THERMODYNAMICS OF AQUEOUS SOLUTIONS

KRISTY M. ERICKSON
B.Sc., University of Lethbridge, 2005

A Thesis
Submitted to the School of Graduate Studies
of the University of Lethbridge
in Partial Fulfillment of the
Requirements for the Degree

[MASTER OF SCIENCE]

Department of Chemistry and Biochemistry
University of Lethbridge
LETHBRIDGE, ALBERTA, CANADA

© Kristy M. Erickson, 2007

A STUDY OF THE THERMODYNAMICS OF AQUEOUS RARE EARTH ELEMENT
CONTAINING TRIFLATE SALT SYSTEMS

KRISTY M. ERICKSON

Approved:

(Print Name)   (Signature)   (Rank)   (Highest   Date
                                                                    Degree)

_____   _____   _____   _____   _____
Supervisor

_____   _____   _____   _____   _____
Thesis Examination Committee
Member

_____   _____   _____   _____   _____
Thesis Examination Committee
Member

_____   _____   _____   _____   _____
External Examiner

_____   _____   _____   _____   _____
Chair, Thesis Examination Committee

"Thermodynamics is not difficult if you can just keep track of what it is you are talking about."

-William F. Giauque, Nobel Laureate 1949
(as cited in Bent, 1972)

ABSTRACT

Relative densities and relative massic heat capacities have been measured for aqueous solutions of triflic acid (CF_3SO_3H), sodium triflate ($NaCF_3SO_3$), gadolinium triflate ($Gd(CF_3SO_3)_3$), dysprosium triflate ($Dy(CF_3SO_3)_3$), neodymium triflate ($Nd(CF_3SO_3)_3$), erbium triflate ($Er(CF_3SO_3)_3$), ytterbium triflate ($Yb(CF_3SO_3)_3$), and yttrium triflate ($Y(CF_3SO_3)_3$) at $T = $ (288.15, 298.15, 313.15, and 328.15) K and $p = 0.1$ MPa. The resulting densities and massic heat capacities have been used to calculate out apparent molar volume and apparent molar heat capacity data for each of the investigated aqueous systems. The concentration dependencies of the apparent molar volumes and apparent molar heat capacities have been modeled using Pitzer-ion interaction equations. Single ion volumes and heat capacities have been calculated using estimates of the apparent molar properties at infinite dilution obtained from the Pitzer-ion interaction equations. These single ion values have, where possible, been compared with those previously reported in the literature.

Also, relative densities have been measured for aqueous solutions of CF_3SO_3H, $Gd(CF_3SO_3)_3$, $Nd(CF_3SO_3)_3$, and $Yb(CF_3SO_3)_3$ at $T = $ (323.15, 348.15, 373.15, and 423.15) K and $p = $ (5.00, 10.00, and 15.00) MPa. The resulting densities have been used to calculate apparent molar volumes. The concentration dependences of these properties have also been modeled using Pitzer-ion interaction equations. The apparent molar volumes have been used to calculate single ion volumes which, in turn, have been compared with those previously reported in the literature.

This thesis also attempts to model the temperature, pressure, and concentration dependencies of the reported apparent molar properties of each system investigated using

an equation of state commonly referred to as the density model. Where possible, the

results of this model have been compared with those results from models previously

reported in the literature.

Acknowledgements

I would first like to thank my parents, Neil and Wanda, and my brother, Jeremy, for all their love and support over the last 20 years of my education and their continuing support for my work in the future. I would also like to thank my friends Allison, Warren, Scott, Troy, Jennifer, and all the Chemistry and Biochemistry graduate students at the University of Lethbridge. Without their help and support, I never would have made it this far, and with so many wonderful memories.

I am greatly indebted to my supervisor, Dr. Andrew Hakin, who allowed me to work in his lab as an undergraduate and subsequently as a graduate student. Without his guidance and support, I surely never would have accomplished all that I have in these past two years. I am also grateful for his trust in my abilities to represent his research at the International Conference on Chemical Thermodynamics (ICCT 2006) gathering in August, 2006. The experience was truly eye opening and it has been a pleasure working with Andy these last two years.

I would like to thank my committee members, Dr. Marc Roussel and Dr. Kenneth Vos for their continuing support and assistance throughout my graduate degree. I would also like to thank Dr. Lee Wilson (University of Saskatchewan) for acting as my external examiner. Appreciation should also be given to Heinz Fischer and Frank Klassen, who helped me modify and reconstruct the high temperature and pressure vibrating tube densimeter that will be discussed in Chapters 3 and 5. They are life savers. Dr. Rene Boeré and Dr. John Vokey also deserve acknowledgements for their enlightening classes on lanthanide chemistry and statistical design. Furthermore, I would like to thank

Table of Contents

List of Tables

xii

List of Figures

1) INTRODUCTION

Thermodynamic properties can be used as a means of probing various solute-solvent and solute-solute interactions within a solution. Until recently, such studies were restricted to near ambient conditions because of instrumental limitations. However, with recent technical advances, investigations of thermodynamic properties over extended temperature and pressure surfaces have begun to increase; and the result is an increased understanding of aqueous solutions removed from ambient conditions. In order to obtain the thermodynamic properties necessary to probe solute-solvent and solute-solute interactions, the techniques of densimetry and calorimetry are employed. These densimetric and calorimetric measurements have been conducted on aqueous rare earth element (REE) containing solutions over an extended range of temperatures and pressures.

Chapter 2 discusses the thermodynamics of aqueous solutions. Various thermodynamic properties and their relationships are presented. These properties and relationships may be used to provide an increased understanding of solute-solvent and solute-solute interactions within solutions. Partial and apparent molar properties are discussed in detail, with reference to the volumetric and calorimetric properties of aqueous salt solutions. Chapter 2 also includes a discussion of Young's rule; that has been used in order to estimate thermodynamic properties for aqueous solutions in which more than one solute is present (such as those presented in this thesis for acidified aqueous salt solutions).

Chapter 3 provides a detailed overview of the experimental equipment and techniques used to make the measurements reported in this thesis. These measurement techniques are described for a Picker-flow microcalorimeter ("Picker" system) and a home-designed and purpose-built high temperature and pressure vibrating tube densimeter. Estimations and calculations of experimental uncertainties associated with the measurements on each instrument are also discussed in detail in this chapter.

Chapter 4 introduces the aqueous REE systems, which are the subject of this study. This chapter contains a detailed analysis of volumetric and calorimetric properties for several aqueous REE triflate salts, trifluoromethanesulfonic (triflic) acid, and sodium triflate using the Picker system at $T = (288.15, 298.15, 313.15, and 328.15)$ K and $p = 0.1$ MPa. These studies compare the calculated volumes and heat capacities of the REE triflates with other such data for REE salts that have been previously studied and presented within the literature. Such comparisons provide a means of looking at the internal consistency of the measurements presented in this study. This chapter also provides an analysis of triflate anion speciation in aqueous solution. This is achieved by comparing the concentration dependences on the apparent molar properties of the investigated REE triflate salts with those previously reported for the REE perchlorate, chloride, and nitrate salt systems.

An extension of the volumetric studies reported in Chapter 4 is provided in Chapter 5. In this chapter a high temperature and pressure vibrating tube densimeter is used to measure the relative densities of aqueous solutions of triflic acid and several REE triflates at $T = (323.15, 348.15, 373.15, and 423.15)$ K and $p = (5.00, 10.00, and$

2

15.00) MPa. These volumetric studies are compared with those previously reported in the literature. The comparison is completed in order to probe the internal consistency of the volumetric measurements of the REE triflates over an extended temperature and pressure surface.

Chapter 6 describes the modeling of the volumetric and calorimetric properties calculated in Chapters 4 and 5 using an equation of state commonly referred to as the density model. The results of this model have been compared to other density model results that have been previously reported for the REE triflates.

Chapter 7 provides a concise summary of the new information presented within this thesis. It also presents some possible future directions for research in this fascinating area of thermodynamics.

2) THE THERMODYNAMICS OF AQUEOUS SOLUTIONS

2.1 Introduction

Investigations of thermodynamic properties of solutions are important because they provide valuable insights into the nature of solute-solvent and solute-solute interactions (Robinson and Stokes, 1965). In solution, the change in the standard state Gibbs energy, $\Delta \overline{G}^0$, is a central property that is related to the equilibrium constant, K, of a reaction or process (Anderson and Crerar, 1993):

$$\Delta \overline{G}^0 = -R \cdot T \cdot \ln K, \tag{2.1}$$

where T is the temperature in Kelvin (K), R is the ideal gas constant that has a value of 8.31451 J·K^{-1}·mol^{-1}, the symbol Δ represents a change, and the superscript "^{0}" represents a standard (fixed) state under specific conditions (the most important fixed conditions being the state and the concentration, or the amount, of substance). The equilibrium constant is perhaps more appropriately known as the activity product (Anderson and Crerar, 1993), where the activity of a species is directly related to a measure of its ability to interact with other species in solution (known as an activity coefficient). Therefore, the change in standard state Gibbs energy can be used to obtain an understanding of solute-solvent and solute-solute interactions that occur within a solution (Robinson and Stokes, 1965).

Measurements of the change in the Gibbs function, ΔG, of a system are limited to studies involving reversible transformations in an electric cell. ΔG values are calculated from these measurements through the Nernst equation and often cannot be adapted to investigations involving solutions (Klotz and Rosenberg, 1972; Anderson and Crerar,

1993). Therefore, experimental investigations turn to higher derivative thermodynamic properties which are more easily measured. Two such properties are volume, V, and isobaric (constant pressure) heat capacity, C_p. The total differential of the Gibbs function, dG, is defined as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp, \tag{2.2}$$

where,

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \tag{2.3}$$

and

$$\left(\frac{\partial G}{\partial T}\right)_p = -S. \tag{2.4}$$

Therefore, the differential of the Gibbs function is directly related to the volume and entropy, S, of a system through minute changes (∂) in temperature, T, and pressure, p (Anderson and Crerar, 1993; Klotz and Rosenberg, 1972):

$$dG = V \cdot dp - S \cdot dT. \tag{2.5}$$

Entropy is also a difficult property to measure. In order to deal with this issue, attention is turned to another measurable higher derivative property, C_p, where:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p. \tag{2.6}$$

Therefore, with a temperature dependent description of C_p and a pressure dependent description of V, the equilibrium constant can be described. Methods by which the volumes and heat capacities of solutions can be precisely measured are described in detail in Chapter 3.

2.2 Activity Coefficients

Figure 2.1 illustrates a simple example that introduces the concept of activity coefficients. In both beakers (1) and (2), the temperature and pressure of the solutions are constant and equal (and the solvent is water). In beaker (1), the sparingly soluble salt, $AB_{(s)}$, undergoes a limited amount of dissociation into its ions, $A^+_{(aq)}$ and $B^-_{(aq)}$ such that a saturated solution is formed. To a first approximation, the solubility constant, K_{sp}, at equilibrium is:

$$K_{sp} = [A^+_{(aq)}] \cdot [B^-_{(aq)}]. \tag{2.7}$$

One could initially assume that the same equation could be used to estimate the K_{sp} of the sparingly soluble salt in beaker (2), but this would not be the case. When $C^+_{(aq)}$ and $D^-_{(aq)}$ are present in beaker (2), the solubility of $AB_{(s)}$ increases, relative to that of beaker (1). As the concentration of both $C^+_{(aq)}$ and $D^-_{(aq)}$ is increased in beaker (2), the solubility of $AB_{(s)}$ in beaker (2) increases even more. An explanation of this observation exploits the concept of "ionic atmospheres". In beaker (2), there is, on average, an excess of negatively charged ions, $D^-_{(aq)}$, situated around each $A^+_{(aq)}$ ion and an excess of positively charged ions, $C^+_{(aq)}$, around each $B^-_{(aq)}$ ion, causing the net forces of ionic attraction between the ions $A^+_{(aq)}$ and $B^-_{(aq)}$ to decrease. Therefore, the solubility of $AB_{(s)}$ in beaker (2) relative to beaker (1) increases (Harris, 2002). To explain this observation, the concept of activity is introduced. In beaker (2), the activities of the ions $A^+_{(aq)}$ or $B^-_{(aq)}$ have been decreased by the presence of the ions $C^+_{(aq)}$ and $D^-_{(aq)}$. The activity, a_i, of each ion, i (either $A^+_{(aq)}$ or $B^-_{(aq)}$), is defined by the following equation:

$$a_i = [i] \cdot \gamma_i, \tag{2.8}$$
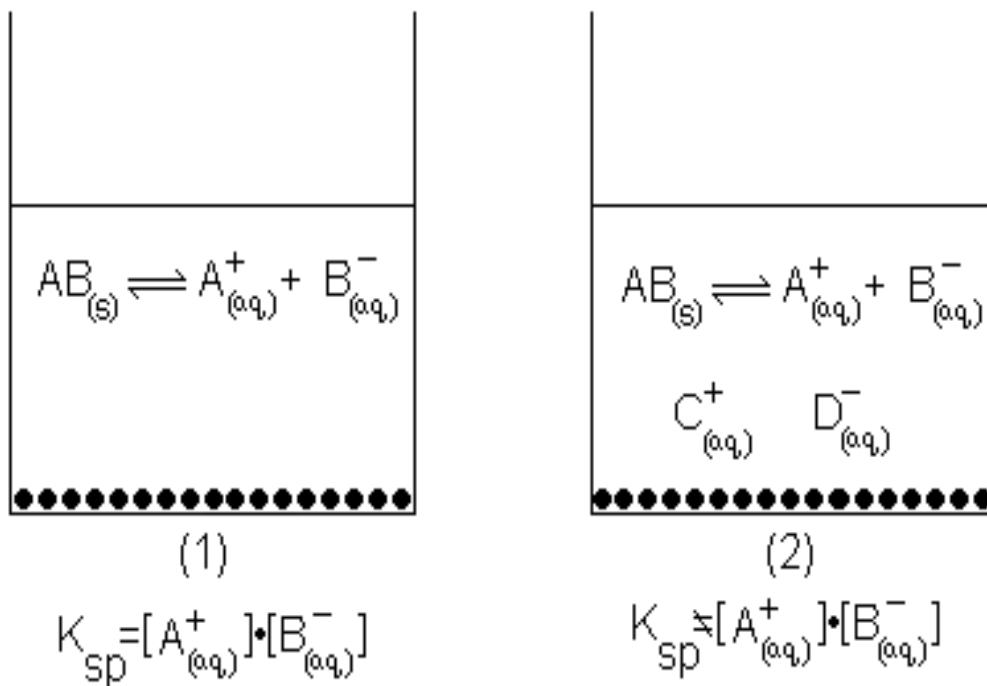
Figure 2.1 The determination of the K_{sp} for $AB_{(s)}$ in order to explain the concept of activity coefficients: beaker (1), a saturated solution of a sparingly soluble electrolyte, $AB_{(s)}$; and beaker (2), a saturated solution containing a sparingly soluble electrolyte, $AB_{(s)}$, and an inert electrolyte which is very soluble and has completely dissociated into its ions, $C^+_{(aq)}$ and $D^-_{(aq)}$ (the dots at the bottom of the beakers represent $AB_{(s)}$ that is not dissolved).

where the activity coefficient, γ_i, is described as a measure of an ion's effectiveness to influence an equilibrium in which it is involved. For beaker (2), equation (2.7) should be written as:

$$K_{sp} = a_{A^+_{(aq)}} \cdot a_{B^-_{(aq)}}$$

$$= [A^+_{(aq)}] \cdot [B^-_{(aq)}] \cdot \gamma_{A^+_{(aq)}} \cdot \gamma_{B^-_{(aq)}}. \tag{2.9}$$

As the concentration of ions in an aqueous solution lowers, activity coefficients for these ions approach a value of 1.0. However, with increasing concentration, the activity

coefficients decrease from 1.0. Also, as the charge on an ion is increased, its activity

coefficient decreases more rapidly with respect to increasing concentration. Therefore,

activity coefficients are known to be dependent upon the ionic strength, I, of a system,

which is a measure of the amount of charged species (or ions) within a solution:

$$I = \left(\frac{1}{2}\right) \cdot \sum_i c_i \cdot z_i^2,$$ (2.10)

where c_i is the concentration of species i and z_i is the corresponding charge. In the

example presented in Figure 2.1, the $AB_{(s)}$ salt in beaker (2) is only sparingly soluble;

therefore I is directly related to the concentrations of $C^+_{(aq)}$ and $D^-_{(aq)}$. With increasing

ionic strength, the tendency of the $A^+_{(aq)}$ and $B^-_{(aq)}$ ions to come together to form a solid is

decreased, as are the activity coefficients of $A^+_{(aq)}$ and $B^-_{(aq)}$. Therefore, the overall

solubility of the salt, $AB_{(s)}$, increases. An example of this ionic strength dependence is

the Debye-Hückel Limiting Law:

$$\log \gamma_{\pm} = -A_Y \cdot |z_+ \cdot z_-| \cdot \sqrt{I},$$ (2.11)

where $\gamma_{\pm}$ is defined as a mean ion activity coefficient, which will be dealt with in more

detail, along with the Debye-Hückel Limiting Law, in Section 2.4.

2.3 Partial and Apparent Molar Properties

A molar property of a solute, where the solute will be designated by a subscripted

"2", is defined as a change in the property, Y_2, of a solution when 1 mole of a solute is

added to a solution. The easiest way to think of this is in terms of the molar volume, V_m,

shown in Figure 2.2, where the volume of the solution increases with respect to the

amount of solute added (Anderson and Crerar, 1993). A dissolved solute has its own

Volume
of solution
(V/cm^3)

Molar volume
$(V_m/cm^3 \cdot mol^{-1})$ $= \dfrac{dV}{dn_2}$

0

Moles of solute
(n_2 /mol)
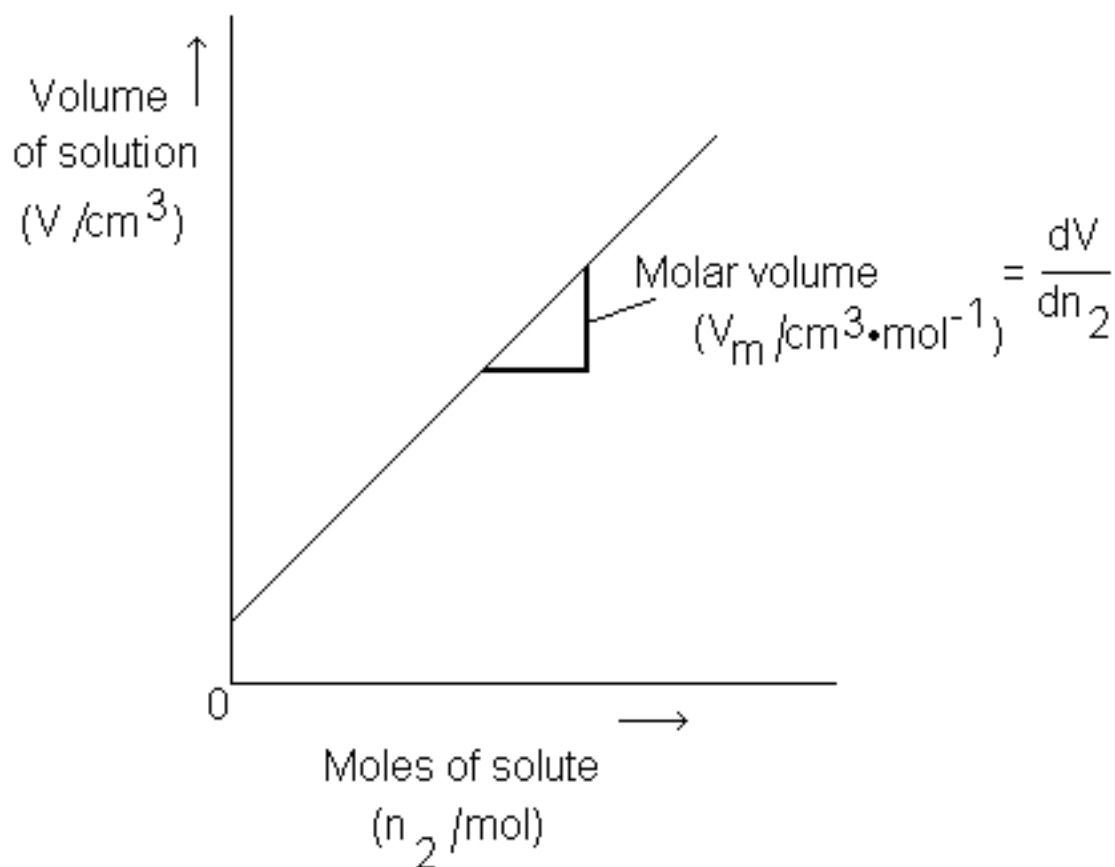
Figure 2.2 A diagram to assist in the explanation of a molar volume (this figure is based on the one presented by Anderson and Crerar,1993).

property, referred to as a partial molar property, $\overline{Y_2}$. Consider Figure 2.3, where there is an extremely large tank containing a 1.00 mol·L^{-1} solution of a solute with a certain volume, shown at position (1). If 1.00 mole of solute is added to this tank of water, the volume will increase to (2), however, the concentration of the other species of the solution will not change by any detectable amount. Therefore, for a two component system, where one component is the solvent and the other is the solute, the total volume of the system can be represented as the sum of the partial molar volumes of the solvent, $\overline{V_1}$, and the solute, $\overline{V_2}$:
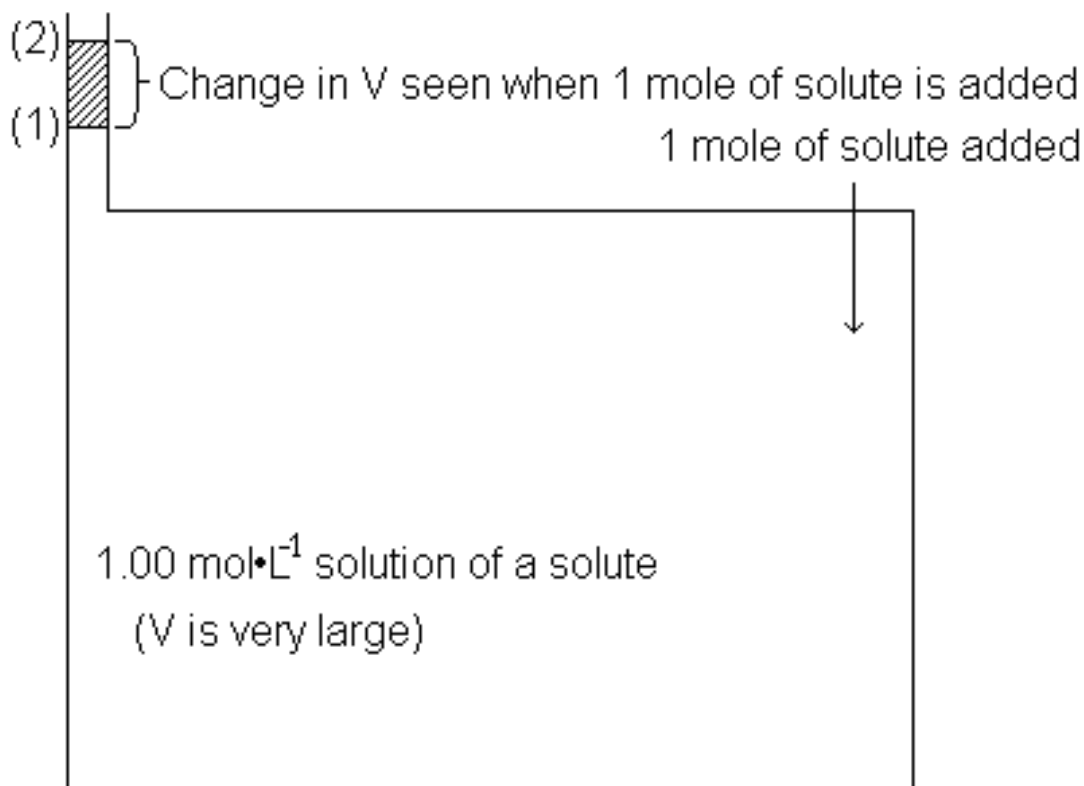
Figure 2.3 A diagram to assist in the explanation of a partial molar volume (this figure is based on the one presented by Anderson and Crerar, 1993).

$$V = n_1 \cdot \overline{V}_1 + n_2 \cdot \overline{V}_2, \tag{2.12}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively, in the solution. The molar volume of the solution is defined by:

$$V_m = x_1 \cdot \overline{V}_1 + x_2 \cdot \overline{V}_2, \tag{2.13}$$

where x_1 and x_2 represent the mole fraction of the solvent and solute, respectively. The partial molar property of a solute is defined as the change in the total property of the system with respect to the change in the number of moles of solute added, with all other variables (T, p, and the amount of solvent) held constant:

$$\overline{Y}_2 = \left(\frac{\partial Y}{\partial n_2} \right)_{T,p,n_1}. \tag{2.14}$$

A common thermodynamic term is a partial molar Gibbs energy, $\overline{G}_2$, that is based on the activity of the solute in the solution with T, p, and the other constituents of the solution being held constant. This value is known as the chemical potential, μ_2:

$$\overline{G}_2 = \mu_2 = \left(\frac{\partial G}{\partial n_2} \right)_{T,p,n_1}, \tag{2.15}$$

where

$$\mu_2 = \mu_2^0 + R \cdot T \cdot \ln a_2, \tag{2.16}$$

and μ_2^0 is the chemical potential of the solution in its standard state.

An alternative, widely used property of the solute is the apparent molar property. The apparent molar volume (for example) is the volume that should be attributed to the solute in solution if it is assumed that the solvent contributes the exact same volume it would if it was in its pure state. Under this assumption, the apparent molar volume of the solute ($V_{2\phi}$) becomes the difference between the total volume (or total molar volume) and the partial molar volume of the pure solvent ($\overline{V}_1^0$) divided by the number of moles (or mole fraction) of solute present:

$$V_{2\phi} = \frac{V - n_1 \cdot \overline{V}_1^0}{n_2} \tag{2.17}$$

$$V_{2\phi} = \frac{V_m - x_1 \cdot \overline{V}_1^0}{x_2}. \tag{2.18}$$

In experimentation, $\overline{V}_1^0$ is generally considered to be constant over the range of solute concentration at constant temperature and pressure (Klotz and Rosenberg, 1972). Hence,

$V_{2\phi}$ can be easily calculated using equation (2.17) or (2.18) when the total volume or molar volume, respectively, is obtained.

Equation (2.17) can be modified in order to find the apparent molar volume of a solute using the density of the solution containing the solute and the density of the pure solvent, ρ_2 and ρ_1, respectively. Assuming there is 1 kilogram (kg) of solvent:

$$n_1 = \frac{1}{M_1}, \text{ therefore } V = \frac{\overline{V}_1^0}{M_1} + m_2 \cdot V_{2\phi},$$

where M_1 is the molar mass of the solvent. Since:

$$\rho_1 = \frac{M_1}{\overline{V}_1^0},$$

equation (2.17) becomes:

$$V = \frac{1}{\rho_1} + m_2 \cdot V_{2\phi},$$

where m_2 is the molality of the solute (which is equivalent to n_2 if 1 kg of solvent is present). The entire mass of the solution will be composed of the mass of the solvent (1 kg) and the mass of the solute ($m_2 \cdot M_2$). Since volume is defined as the mass divided by the density, the equation for V becomes:

$$\frac{1 + m_2 \cdot M_2}{\rho_2} = \frac{1}{\rho_1} + m_2 \cdot V_{2\phi}.$$

By rearranging this equation and solving for $V_{2\phi}$, an equation for the apparent molar volume of the solute is found:

$$V_{2\phi} = \frac{\rho_2 - \rho_1}{m_2 \cdot \rho_2 \cdot \rho_1} + \frac{M_2}{\rho_2}. \tag{2.19}$$

Since there is also interest in the calculation of heat capacities, an equation for the

apparent molar heat capacity, $C_{p,2\phi}$, is also needed. The equation for $C_{p,2\phi}$ is similar to equation (2.19):

$$C_{p,2\phi} = M_2 \cdot c_{p2} + \frac{c_{p2} - c_{p1}}{m_2},$$
(2.20)

where c_{p2} is the massic (specific) heat capacity of the solution and c_{p1} is the massic heat capacity of the solvent.

Using equations (2.12) and (2.14), the apparent molar property of a solute is related to its partial molar property through equation (2.21):

$$\overline{Y}_2 = Y_{2\phi} + \left(\frac{\partial Y_{2\phi}}{\partial n_2} \right)_{n_1} \cdot n_2.$$
(2.21)

As n_2 approaches 0, $\left(\dfrac{\partial Y_{2\phi}}{\partial n_2} \right)_{n_1}$ also approaches 0. Therefore, at infinite dilution (a

theoretical point at which only 1 mole of solute exists in an extremely large volume of water, and where only solute-solvent interactions are present within the aqueous solution) this apparent molar property, known as Y_2^0, of the solute equals the partial molar property of the solute (V_2^0 is the standard term used to represent the apparent molar volume at infinite dilution and C_{p2}^0 is the standard term used to represent the apparent molar heat capacity at infinite dilution (Anderson and Crerar, 1993; Klotz and Rosenberg, 1972)). This becomes important in order to obtain a value for the partial molar volume or heat capacity of a system (which normally cannot be calculated directly from experimentation) that represents solute-solvent interactions within a solution.

13

2.4 Debye-Hückel Theory and Pitzer-ion Interaction

When considering the formation of an ionic atmosphere, γ_i becomes an important variable to represent the deviation from equilibrium and hence, the degree of various interactions between ions within a solution. For aqueous electrolytes, the positive and negative ions of the electrolyte cannot be dealt with separately; therefore a mean ion activity coefficient, $\gamma_\pm$, is used to represent the activity of the parent electrolyte solute dissolved within water:

$$\gamma_\pm = \left(\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-} \right)^{\frac{1}{\nu}}, \tag{2.22}$$

where ν_+ and ν_- represent the stoichiometric number of positively and negatively charged species and ν is the sum of ν_+ and ν_-. γ_+ and γ_- are the activity coefficients of the positive and negative ions, respectively.

Combining equations (2.1) and (2.16) (Robinson and Stokes, 1965), an equation is obtained that describes the chemical potential of a simple 1:1 electrolyte salt, designated as *AB*:

$$\mu_{AB} = \mu_{AB}^0 + \nu \cdot R \cdot T \cdot \ln(a_{AB})$$

$$= \mu_{AB}^0 + \nu \cdot R \cdot T \cdot \ln([AB] \cdot \gamma_{\pm(AB)}). \tag{2.23}$$

Using equations (2.3), (2.6), and (2.23), the partial molar volume, $\overline{V}_2$, and partial molar heat capacity, $\overline{C}_{p2}$, of a solute can be presented in terms of $\gamma_\pm$:

$$\overline{V}_2 = \left(\frac{\partial \mu_2}{\partial p} \right)_T$$

$$= V_2^0 - \nu \cdot R \cdot T \cdot \left(\frac{\partial \ln \gamma_\pm}{\partial p} \right)_{m,T} \tag{2.24}$$

$$\overline{C}_{p2} = T \cdot \left(\frac{\partial S}{\partial T} \right)_p$$

$$= C_{p2}{}^0 - v \cdot R \cdot T \cdot \left(T \cdot \frac{\partial^2 \ln \gamma_\pm}{\partial T^2} + 2 \cdot \frac{\partial \ln \gamma_\pm}{\partial T} \right)_{m,p}. \tag{2.25}$$

where the "m" represents a constant composition for the partial derivative.

Debye and Hückel (1923, 1924) attempted to derive a way of calculating the mean ionic activity coefficient of an electrolyte in very dilute aqueous solutions (Anderson and Crerar, 1993). The result was that the mean ionic activity coefficient was represented in terms of the unit charge, z_i, of each ion (represented as z_+ for a positive ion and z_- for a negative ion) in the solute, the ionic strength, and the average effective diameter, $\overset{o}{a}$ (in angstroms), of the solute ions (Robinson and Stokes, 1965; Klotz and Rosenberg, 1972):

$$\log \gamma_\pm = \frac{-A_\gamma \cdot |z_+ \cdot z_-| \cdot \sqrt{I}}{I + \overset{o}{a} \cdot B_\gamma \cdot \sqrt{I}}. \tag{2.26}$$

A_γ and B_γ are constants based on the charge of an electron, e, the dielectric constant of water, ε, Avogadro's number, N_a, Boltzman's constant, k, ρ_1, and T:

$$A_\gamma = \sqrt{\frac{2 \cdot \pi \cdot N_a \cdot \rho_1}{1000}} \cdot \frac{e^3}{(k \cdot \varepsilon \cdot T)^{\frac{3}{2}}} \tag{2.27}$$

$$B_\gamma = \sqrt{\frac{8 \cdot \pi \cdot N_a \cdot \rho_1}{1000 \cdot k \cdot \varepsilon \cdot T}}. \tag{2.28}$$

If I is sufficiently small, equation (2.26) simplifies such that it becomes independent of long-range coulombic interactions between the solute species. This equation is known as the Debye-Hückel Limiting Law (DHLL), as shown in equation (2.11), and indicates that

there is a linear ionic strength dependence on $\gamma_\pm$. A_Y (in equation (2.11)) is a temperature and pressure dependent Debye-Hückel constant and takes on the following forms in the studies of the molar volume (known as A_V) and molar heat capacity (known as A_J), respectively:

$$A_V = 2 \cdot R \cdot T \cdot \left(\frac{\partial A_\gamma}{\partial p} \right)_T \qquad\qquad (2.29)$$

$$A_J = 2 \cdot R \cdot T^2 \cdot \left(\frac{\partial^2 A_\gamma}{\partial T^2} \right)_p . \qquad\qquad (2.30)$$

Values of A_V and A_J used in this thesis have been reported by Archer (1990) over large temperature and pressure ranges. A_γ is equal to $3 \cdot A_\phi$ (Pitzer, 1971; Stokes in Pytcowicz, 1979), where A_ϕ is the Debye-Hückel constant for the osmotic coefficient of water (which is a measure of the activity for water) that has also been reported by Archer (1990) over large temperature and pressure ranges.

As a system approaches infinite dilution, the partial and apparent molar properties become equal and $\gamma_\pm$ values in equations (2.24) and (2.25) approach unity. Therefore the general DHLL equation for an apparent molar property, $Y_{2\phi}$, becomes:

$$Y_{2\phi} = Y_2^{\,0} + \frac{v}{2} \cdot A_Y \cdot | z_+ \cdot z_- | \cdot \sqrt{I} , \qquad\qquad (2.31)$$

if the DHLL slopes are accepted in the dilute region.

Pitzer (Pitzer, 1991; Stokes in Pytkowicz, 1979) elaborated on the work of Debye and Hückel by including higher order interaction terms (that represent solute-solute interactions in solution, also referred to as virial expansion coefficients). These terms

account for various interactions independent of T and p and are assumed to be an average of clusters over the entire system.

Since activities are a representation of solute-solvent and solute-solute interactions in solution, it makes sense to discuss Pitzer's work in terms of the Gibbs function. The excess Gibbs function, G^{EX}, is a representation of the non-ideal contributions (the contributions associated with solute-solute interactions) in a solution with respect to the Gibbs function:

$$G = G^{EX} + G^0, \tag{2.32}$$

where G^0 is a representation of the ideal contributions (the contributions associated with solute-solvent interactions) in a solution. Since the solvent is in abundance, the solute-solute interactions are described by the various potentials of force present in the solvent, and not the interactions between individual solute molecules (Pitzer, 1991). G^{EX} has been defined by:

$$\frac{G^{EX}}{R \cdot T} = n_1 \cdot f(I) + \frac{I}{n_w} \cdot \sum_i \cdot \sum_j \lambda_{ij} \cdot n_i \cdot n_j$$

$$+ \frac{1}{n_1^2} \cdot \sum_i \cdot \sum_j \cdot \sum_k \mu_{ijk} \cdot n_i \cdot n_j \cdot n_k, \tag{2.33}$$

where λ_{ij} and μ_{ijk} represent the virial coefficients for short range doublet and triplet interactions for the dissolved electrolyte solute within the solvent, and:

$$f(I) = \frac{\left[1 - \left(1 + \alpha \cdot I^{1/2}\right) \cdot \exp\left(- \alpha \cdot I^{1/2}\right)\right]}{\left(\alpha^2 \cdot I\right)}. \tag{2.34}$$

$\alpha = 2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ and $f(I)$ is used to define the long-range interaction effects within a solution (Pitzer, 1991; Stokes in Pytkowicz, 1979).

Looking back to the equations for V and C_p (equations (2.3) and (2.6)), the volume and isobaric heat capacity, respectively, can be represented in terms of G^{EX}:

$$V = V_2^0 + \left(\frac{\partial G^{EX}}{\partial p}\right)_{T,m} \tag{2.35}$$

$$C_p = C_{p2}^0 + \left(\frac{\partial\left(-T^2 \cdot \left(\frac{\partial\left(G^{EX}/T\right)}{\partial T}\right)_{p,m}\right)}{\partial T}\right)_{p,m}. \tag{2.36}$$

Using the definition for an apparent molar property (equation (2.17)) and the relationship between an apparent and partial molar property (equation (2.21)), the apparent molar volume and apparent molar heat capacity of a solute can subsequently be modeled as a function of solute molality, m_2 using equations (2.37) and (2.38), respectively:

$$V_{2\phi} = V_2^0 + \frac{v \cdot |z_+ \cdot z_-| \cdot A_V \cdot \ln(1 + b \cdot \sqrt{I})}{2 \cdot b}$$
$$+ 2 \cdot (v_+ \cdot v_-) \cdot R \cdot T \cdot m_2 \cdot \left(\beta^{(0)V} + 2 \cdot \beta^{(1)V} \cdot f(I)\right) + C^V \cdot m_2 \tag{2.37}$$

$$C_{p,2\phi} = C_{p2}^0 + \frac{v \cdot |z_+ \cdot z_-| \cdot A_J \cdot \ln\left(1 + b \cdot \sqrt{I}\right)}{2 \cdot b}$$
$$- 2 \cdot (v_+ \cdot v_-) \cdot R \cdot T^2 \cdot m_2 \cdot \left(\beta^{(0)J} + 2 \cdot \beta^{(1)J} \cdot f(I)\right) + C^J \cdot m_2, \tag{2.38}$$

where $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$. $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ are all fitting parameters related to the second and third virial activity coefficients. C^V and C^J do not have to be considered as long as the molality of the solute stays below 1.0 mol·kg^{-1} (Pitzer, 1991). Through least squares multiple regression analyses, the values of V_2^0 and C_{p2}^0 can be determined using equations (2.37) and (2.38) (for solutes of interest over temperature and pressure surfaces).

2.5 The "Density" Model

Marshall (1970) observed that the natural log of an equilibrium constant has a linear dependence with respect to the isothermal compressibility coefficient of water, β, where:

$$\beta = -\frac{1}{V} \cdot \left(\frac{\partial V}{\partial p} \right)_T$$

$$= \frac{1}{\rho_1} \cdot \left(\frac{\partial \rho_1}{\partial p} \right)_T. \tag{2.39}$$

According to equation (2.1), the standard state change in Gibbs energy is related to K. Hence, equations (2.35) and (2.36) can be used to find equations for V_2^0 and C_{p2}^0 in terms of β. This method (referred to as the density model) has been exploited by Xiao *et al.* (1997b), Tremaine *et al.* (1997), Mesmer *et al.* (1988), Gates *et al.* (1982), and Simonson *et al.* (1994) using a variety of different equations in order to describe solute-solvent interactions within a solution over large surfaces of temperatures and pressures.

The general assumption is that the property of the solute dissolved within a certain solvent will behave in a similar manner as the property of the solvent itself over the temperature and pressure surface. Therefore, the property of the solvent is mapped over the conditions of interest and the resulting equation (referred to as a global fit) is applied to the calculated thermodynamic property of the solute in order to probe the temperature and pressure dependences of the solute's property.

2.6 Young's Rule

In the studies presented in this thesis, the salt solutions investigated need to be acidified in order to ensure that the salt remains in a fully dissociated state (to prevent

hydrolysis). Hence, the solutions contain more than one solute. As a result, thermodynamic investigations of these solutions are not that simple when compared to those described above. Since an additional solute is present within the solution (the acid), it must be dealt with in order to investigate the actual dissolved solute of interest.

Young's additivity rule (Young and Smith, 1954) permits the experimental apparent molar property of a multi-solute containing solution to be estimated as the sum of the apparent molar properties of each of the two solutes (referred to as "2" and "3" in this thesis, where solute "2" is the solute of interest):

$$Y_{\phi,\exp t} = \left(\frac{m_2}{m_2 + m_3} \right) \cdot Y_{2\phi} + \left(\frac{m_3}{m_2 + m_3} \right) \cdot Y_{3\phi} + \delta, \tag{2.40}$$

where,

$$\delta = k_{2,3} \cdot \left(\frac{m_2 \cdot m_3}{m_2 + m_3} \right) \cdot I. \tag{2.41}$$

$Y_{2\phi}$ is the property value of solute "2" if only it were in solution (assuming that this pure solute in solution exists at the same ionic strength as the solution under investigation). $Y_{3\phi}$ is the property values for solute "3", if only it were in solution. Variables m_2 and m_3 represent the corresponding molalities of solutes "2" and "3", respectively, while $k_{2,3}$ is a binary interaction term. In the systems studied in this thesis, a common anion exists in solutes "2" and "3". Therefore, in solution, it is assumed that the interaction of the positive ion from solute "2" with the negative ion from solute "2" will be the same as the interaction of the positive ion from solute "2" with the negative ion from solute "3". Therefore $k_{2,3}$ becomes negligible, especially when $m_2 > m_3$ (as is the case for the systems investigated in this thesis). From equation (2.40), $Y_{2\phi}$ values may be calculated (if m_2 and

m_3 are known, and $Y_{3\phi}$ and $Y_{\phi,expt}$ are measured). These measurement techniques will be explained in detail in Chapters 3, 4, and 5.

3) EXPERIMENTAL EQUIPMENT

3.1 Introduction

Density and heat capacity measurements are important because they can be used to provide information on bulk solute-solvent and solute-solute interactions within a system. As described in Chapter 2, entropies, which provide information on the order of a system, may be obtained from the integration of the temperature dependences of isobaric heat capacity data. Density measurements can be used to determine the pressure and temperature dependences of a volume of a system. A current push within the field of solution thermodynamics is to make precise density and heat capacity measurements at higher temperatures and pressures. Such measurements can provide thermodynamic information that is necessary to increase the understanding of the nature of solute-solvent and solute-solute interactions under extreme temperature and pressure conditions.

Two instruments were used to make the thermodynamic measurements reported in this thesis. One of these is an instrument that is generally referred to as the "Picker". The Picker consists of a Sodev O2D vibrating tube densimeter connected in series with a Picker-flow microcalorimeter. The instrument measures relative densities and massic heat capacities at ambient pressure ($p = 0.1$ MPa) and temperatures in the range $T = 288.15$ K to $T = 328.15$ K. Such measurements can be used in the manner presented in Chapter 2 to calculate apparent molar volumes and apparent molar heat capacities of both aqueous and non-aqueous solutions. The other instrument featured in this study is a recently modified (within the last year) and purpose-built high temperature and pressure vibrating tube densimeter. This instrument is capable of measuring precise relative

22

densities for aqueous solutions in a temperature range from ambient to $T = 623.15$ K and a pressure range from ambient to $p = 15.00$ MPa.

3.2 The Picker

3.2.1 The Sodev O2D Vibrating Tube Densimeter

Due to their high sensitivity and precision, vibrating tube densimeters have become the instrument of choice with respect to the measurement of solution densities (Picker *et al.*, 1974). The motion of the vibrating tube within the densimeter resembles that of a harmonic oscillator:

$$\omega_u = \sqrt{\frac{K}{m}},$$ (3.1)

where ω_u is the un-damped resonance frequency of a harmonic oscillator, K is the spring constant, and m is the mass of both the vibrating tube and the system it contains. Variable "m" is the only variable that can cause a change in ω_u since the volume of the tube is constant under constant temperature and pressure conditions. Therefore, a change in m will cause a change in the period of vibration, τ, of the tube, where τ is defined by:

$$\tau = \frac{2 \cdot \pi}{\omega_u}.$$ (3.2)

The density (ρ_2) of a system of interest may be determined from the density of water (ρ_1) and the measured periods of vibration of the vibrating tube when it contains either the system of interest (τ_2) or water (τ_1):

$$\rho_2 - \rho_1 = k \cdot (\tau_2^2 - \tau_1^2).$$ (3.3)

To determine the densimeter constant, k, at a particular temperature and pressure of

interest, a calibration experiment is performed. In this calibration, water and air are used as reference systems. The period of oscillation of the vibrating tube is measured when it contains pure water (referred to as τ_1 in the calibration) and air (referred to as τ_2 in the calibration). The densities of pure water (ρ_1 in the calibration; values reported in Kell, 1967) and air (ρ_2 in the calibration) are either well known to high precision over the surface of temperatures and pressures of study ($T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa) or can easily be calculated. With known values of ρ_1 and ρ_2, and measured values of τ_1 and τ_2, the densimeter constant can be easily calculated by appropriately arranging equation (3.3). Once k has been calculated at the temperature and pressure of interest, the unknown density of a system of interest (now referred to as ρ_2) may be obtained by measuring the time period of oscillation of the tube containing the system of interest, τ_2, relative to that of pure water, τ_1, using equation (3.3). In order to ensure that any small deviations in the set temperature or pressure of the system are accounted for, an average value of k is determined from two calibration experiments.

A schematic for the Sodev O2D vibrating tube densimeter is shown in Figure 3.1. At the core of the densimeter is a vibrating tube that is positioned within a temperature regulated environment. Temperature is maintained to within several thousandths of a Kelvin with the use of a TechnoEurop closed loop thermostat (a). A U-shaped tube (b) is soldered onto a brass plate (c). A magnetic pickup (d) is used to keep the tube vibrating with the use of a detector drive circuit system that locks to the frequency of the tube and triggers a resonant vibration (Picker *et al.*, 1974; Lukacs, 2003). A Phillips PM 6611 universal counter that averages every 10 000 counts is used to measure the time period of oscillation of the tube. These measurements are transferred to a PC for storage via a

24
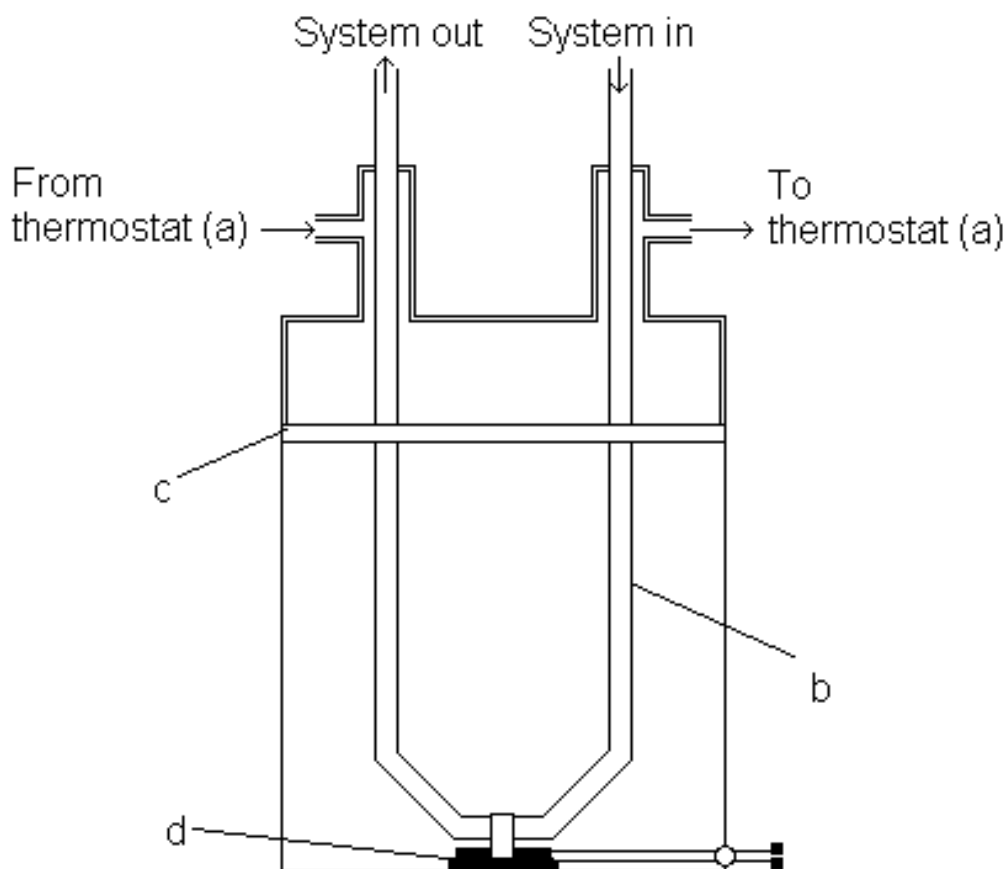
Figure 3.1 Schematic of the Sodev O2D vibrating tube densimeter: (a), circulating thermostat bath; (b), vibrating tube; (c), brass plate; (d), magnetic pickup (This schematic is re-drawn from the one presented in Picker *et al.*, 1974).

serial interface. The time periods collected in this manner are used within equation (3.3) to calculate relative densities with an uncertainty estimated to be $\delta\rho = \pm 5 \times 10^{-6}$ g·cm^{-3} (Marriott, 1999).

When performing a measurement, gravity feed is used to transfer the solvent and solution of interest into the vibrating tube densimeter. An output similar to the one shown in Figure 3.2 is obtained. The solvent is allowed to run both before and after (see
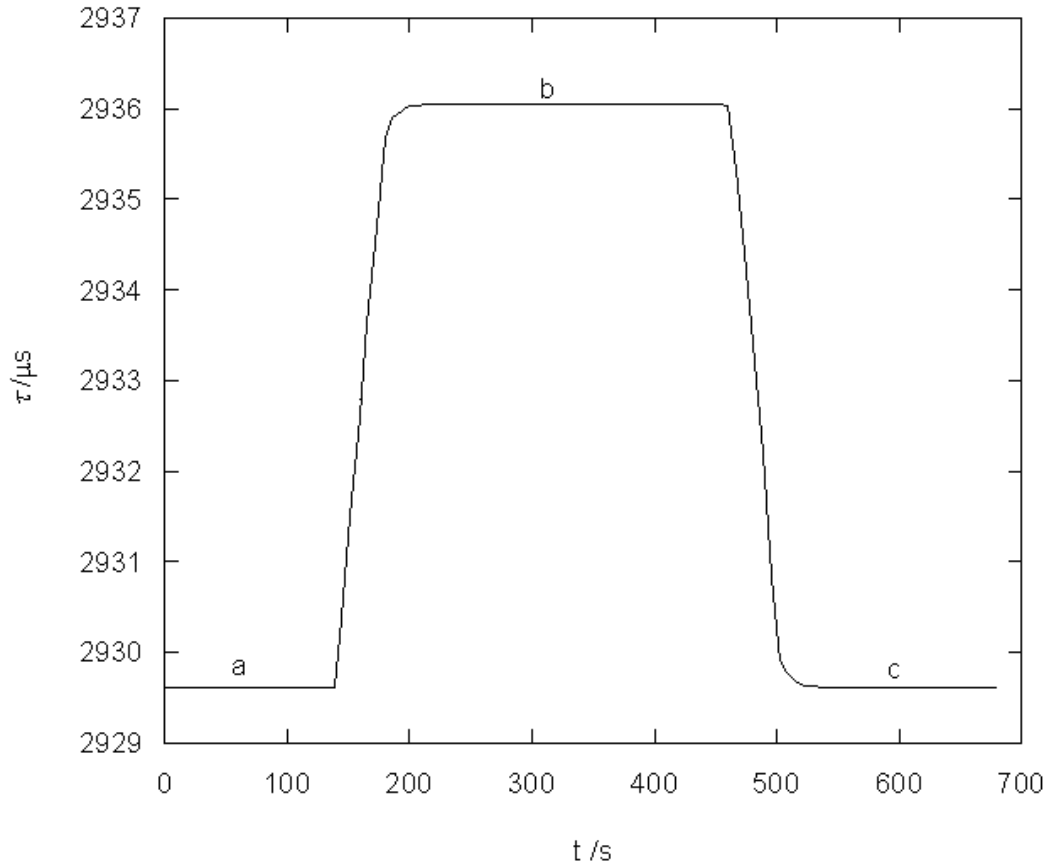
Figure 3.2 A plot of time period of vibration against time for the Sodev O2D vibrating tube densimeter: (a) solvent flow before system of interest; (b) system of interest flow; (c) solvent flow after system of interest.

areas labeled as (a) and (c) in Figure 3.2) the solution of interest, the area labeled (b), in order to compensate for any slow drift in the period of vibration of the tube over the course of the experiment. Densities determined in this manner are used to calculate apparent molar volumes for the system of interest (as shown in equation (2.19)).

Uncertainties in the calculation of apparent molar volumes are determined through the standard propagation of error method. In this method, the overall uncertainty in an apparent molar volume is related to the uncertainties associated with the density and the concentration of the solution of interest:

26

Table 3.1 A comparison of apparent molar volume values at infinite dilution, V_2^0, for NaCl$_{(aq)}$ solutions at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa: those calculated in this study[a] with those reported by Marriott (1999)[b], Archer (1992)[c], Millero (1970)[d], and Dessauges *et al.*, (1980)[e]

T /(K)	V_2^0[a] /(cm³·mol⁻¹)	V_2^0[b] /(cm³·mol⁻¹)	V_2^0[c] /(cm³·mol⁻¹)	V_2^0[d] /(cm³·mol⁻¹)	V_2^0[e] /(cm³·mol⁻¹)
288.15	15.64(0.04)	15.49(0.07)	15.551(0.004)	15.57(0.01)	15.63
298.15	16.644(0.002)	16.62(0.01)	16.64(0.01)	16.62	16.62
313.15	17.31(0.02)	17.54(0.01)	17.58(0.02)		
328.15	17.75(0.04)	17.72(0.02)	18.03(0.02)	17.91	

$$\left(\delta V_{2\phi}\right)^2 = \left(\frac{\partial V_{2\phi}}{\partial \rho_2}\right)^2 \cdot \delta\rho_2{}^2 + \left(\frac{\partial V_{2\phi}}{\partial m_2}\right)^2 \cdot \delta m_2{}^2. \tag{3.4}$$

Combining equations (2.19) and (3.4), the calculation for $\delta V_{2\phi}$ simplifies to:

$$\delta V_{2\phi} = \left(M_2 + \frac{1000}{m_2}\right) \cdot \frac{\delta\rho_2}{\rho_2{}^2} + \left(1000 \cdot \frac{(\rho_2 - \rho_1)}{m_2{}^2 \cdot \rho_2 \cdot \rho_1}\right) \cdot \delta m_2. \tag{3.5}$$

To track the precision of the vibrating tube densimeter over the course of this study, calibrations were routinely performed using reference NaCl$_{(aq)}$ solutions. Apparent molar volumes for NaCl$_{(aq)}$ were calculated as a function of molality using equation (2.19) at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa. These values were subsequently used to calculate apparent molar volumes at infinite dilution, V_2^0, using equation (2.37), which then were compared to V_2^0 values previously reported by Marriott (1999), Archer (1992), Millero (1970), and Dessauges *et al.* (1980). This comparison is presented in Table 3.1. As can be seen, the V_2^0 values calculated in this study are in good agreement with those V_2^0 values reported in previous studies. Due to this agreement, a high degree of confidence is placed in the precision of measurements obtainable from the Sodev O2D vibrating tube densimeter used in the studies presented in this thesis.

3.2.2 The Picker-flow Microcalorimeter

Connected in series to the Sodev O2D vibrating tube densimeter is the Picker-flow microcalorimeter. The Picker-flow microcalorimeter is used to determine the relative heat capacities of aqueous and non-aqueous solutions with high precision.

In flow calorimetry (Picker *et al.*, 1971; Desnoyers *et al.*, 1976) a temperature gradient is established through the continuous heating of a system of interest (a liquid) as it is allowed to flow through the instrument. The system of interest is pre-thermostated to a set temperature of interest and a volumetric heat capacity, σ_s, is calculated based on an applied power required to add thermal energy to the system, w_o, the change in temperature resulting from the applied power, ΔT, and the flow rate of the liquid, f:

$$\sigma_s = \frac{w_o}{f \cdot \Delta T}.$$
(3.6)

The massic heat capacity of a solute of interest is related to the volumetric heat capacity of that system and its corresponding density:

$$c_{p2} = \frac{\sigma_s}{\rho_2}.$$
(3.7)

In the case of the Picker-flow microcalorimeter, a twin cell approach is used to establish the temperature gradient. A schematic diagram of the Picker-flow microcalorimeter is shown in Figure 3.3. In an initial calibration, the two thermistor detectors (d), D_1 and D_2, are nulled such that their temperature readings, T_1 and T_2, are equal to the temperature of interest, T_0. T_0 is the temperature that the solvent (water, in these studies) and the system of interest attain once they have entered the thermostated calorimeter. The calorimeter is thermostated by a water jacket (a) using a TechnoEurop thermostat bath. During the experiment, thermal energy is added to the solvent by supplying power, w_o, to the two

28
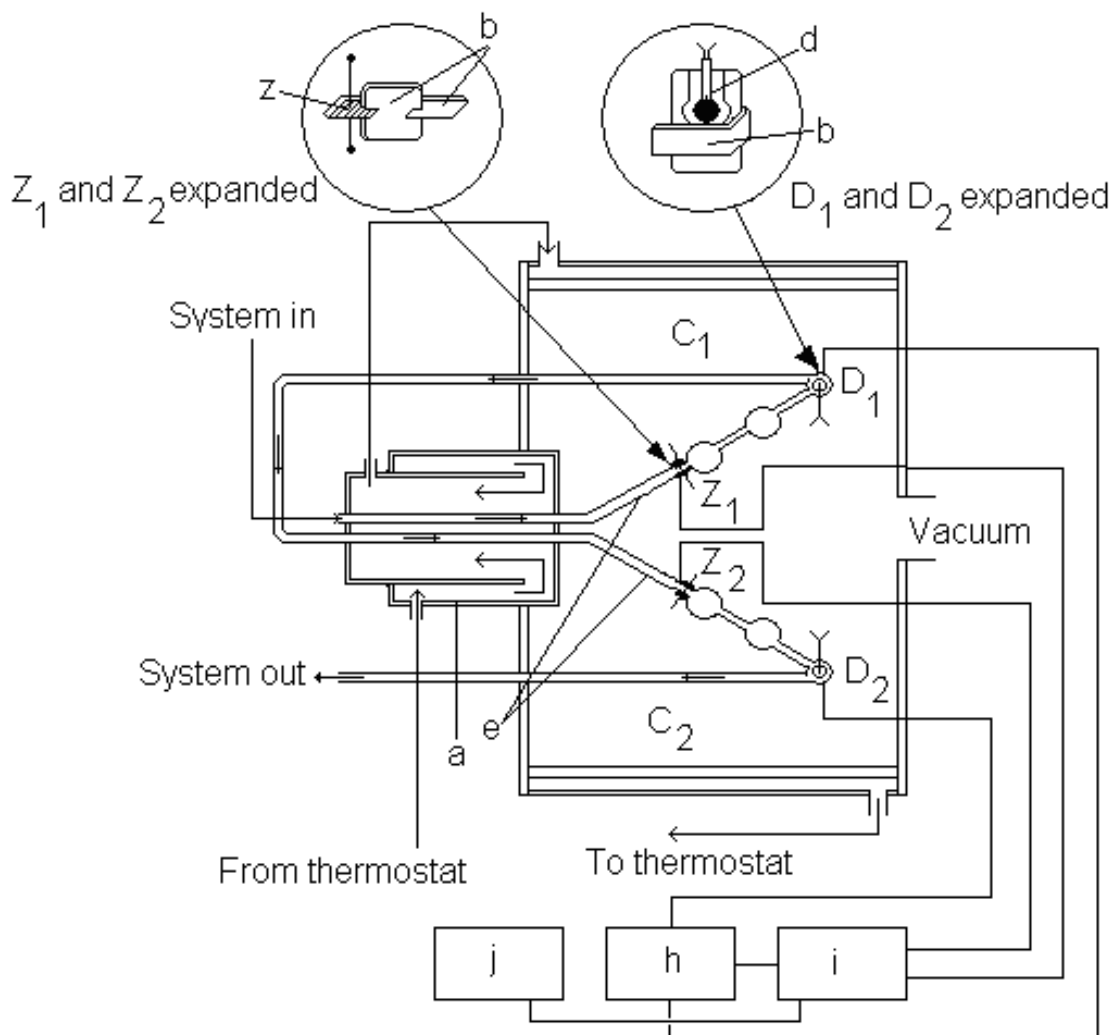
Figure 3.3 Schematic diagram of the Picker-flow microcalorimeter: (a), pre-thermostated water jacket; (b), flattened parts of the stainless-steel tubing; (d), thermistor detectors; (e) un-flattened stainless steel tubing; (h), HP3456A digital voltmeter; (i), feedback circuit; (j), IBM computer; (z), zener diode (Schematic is a re-drawing from the schematic presented in Picker *et. al*, 1971).

cells, C_1 and C_2, via two zener diodes (z), Z_1 and Z_2. Z_1 and Z_2 are Germanium chips that

are soldered onto flattened parts of the stainless-steel tubing (b) of the calorimeter in

order to allow maximum thermal contact (Picker *et al.*, 1971). Through a feedback

circuit (i), power is supplied either to Z_1 or Z_2 in order to ensure that D_1 and D_2 have

identical readouts. When solvent is flowing through the un-flattened stainless steel

tubing (e) in both C_1 and C_2, the power supplied to Z_1 and Z_2 are almost identical. If a solution of a higher heat capacity enters C_1 but not C_2, then the power supplied to Z_1 will be increased in order to ensure that both D_1 and D_2 have the same readouts. The difference in power supplied to Z_1 with respect to Z_2 (known as Δw) is measured as a voltage change by a HP3456A digital voltmeter (h) and subsequently recorded using an IBM computer (j). In the experiments, the flow rate of liquid through the cells is kept constant via gravity feed and careful adjustment of the liquid levels. Therefore:

$$w_s = w_o + \Delta w, \tag{3.8}$$

where w_s is the total power supplied to Z_1 in order to add thermal energy to the solution such that D_1 and D_2 have the same readout. Since the voltage change is proportional to the relative heat capacity of the solution, the volumetric heat capacity therefore becomes:

$$\frac{\sigma_s}{\sigma_1} = 1 + \frac{\Delta w}{w_o}, \tag{3.9}$$

where σ_1 is the volumetric heat capacity of pure water. Using equation (3.8), the massic heat capacity of the system may be calculated using the following equation:

$$\frac{c_{p2}}{c_{p1}} = \frac{\sigma_s \cdot \rho_1}{\sigma_1 \cdot \rho_2}$$

$$= \frac{\rho_1}{\rho_2} \cdot \left(1 + \frac{\Delta w}{w_o}\right). \tag{3.10}$$

A diagram of a typical readout obtained from the Picker-flow microcalorimeter is shown as Figure 3.4. Initially, the baseline, w_o, is obtained with the reference solution (solvent) running through both cells, C_1 and C_2 (a). At this point, approximately the same amount of power is supplied to Z_1 and Z_2 to ensure that D_1 and D_2 have identical readouts. Therefore, the Δw is approximately 0. As a solution with a higher heat capacity
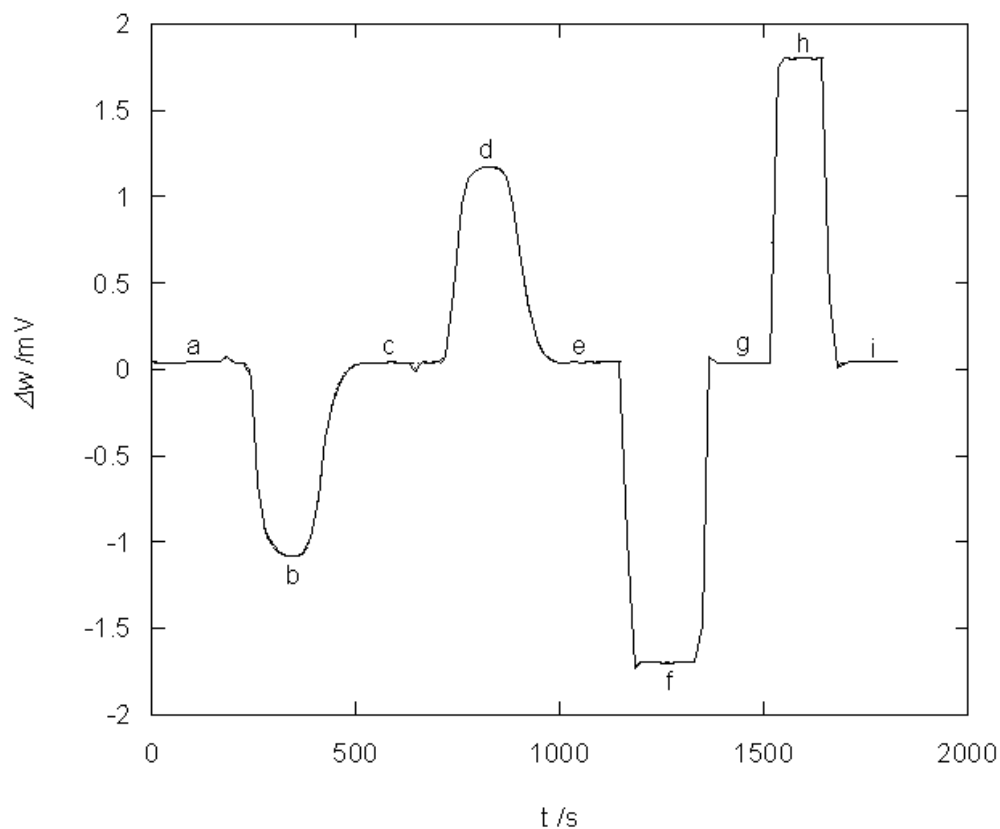
Figure 3.4 A typical output signal of Δw against time for the Picker-flow microcalorimeter.

enters C_1 (b), the power supplied to Z_1 is raised in order to maintain the same readout

from D_1 and D_2. This can be seen as a deflection along the Δw axis.   Eventually, cell C_2

is filled with the solution and the power supplied to Z_1 is reduced in order to ensure that

D_1 and D_2 again, have the same readout. At this point (c), the Δw goes back to

approximately 0 as both cells contain the solution of interest. At this stage, the solvent is

reintroduced into C_1 and the Δw profile is reversed (d-e). An electrical calibration is

performed by subtracting a given power from w_o for each zener (f-i). A measurement of

the Δw deflections associated with the calibration enables the calculation of a constant. This constant can then be used along with the Δw deflections seen in (b) and (d) to determine the massic heat capacity of the solution using equation (3.10).

To ensure a precise calculation of the calibration constant, an optimal flow rate must be used within the system. At this optimal flow rate, the calibration peaks, (f) and (h) in Figure 3.4 rapidly approach maxima and then plateau. When such peaks exist, the Δw deflection is easy to determine, as is the calibration constant.

Although, as shown in Figure 3.3, the calorimeter chamber containing the cells is evacuated (to $p = 2 \times 10^{-3}$ mbar, using a D4A direct drive vacuum pump and Edwards E50 Air-cooled diffusion pump), there remains a small amount of thermal transfer from the cells C_1 and C_2 to the surroundings. Therefore, a constant, known as an F-factor, is calculated to account for this heat loss. By using an agreed upon set of heat capacities for the aqueous sodium chloride system, a comparison is made between the selected volumetric heat capacities (Perron *et al.*, 1975) and those measured with the Picker system (Desnoyers *et al.*, 1976). The value of this Picker system's F-factor has been determined to be 1.01609 ± 0.0076 and has been calculated using equation (3.11):

$$F = \left(\frac{w_o^*}{w_s^*}\right) \cdot \frac{w_s}{w_o}, \tag{3.11}$$

where the variables containing an "*" represent the standard data of Perrron *et al.* (1975). The uncertainty in massic heat capacities associated with the Picker instrument is estimated to be $\delta c_p = \pm 7 \times 10^{-5}$ J·K^{-1}·mol^{-1} (Marriott, 1999).

A continuous flow of solvent and solution through the Picker is ensured with the use of a four-way liquid chromatography valve. This is done to avoid the introduction of

air pockets between the introduction of solvent and the sample into the instrument that could cause a rapid increase in power supplied to either Z_1 or Z_2. Such power surges could potentially cause damage to the feedback circuit.

The massic heat capacity data for a solution of interest, calculated from the measured voltages, equation (3.10), and the massic heat capacity of water, can be used to calculate the apparent molar heat capacity, $C_{p,2\phi}$, of the solution (as shown in equation (2.20)), where values for c_{p1} were taken from Stimson (1955). Relative uncertainties for the apparent molar heat capacities may be calculated using equation (3.12):

$$\left(\delta C_{p,2\phi}\right)^2 = \left(\frac{\partial C_{p,2\phi}}{\partial c_{p2}}\right)^2 \cdot \delta c_{p2}{}^2 + \left(\frac{\partial C_{p,2\phi}}{\partial m_2}\right)^2 \cdot \delta m_2{}^2$$

$$\delta C_{p,2\phi} = \left(M_2 + \frac{1000}{m_2}\right) \cdot \delta c_{p2} + \left(1000 \cdot \frac{c_{p2} - c_{p1}}{m_2^2}\right) \cdot \delta m_2. \tag{3.12}$$

Similar to the Sodev O2D vibrating tube densimeter, periodic calibrations were performed using aqueous solutions of NaCl in order to show the continued precision of the calorimeter. Calculated apparent molar heat capacities, $C_{p,2\phi}$, of NaCl$_{(aq)}$ (calculated using equation (2.20)) were used in equation (2.38) to calculate apparent molar heat capacities at infinite dilution, $C_{p2}{}^0$, at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and at $p = 0.1$ MPa. These $C_{p2}{}^0$ values have been compared with those $C_{p2}{}^0$ values reported by Marriott (1999), Archer (1992), and Desnoyers $et\ al.$ (1976). This comparison is shown in Table 3.2 and indicates that there is good agreement between the calculated $C_{p2}{}^0$ values reported in this study and those previously reported at each temperature of interest. Such agreements provide a high degree of confidence in the precision of measurements for the calorimeter over the course of the studies presented in this thesis.

Table 3.2 A comparison of apparent molar heat capacity values at infinite dilution, C_{p2}^0, for $NaCl_{(aq)}$ solutions at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa: those calculated in this study[f] using a Picker-flow microcalorimeter compared to those reported by Marriott (1999)[g], Archer (1992)[h], and Desnoyers *et al.* (1976)[i]

T /(K)	$C_{p2}^{0\,f}$ /(J·K⁻¹·mol⁻¹)	$C_{p2}^{0\,g}$ /(J·K⁻¹·mol⁻¹)	$C_{p2}^{0\,h}$ /(J·K⁻¹·mol⁻¹)	$C_{p2}^{0\,i}$ /(J·K⁻¹·mol⁻¹)
288.15	-107.5(0.5)	-107(2)	-108.3(0.2)	
298.15	-85.33(0.08)	-85.7(0.4)	-84.6(0.2)	-84.4
313.15	-67.4(0.8)	-68.9(0.4)	-65.8(0.3)	
328.15	-59.1(0.3)	-59(1)	-58.92(0.09)	

3.2 The High Temperature and Pressure Vibrating Tube Densimeter

A high temperature and pressure vibrating tube densimeter was recently modified to measure densities for selected solutions, relative to those of the solvent. Such measurements were performed over an extended range of temperatures and pressures, significantly larger than those that can be provided by the Sodev O2D densimeter described previously. The general design of the instrument has been previously reported (Lukacs, 2003; Marriott, 1998; Hakin *et al.*, 2004a; Hakin *et al.*, 1998), but this new model offers enhanced temperature control.

Like the Sodev O2D vibrating tube densimeter, the high temperature and pressure vibrating tube densimeter makes use of equations (3.1), (3.2), and (3.3) to obtain the relative density of a solution. Solutions of $NaCl_{(aq)}$ of precisely known molalities are used as the calibrating system together with pure water. The densities of $NaCl_{(aq)}$ and pure water have been well modeled over the temperature and pressure ranges of interest by Archer (1992). Using Archer's (1992) equation of state program for $NaCl_{(aq)}$, the densities of solutions of $NaCl_{(aq)}$ at selected temperatures, pressures, and molalities can be calculated. Archer's program also yields density data for pure water. Using the
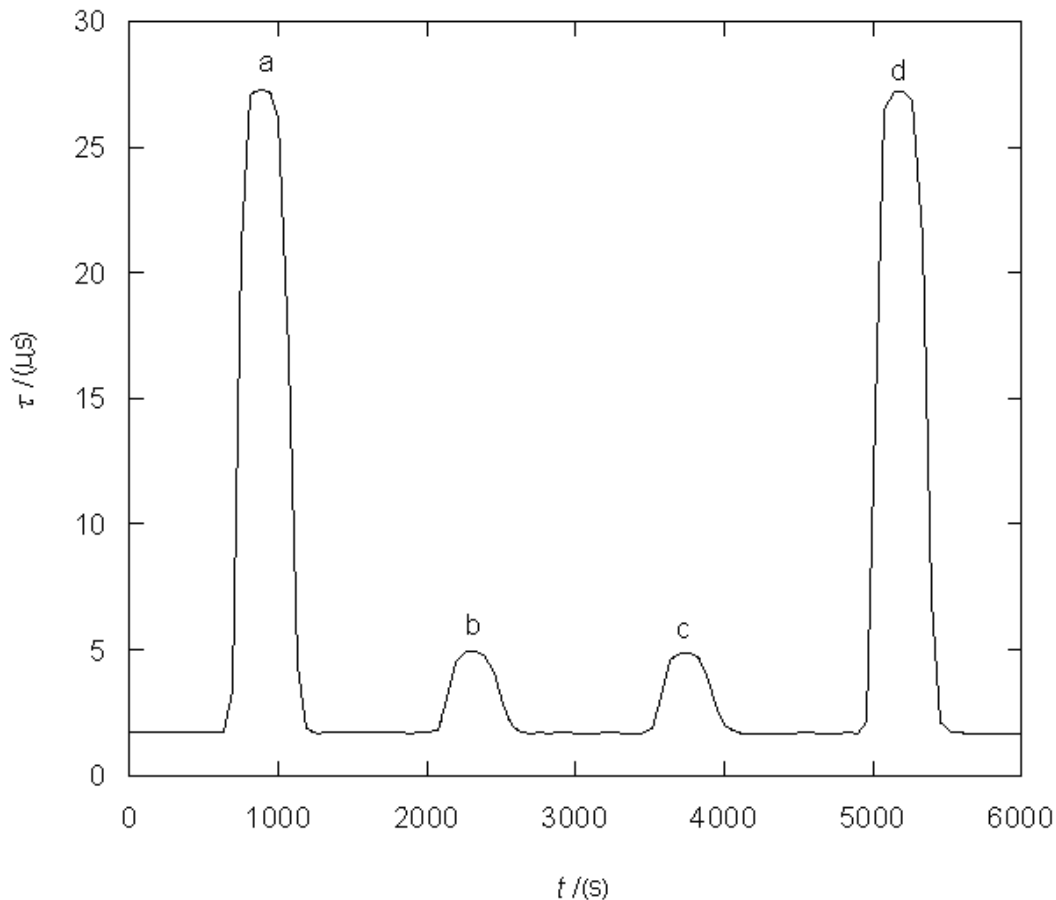
Figure 3.5 A plot of time period of vibration against time for the high temperature and pressure vibrating tube densimeter (at $T = 373.15$ K and $p = 5.00$ MPa for $Yb(CF_3SO_3)_{3(aq)}$).

method described above for the Sodev O2D vibrating tube densimeter, the relative

density of a solution of interest can be determined using equation (3.3). To minimize

errors associated with temperature and pressure differences experienced, the densimeter

constant is determined several times throughout an experimental run and is averaged. A

typical readout from an experimental run is shown in Figure 3.5. The peaks (a) and (d)

are those for a solution of $NaCl_{(aq)}$ of precisely known molality (in this case

$m = 5.3322$ mol·kg^{-1}) and peaks (b) and (c) are associated with the solution of interest (in

this case, $Yb(CF_3SO_3)_{3(aq)}$, $m = 0.06638$ mol·kg^{-1}). The relative uncertainty in the density measurements of the vibrating tube densimeter is described by equation (3.13):

$$\delta\Delta\rho_e = \left(\delta\Delta\rho_r{}^2 + \delta\Delta\rho_s{}^2\right)^{1/2},$$
(3.13)

where $\delta\Delta\rho_e$ is the probable random error of the density calculation based on the deviation between two peaks of the same type (either $NaCl_{(aq)}$ calibration peaks or system peaks, as shown in Figure 3.5). $\delta\Delta\rho_r$ is the difference between the calibration peaks and $\delta\Delta\rho_s$ is the difference between the two system of interest peaks. The calculation of the relative uncertainty of the apparent molar volume for each system of interest, using equation (3.14) (Hakin *et al.*, 1998; Marriott, 1998), is:

$$\delta V_{2\phi} = -\left(M_2 + \frac{1000}{m_2}\right)\cdot\frac{\delta\Delta\rho_e}{\rho_2{}^2} + \left(1000\cdot\frac{(\rho_2 - \rho_1)}{m_2{}^2\cdot\rho_2\cdot\rho_1}\right)\cdot\delta m_2.$$
(3.14)

A schematic of the high temperature and pressure vibrating tube densimeter is shown as Figure 3.6. Purified and degassed water (a) is used as a reference solvent and is pumped (at a constant rate of 0.4 mL·min^{-1}) into the densimeter using a Waters 501 HPLC pump (b). A set of two Rheodyne 7125 manual injection valves (c) connected with 316 stainless steel tubing permits the solvent to flow into the densimeter and also allows for the introduction of solution samples through sample loops of precisely known volume. When an injection valve is in the load position (1), a solution can be loaded into the sample loop and the solvent is allowed to pass through into the densimeter. In the inject position (2), the loaded sample solution travels into the densimeter. The actual vibrating tube is housed within a Varian 3700 gas chromatograph oven (d) capable of reaching temperatures of $T = 623.15$ K whilst maintaining that temperature to

36
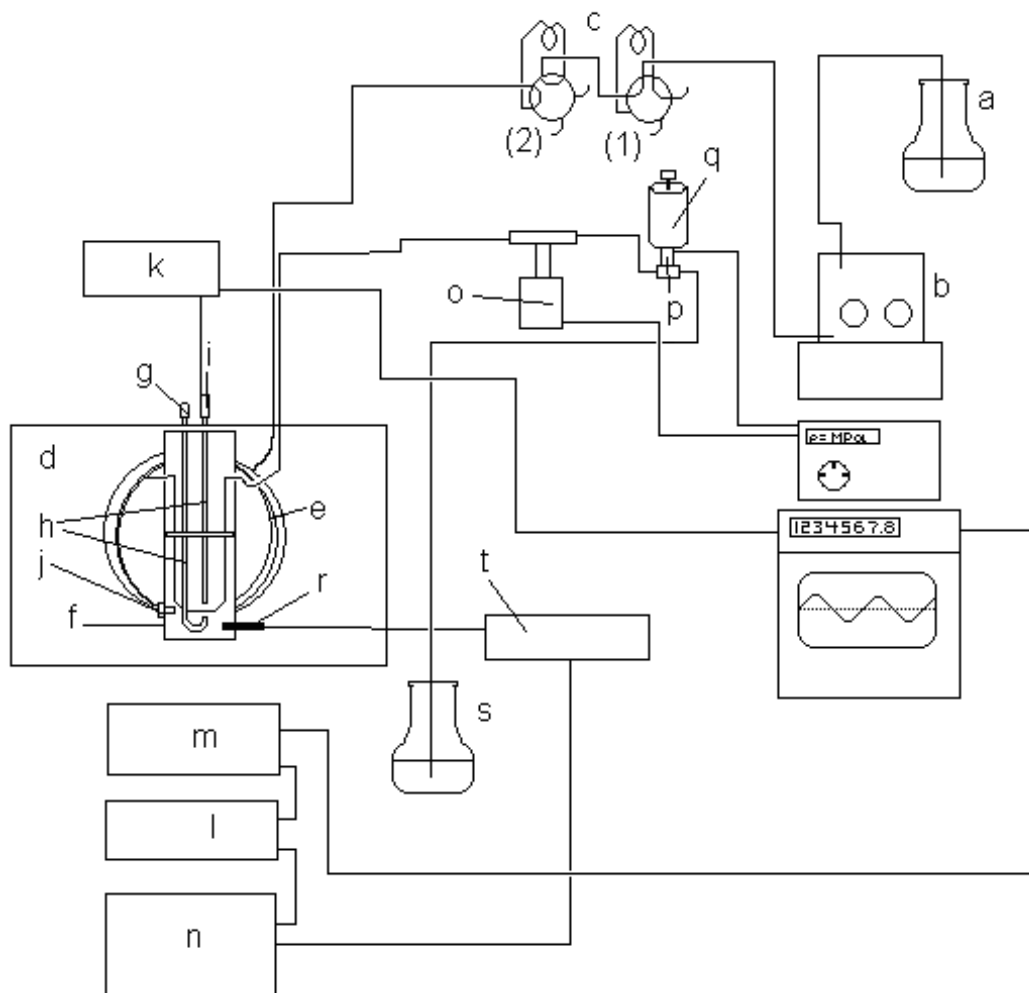
Figure 3.6 Schematic of the high temperature and pressure vibrating tube densimeter: (a), flask of reference polished and de-gassed $H_2O_{(l)}$; (b), Waters 501 HPLC pump; (c), Rheodyne 7125 injection valves; (d), Varian 3700 gas chromatography oven; (e), pre-heater coil; (f), brass block; (g), LED source; (h), glass rods; (i), LED detector; (j), permanent magnet; (k), Optoelectronics 8040 multifunction counter/timer; (l), PC; (m), RS232 interface; (n), IEEE 488 serial interface board; (o), Omega 940714 pressure transducer; (p), Swagelok SS-SS2 low-flow needle valve; (q), Intelligent Motion Systems, Inc. M2-2232-D stepping motor; (r), platinum resistance probe; (s), waste; (t), Hewlett Packard 34401A multimeter.

$T = \pm 0.1$ K with the use of a circulating fan. Stainless steel tubing that carries either the

solvent or the solution enters the oven and a pre-heater coil (e) in order to allow the

system of interest to come to thermal equilibrium. The vibrating tube is connected to a

brass block (f) that is designed to float freely within the oven. This is necessary because the fan within the oven causes additional vibration that interferes with the vibration of the tube. The period of vibration of the tube is determined using an optical LED source (g), two glass rods (h), and an optical detector (i). Light from the LED light source travels down the curved glass source rod and then up the straight glass detector rod to the optical detector. An alternating current is passed through the vibrating tube and creates a magnetic field. A permanent magnetic pickup (j) ensures the continuous vibration of the tube throughout the experiment. When the tube vibrates in and out of the path of the light traveling along the glass rods, the amount of light that reaches the optical detector varies. The resulting signal takes the form of a sine wave that is electronically transformed into a square wave. The square wave is the signal that is inputted to an Optoelectronics 8040 multifunction counter/timer (k). The counter and software program constantly averages multiples of 1 000 counts which are subsequently stored in a PC (l) via an RS232 (m) serial interface. The temperature within the oven is monitored using a platinum resistance probe (r) that is connected to an HP 33401A multimeter (t) that in turn is IEEE 488 interfaced (n) to the PC. Once the solution or solvent has passed through the oven, it heads past an Omega 940714 pressure transducer (o) that forms part of a home-built electronic pressure control system, which also contains a feedback circuit connected to a Swagelok SS-SS2 low-flow needle valve (p). The operation of the needle valve is controlled by an Intelligent Motion Systems, Inc. M2-2232-D stepping motor (q). The pressure control system permits pressure regulation of $\delta p = \pm \ 0.01$ MPa up to pressures of $p = 15.00$ MPa. After passing through the pressure control system, all fluids are discarded into a waste container (s).

The precision of this recently modified vibrating tube densimeter has been determined by measuring the densities of aqueous NaBr solutions of precisely known molalities, and comparing these densities with those which may be calculated using Archer's program for $NaBr_{(aq)}$ (Archer, 1991). A comparison of measured relative densities, ρ_{expt}, and calculated apparent molar volumes, $V_{2\phi}$ (calculated using equation (2.19)), with those reported by Archer ($\rho_{(archer)}$ and $V_{2\phi(archer)}$, 1991) for $NaBr_{(aq)}$ is provided in Table 3.3. The maximum deviation from the expected density is approximately $\delta\rho = \pm\ 5\times10^{-5}\ g\cdot cm^{-3}$, but generally lies within the part per million range. The main exception appears to be a point for $NaBr_{(aq)}$ at $T = 348.15$ K and $p = 15.00$ MPa, with a molality $m = 0.4188$ mol·kg^{-1} (shown in Table 3.3). Reasons for this single discrepancy are not known. Figure 3.7 provides an additional visual aid to show these maximum deviations presented in Table 3.3, at all temperatures and pressures of interest.
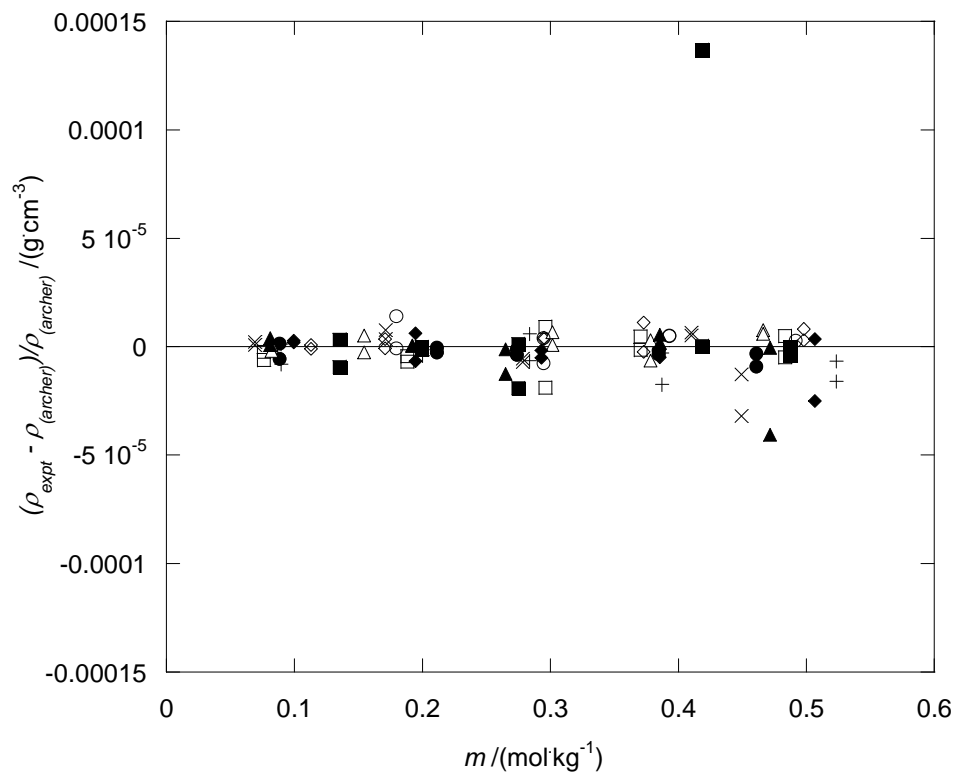
Figure 3.7 Deviations in the experimental densities, ρ_{expt}, for NaBr$_{(aq)}$ (those obtained experimentally using the modified vibrating tube densimeter compared to those calculated using the values reported by Archer ($\rho_{(archer)}$, 1991)): $\bullet$, T = 323.15 K, p = 5.00 MPa; $\times$, T = 323.15 K, p = 10.00 MPa; $+$, T = 323.15 K, p = 15.00 MPa; $\square$, T = 348.15 K, p = 5.00 MPa; $\diamondsuit$, T = 348.15 K, p = 10.00 MPa; $\blacksquare$, T = 348.15 K, p = 15.00 MPa; $\triangle$, T = 373.15 K, p = 5.00 MPa; $\blacktriangle$, T = 373.15 K, p = 10.00 MPa; $\circ$, T = 373.15 K, p = 15.00 MPa; and $\blacklozenge$, T = 423.15 K, p = 10.00 MPa.

Table 3.3 Comparison of ρ_{expt} and $V_{2\phi}$ of NaBr$_{(aq)}$ determined using the modified vibrating tube densimeter with values that were calculated using Archer's (1991) program for NaBr$_{(aq)}$

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	ρ_{expt} /(g·cm^{-3})	$V_{2\phi}$ /(cm^3·mol^{-1})	$10^6(\rho_{expt} - \rho_{(archer)})$ /(g·cm^{-3})	$V_{2\phi} - V_{2\phi(archer)}$ /(cm^3·mol^{-1})
			T = 323.15 K, p = 5.00 MPa			
323.98	5.007	0.0883	0.99655	25.59	1.64286	-0.02
323.97	5.009	0.0883	0.99654	25.67	-5.56896	0.06
323.97	5.008	0.2114	1.00586	25.94	-2.63752	0.02
323.98	5.008	0.2114	1.00585	25.93	-0.56335	0.01
324.00	5.008	0.2737	1.01051	26.05	-3.82903	0.02
324.00	5.007	0.2737	1.01051	26.04	-1.19865	0.01
324.00	5.007	0.3846	1.01877	26.21	-3.43574	0.01
324.00	5.007	0.3846	1.01877	26.21	-1.62271	0.01
324.01	5.007	0.4609	1.02440	26.32	-9.30242	0.02
324.01	5.006	0.4609	1.02441	26.31	-3.23682	0.01
			T = 323.15 K, p = 10.00 MPa			
324.05	10.015	0.0691	0.99720	25.67	0.92594	-0.02
324.05	10.014	0.0691	0.99720	25.65	2.30000	-0.04
324.05	10.015	0.1711	1.00493	25.96	3.43262	-0.01
324.05	10.014	0.1711	1.00493	25.94	7.82015	-0.03
324.04	10.014	0.2783	1.01298	26.20	-5.57986	0.02
324.04	10.016	0.2783	1.01298	26.20	-7.17799	0.02
324.05	10.017	0.4101	1.02279	26.36	5.20267	-0.01
324.05	10.016	0.4101	1.02279	26.36	6.57420	-0.01
324.05	10.016	0.4493	1.02567	26.45	-13.1402	0.03
324.05	10.017	0.4493	1.02565	26.49	-32.7851	0.07
			T = 323.15 K, p = 15.00 MPa			
324.24	15.016	0.0896	1.00079	25.88	1.33564	-0.02
324.24	15.022	0.0896	1.00078	26.00	-8.05667	0.10
324.24	15.016	0.2001	1.00915	26.18	-1.48872	0.01
324.24	15.013	0.2001	1.00914	26.20	-4.04711	0.03
324.24	15.016	0.2838	1.01542	26.35	-6.43588	0.03
324.24	15.014	0.2838	1.01543	26.30	6.07333	-0.02
324.23	15.014	0.3872	1.02311	26.48	-3.06150	0.01
324.23	15.014	0.3872	1.02310	26.52	-17.7409	0.05
324.23	15.013	0.5236	1.03316	26.65	-6.80117	0.02
324.23	15.013	0.5236	1.03315	26.67	-16.5676	0.04

Table 3.3 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	ρ_{expt} /(g·cm^{-3})	$V_{2\phi}$ /(cm^3·mol^{-1})	$10^6(\rho_{expt} - \rho_{(archer)})$ /(g·cm^{-3})	$V_{2\phi} - V_{2\phi(archer)}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 5.00$ MPa			
349.14	5.013	0.0763	0.98220	25.84	-2.48360	0.04
349.14	5.011	0.0763	0.98220	25.89	-5.93718	0.09
349.14	5.011	0.1886	0.99059	26.19	-4.21927	0.03
349.14	5.009	0.1886	0.99060	26.18	-6.77202	0.02
349.14	5.007	0.2962	0.99857	26.38	8.99591	-0.01
349.14	5.009	0.2962	0.99854	26.47	-18.8805	0.08
349.13	5.010	0.3704	1.00402	26.52	4.63119	0.00
349.14	5.009	0.3704	1.00401	26.53	-1.56943	0.01
349.14	5.011	0.4832	1.01223	26.70	-4.92276	0.01
349.13	5.009	0.4832	1.01224	26.68	4.94061	-0.01
			$T = 348.15$ K, $p = 10.00$ MPa			
349.15	10.012	0.1129	0.98713	26.10	-0.97158	0.01
349.15	10.012	0.1129	0.98713	26.08	0.76766	-0.01
349.16	10.011	0.1708	0.99145	26.24	3.47652	-0.02
349.16	10.010	0.1708	0.99145	26.27	-0.62556	0.01
349.16	10.013	0.2949	1.00064	26.52	4.33086	-0.01
349.16	10.012	0.2949	1.00064	26.53	3.48529	0.00
349.17	10.011	0.3730	1.00637	26.68	-2.29765	0.02
349.16	10.016	0.3730	1.00638	26.64	11.1125	-0.02
349.16	10.016	0.4979	1.01547	26.84	3.11726	0.00
349.16	10.011	0.4979	1.01547	26.83	8.23859	-0.01
			$T = 348.15$ K, $p = 15.00$ MPa			
349.57	15.018	0.1355	0.99074	26.28	3.13795	-0.03
349.58	15.016	0.1355	0.99071	26.38	-9.14684	0.07
349.58	15.016	0.1998	0.99551	26.49	-1.40172	0.02
349.58	15.020	0.1998	0.99551	26.48	-0.12824	0.01
349.57	15.016	0.2752	1.00108	26.71	-19.2727	0.08
349.58	15.024	0.2752	1.00110	26.63	1.14695	0.00
349.57	15.016	0.4188	1.01162	26.87	0.34217	0.01
349.58	15.016	0.4188	1.01175	26.53	138.270	-0.33
349.56	15.016	0.4875	1.01661	26.96	-0.08459	0.00
349.57	15.016	0.4875	1.01660	26.97	-4.18457	0.01

Table 3.3 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	ρ_{expt} /(g·cm^{-3})	$V_{2\phi}$ /(cm^3·mol^{-1})	$10^6(\rho_{expt} - \rho_{(archer)})$ /(g·cm^{-3})	$V_{2\phi} - V_{2\phi(archer)}$ /(cm^3·mol^{-1})
			$T = 373.15$ K, $p = 5.00$ MPa			
374.10	5.012	0.0824	0.96619	25.27	-1.80582	0.02
374.10	5.011	0.0824	0.96619	25.24	0.74309	0.00
374.10	5.010	0.1545	0.97155	25.58	-2.64102	0.03
374.11	5.010	0.1545	0.97156	25.54	5.14414	-0.01
374.12	5.011	0.3019	0.98240	25.94	6.71470	-0.02
374.12	5.012	0.3019	0.98239	25.97	0.75062	0.01
374.12	5.012	0.3784	0.98796	26.14	-6.27979	0.02
374.12	5.011	0.3784	0.98797	26.12	2.90901	0.00
374.12	5.012	0.4661	0.99431	26.27	7.63784	-0.01
374.12	5.009	0.4661	0.99431	26.28	5.91048	0.00
			$T = 373.15$ K, $p = 10.00$ MPa			
374.16	10.017	0.0812	0.96837	25.37	3.89253	-0.05
374.15	10.024	0.0812	0.96837	25.41	0.84275	-0.01
374.15	10.019	0.1923	0.97662	25.85	0.30770	0.00
374.16	10.023	0.1923	0.97662	25.85	0.52846	0.00
374.15	10.022	0.2649	0.98195	26.10	-12.3824	0.05
374.15	10.025	0.2649	0.98196	26.06	-1.22766	0.01
374.16	10.022	0.3854	0.99074	26.30	1.88608	0.00
374.16	10.022	0.3854	0.99074	26.29	5.34098	-0.01
374.16	10.022	0.4716	0.99694	26.54	-40.3372	0.09
374.16	10.021	0.4716	0.99697	26.46	-0.48039	0.01
			$T = 373.15$ K, $p = 15.00$ MPa			
374.60	15.020	0.1794	0.97763	25.97	13.7914	0.00
374.59	15.025	0.1794	0.97763	25.98	-0.79835	0.01
374.58	15.014	0.2948	0.98610	26.30	-7.40006	0.03
374.59	15.020	0.2948	0.98610	26.26	3.99878	-0.01
374.58	15.027	0.3931	0.99327	26.45	4.97403	-0.01
374.57	15.027	0.3931	0.99327	26.45	5.11057	-0.01
374.59	15.029	0.4919	1.00039	26.62	2.78765	-0.01
374.58	15.027	0.4919	1.00040	26.63	2.85859	0.00

Table 3.3 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	ρ_{expt} /(g·cm^{-3})	$V_{2\phi}$ /(cm^3·mol^{-1})	$10^6(\rho_{expt} - \rho_{(archer)})$ /(g·cm^{-3})	$V_{2\phi} - V_{2\phi(archer)}$ /(cm^3·mol^{-1})
T = 423.15 K, p = 10.00 MPa
423.88	10.025	0.0996	0.92926	22.07	1.91207	-0.02
423.91	10.019	0.0996	0.92923	22.06	2.54658	-0.02
423.92	10.024	0.1946	0.93631	22.71	-6.29275	0.04
423.92	10.020	0.1946	0.93632	22.64	5.74889	-0.03
423.92	10.027	0.2928	0.94355	23.11	-1.50971	0.01
423.91	10.021	0.2928	0.94355	23.12	-4.89092	0.02
423.90	10.025	0.3854	0.95032	23.44	-4.71557	0.02
423.91	10.023	0.3854	0.95032	23.42	-1.13566	0.01
423.91	10.018	0.5069	0.95910	23.75	3.30165	0.00
423.89	10.018	0.5069	0.95909	23.81	-23.9129	0.05

4) THERMOCHEMICAL STUDY OF AQUEOUS SOLUTIONS OF THE RARE EARTH ELEMENT (REE) TRIFLATES AT AMBIENT PRESSURE AND NEAR AMBIENT TEMPERATURES

4.1. Introduction

As discussed in Chapter 2, volume and heat capacity data can provide information which can be used to understand the nature of solute-solvent and solute-solute interactions within a solution. The ultimate goal of this thesis is to provide such data, with a focus on aqueous rare earth element (REE) containing salt solutions.

Previous work on aqueous REE metal containing salt systems has focused on the volumetric and calorimetric studies of aqueous perchlorates, nitrates, chlorides, and sulfates (Hakin *et al.*, 2003a, 2003b, 2004b, 2005; Marriott *et al.*, 2001) at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa. Additional studies on $Yb(ClO_4)_{3(aq)}$ have been completed at $T = (323.15, 348.15, 373.15, 398.15,$ and $423.15)$ K and $p = (10.0, 20.0,$ and $30.0)$ MPa (Hakin *et al.*, 2004a). The earlier work of Spedding *et al.* (1966a, 1966b, 1975a, 1975b, 1979) also reported apparent molar volumes and heat capacities for a variety of aqueous REE salt solutions. However, much of Spedding's previous work was restricted to the temperature and pressure conditions $T = 298.15$ K and $p = 0.1$ MPa. Therefore, one aim of the work presented in this chapter is to compare the single ion volumes and heat capacities obtained from studies of aqueous REE triflate systems with those previously reported in the literature (Hakin *et al.*, 2003a, 2003b, 2004b, 2005; Marriott *et al.*, 2001; Xiao *et al.*, 1996a, 1996b, 1997a). In addition, another goal is to extend the temperature surface of the volumetric and calorimetric

properties of aqueous REE salt systems to temperatures and pressures that may be more suited to their growing commercial and industrial importance.

The REEs have a wide variety of important industrial applications. They are commonly used in the manufacture of high field strength magnets, as glazes in ceramics, as neutron absorbers in nuclear reactors, and as phosphors in cathode ray tubes. Despite the name, the natural abundances of these elements in the earth's crust (with the exception of promethium) surpass that of mercury (Cotton and Wilkinson, 1988; Lide, 1999-2000). However, they have proven difficult to extract from their ores. Therefore, fundamental thermodynamic data for the aqueous REE metal ions are of significant importance in order to assist in the extraction processes commonly used (Sabot and Maestro, 1995). To further explore the properties of the REE salts, this thesis has focused on the triflate salts. The triflate (trifluoromethanesulfonate) anion is not prone to oxidation at higher temperatures or speciation in aqueous solutions that commonly affects the Cl^-, NO_3^-, and SO_4^{2-} anions (Marriott et $al.$, 2001; Rard et $al.$, 1977, 1979, 1981, 1982). Hence, volumetric and calorimetric measurements on the aqueous REE triflates ($R(CF_3SO_3)_3$) should, in theory, yield more precise single ion data for the trivalent REE metal cations (Erickson et $al.$, 2007).

4.2. Trifluoromethanesulfonic Acid in Aqueous Solution

4.2.1. Experimental

Trifluoromethanesulfonic acid (triflic acid, CF_3SO_3H) was obtained from Aldrich Chemical Company (98%, Catalog No. 15853-4). In order to reduce any hazards

associated with the concentrated acid, stock samples were diluted to 6.0 mol·L^{-1} using

water that was polished to a resistance of 18.3 MΩ using an Osmotics model Aries

high-purity D.I. loop. Gravimetric analysis (Skoog and West, 1982) determined the

sulfate ion content of the 6.0 mol·L^{-1} triflic acid to be less than 0.05 mol % (through

precipitated $BaSO_{4(s)}$). The $CF_3SO_3H_{(aq)}$ was further diluted to a molarity of

$c = 0.22$ mol·L^{-1} using the polished water and was standardized against

tris(hydroxymethylamino)methane (THAM) obtained from the Fisher Scientific

Company (0.9999 mol fraction, Catalog No. T-395). Stock solutions of THAM were

made by mass to ± 0.00001 g using a Mettler Toledo AT201 analytical balance. Methyl

red was used as an endpoint indicator in these titrations. The titrations were repeated at

least three times to ensure a higher degree of precision (less than 0.5 mol % deviation).

All subsequent solutions of the acid used for thermodynamic measurements were made

by mass to ± 0.00001 g on the molality concentration scale by dilution with polished

water. The solutions were placed in securely sealed volumetric flasks and used within 24

hours of their preparation.

4.2.2. Results and conclusions

Density and heat capacity measurements were obtained using the Picker

instrument described in Chapter 3. Apparent molar volumes, $V_{3\phi}$, and apparent molar

heat capacities, $C_{p,3\phi}$, for triflic acid (previously defined as $V_{2\phi}$ and $C_{p,2\phi}$ in Chapter 2)

were calculated using equations (2.19) and (2.20), respectively, using measured relative

densities, ρ_{expt}, and massic heat capacities, $c_{p,expt}$ (where ρ_{expt} and $c_{p,expt}$ are synonymous

with ρ_2 and c_{p2}, previously identified in Chapter 2). M_3 is the molar mass of triflic acid,

which was identified as M_2 in equations (2.19) and (2.20). Calculated values of $\rho_{expt} - \rho_l$, $V_{3\phi}$, $((c_{p,expt} \cdot \rho_{expt})/(c_{p1} \cdot \rho_l)) - 1$, and $C_{p,3\phi}$ for each investigated solution of known concentration are reported in Table 4.1 along with their calculated relative uncertainties (reported in parentheses, and calculated using the standard propagation of error method described in Chapter 3).

It was necessary to determine the apparent molar properties of aqueous triflic acid for two reasons. First, the apparent molar properties are required in the use of Young's rule that permits the calculation of apparent molar properties of aqueous REE salt systems from solutions of the acidified REE salt solution. Second, the apparent molar properties of triflic acid can be used to obtain single ion information for the aqueous triflate anion.

Although the apparent molar properties for triflic acid, and therefore the triflate anion, were determined, the ionic strength range used in this study was not sufficient over the temperature range $T = (288.15, 298.15, 313.15,$ and $328.15)$ K. Therefore, a combination of the apparent molar properties of $CF_3SO_3H_{(aq)}$ presented in this thesis and those reported by Xiao *et al.* (2001) were combined and subjected to least squares regression analyses at each temperature. Equations (2.37) and (2.38) were used to model the concentration dependences of the apparent molar volume and apparent molar heat capacity sets, respectively. The appropriately calculated Debye-Hückel term (the term in equation (2.37) or (2.38) containing either A_V or A_J, respectively) was subtracted from the apparent molar volume or heat capacity in order to form the dependent variable for each regression. Estimates of the apparent molar properties at infinite dilution for the acid, V_3^0 and C_{p3}^0 (previously identified as V_2^0 and C_{p2}^0 in equations (2.37) and (2.38),
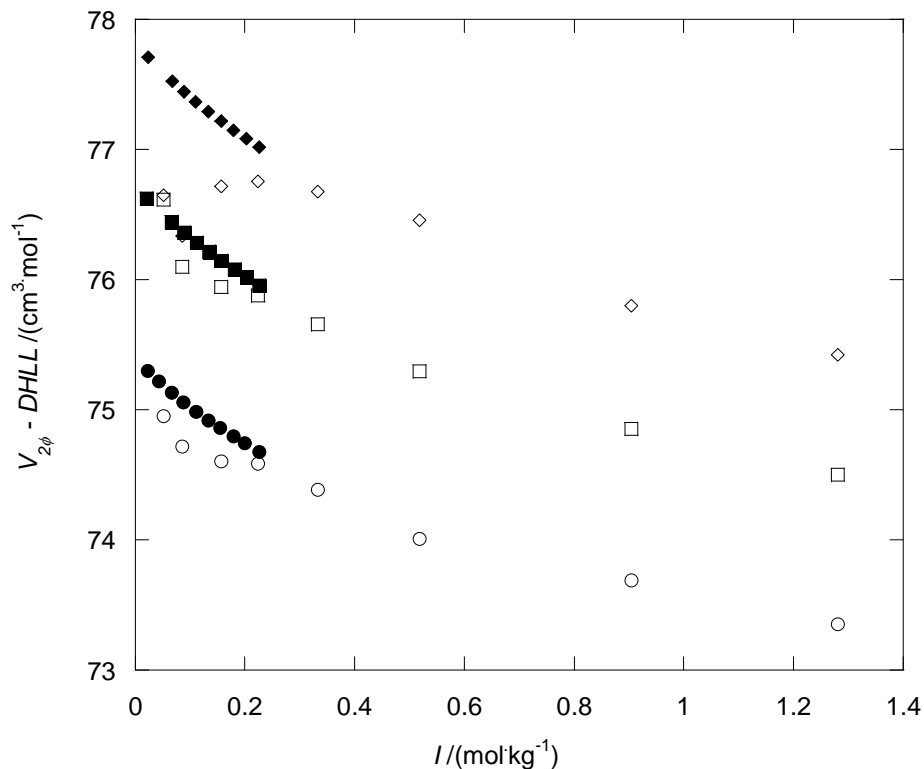
Figure 4.1 Comparison of the ionic strength dependence of $V_{3\phi}$ - *DHLL* values obtained from equation (2.37) for $CF_3SO_3H_{(aq)}$ with those calculated from the study by Xiao *et al.* (2001): •, current study at $T = 298.15$ K; ○ Xiao *et al.* (2001) at $T = 298.15$ K; ■, current study at $T = 313.15$ K; □, Xiao *et al.* (2001) at $T = 313.15$ K; ◆, current study at $T = 328.15$ K; ◇ Xiao *et al.* (2001) at $T = 328.15$ K.

respectively), and values for the parameters $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, $\beta^{(1)J}$, C^V, and C^J were

obtained from the regression analyses and are reported, along with their standard errors,

in Table 4.2. Table 4.2 also compares the values obtained in this study with those

reported by Xiao *et al.* (2001). Figure 4.1 presents a comparison of the ionic strength

dependences of $V_{3\phi}$ - *DHLL* values obtained from measurements conducted in this study

at $T = $ (298.15, 313.15, and 328.15) K and $p = 0.1$ MPa for $CF_3SO_3H_{(aq)}$ with those

previously reported by Xiao *et al.* (2001). The figure indicates good agreement between data sets. The same is true for the C_{p3}^0 values, although they are not shown in this thesis.

Subsequent global modeling was conducted in order to determine the temperature dependences of the factors V_3^0, C_{p3}^0, $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, $\beta^{(1)J}$, C^V, and C^J within equations (2.37) and (2.38). The following equations were utilized:

$$V_3^0 = a_1 + \frac{a_2}{(T - \theta)} + a_3 \cdot T, \tag{4.1}$$

$$\beta^{(0)V} = a_4 + a_5 \cdot T, \tag{4.2}$$

$$\beta^{(1)V} = a_6, \tag{4.3}$$

$$C^V = a_7, \tag{4.4}$$

$$C_{p3}^0 = c_1 + \frac{c_2}{(T - \theta)^2} + c_3 \cdot T, \tag{4.5}$$

$$\beta^{(0)J} = \frac{c_4}{T} + c_5 + c_6 \cdot T, \tag{4.6}$$

$$\beta^{(1)J} = \frac{c_7}{T} + c_8 + c_9 \cdot T, \tag{4.7}$$

$$C^J = c_{10}, \tag{4.8}$$

where θ is equal to 228 K. The model is based on the equations reported by Xiao *et al.* (1997b) for aqueous solutions of triflic acid and its sodium salt. Values for the a_i parameters (i = 1 to 7) and c_j parameters (j = 1 to 10) for equations (4.1) to (4.8) are reported in Table 4.3. It was found that the parameters $\beta^{(1)V}$, C^V, and C^J were independent of temperature, whereas V_3^0, C_{p3}^0, $\beta^{(0)V}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ were all well modeled well using equations (4.1) to (4.2) and (4.5) to (4.7) over the investigated temperature range. The $V_{3\phi}$ and $C_{p,3\phi}$ values calculated for $CF_3SO_3H_{(aq)}$ using equations (4.1) to (4.2)

Figure 4.2 Comparison of $V_{3\phi}$ values (as a function of molality) calculated using equation (2.19) ($V_{3\phi}$(calc)) with those calculated using equation (2.37) and the fitting parameters to equations (4.1) to (4.4) ($V_{3\phi}$(global)) for $CF_3SO_3H_{(aq)}$ at: •, T = 288.15 K; ×, T = 298.15 K; +, T = 313.15 K; and □, T = 328.15 K; and p = 0.1 MPa (the dashed lines represent the standard error).

and (4.5) to (4.7) over the investigated temperature range. The $V_{3\phi}$ and $C_{p,3\phi}$ values

calculated for $CF_3SO_3H_{(aq)}$ using equations (2.19) and (2.20) ($V_{3\phi}$ (calc) and $C_{p,3\phi}$ (calc))

have been compared to those $V_{3\phi}$ and $C_{p,3\phi}$ values for $CF_3SO_3H_{(aq)}$ calculated using

equations (2.37) and (2.38) and the calculated fitting parameters a_1 to a_7 and c_1 to c_{10} for

equations (4.1) to (4.8) ($V_{3\phi}$ (global) and $C_{p,3\phi}$ (global)), respectively, in Figures 4.2 and

Figure 4.3 Comparison of $C_{p,3\phi}$ values (as a function of molality) calculated using equation (2.20) ($C_{p,3\phi}$(calc)) with those calculated using equation (2.38) and the fitting parameters to equations (4.5) to (4.8) ($C_{p,3\phi}$(global)) for $CF_3SO_3H_{(aq)}$ at: •, $T = 288.15$ K; ×, $T = 298.15$ K; +, $T = 313.15$ K; and □, $T = 328.15$ K; and $p = 0.1$ MPa (the dashed lines represent the standard error).

4.3. As can be seen, there is good agreement between these values over the temperature range of study. Therefore, the temperature dependent models presented above used to describe the apparent molar properties of the triflic acid were subsequently used in combination with Young's rule in order to determine the apparent molar properties for the aqueous REE triflate salts presented in this thesis.

Table 4.1 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of CF_3SO_3H at known concentration at $T = $ (288.15, 298.15, 313.15, and 328.15) K and $p = 0.1$ MPa

m_3	$\rho_{expt} - \rho_l$	$V_{3\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p,3\phi}$
/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})
		$T = 288.15$ K		
0.0222	0.00167	74.9(0.7)	-0.00082	156(3)
0.0444	0.00333	74.8(0.6)	-0.00164	156(2)
0.0667	0.00499	74.8(0.6)	-0.00249	154(2)
0.0882	0.00659	74.9(0.6)	-0.00326	156(2)
0.1109	0.00826	74.9(0.5)	-0.00410	156(2)
0.1339	0.00996	75.0(0.5)	-0.00488	158(2)
0.1574	0.01168	75.0(0.5)	-0.00580	156(2)
0.1799	0.01333	75.0(0.5)	-0.00658	157(2)
0.2026	0.01499	75.0(0.5)	-0.00736	158(2)
0.2259	0.01669	74.9(0.5)	-0.00824	156(2)
		$T = 298.15$ K		
0.0222	0.00163	76.6(0.7)	-0.00088	156(4)
0.0427	0.00315	76.0(0.6)	-0.00149	165(2)
0.0659	0.00485	76.0(0.6)	-0.00232	167(2)
0.0878	0.00646	76.1(0.6)	-0.00306	168(2)
0.1112	0.00816	76.1(0.5)	-0.00385	168(2)
0.1338	0.00980	76.1(0.5)	-0.00465	168(2)
0.1548	0.01131	76.1(0.5)	-0.00535	169(2)
0.1794	0.01309	76.1(0.5)	-0.00624	168(2)
0.1994	0.01454	76.1(0.5)	-0.00691	169(2)
0.2259	0.01644	76.1(0.5)	-0.00786	168(2)
		$T = 313.15$ K		
0.0211	0.00153	77.3(0.7)	--------	--------
0.0438	0.00317	77.5(0.6)	-0.00149	177(2)
0.0658	0.00476	77.4(0.6)	-0.00221	177(2)
0.0883	0.00637	77.4(0.6)	-0.00295	177(2)
0.1121	0.00807	77.5(0.5)	-0.00377	178(2)
0.1343	0.00966	77.5(0.5)	-0.00449	178(2)
0.1568	0.01125	77.5(0.5)	-0.00525	178(2)
0.1808	0.01295	77.5(0.5)	-0.00605	178(2)
0.2034	0.01454	77.5(0.5)	-0.00686	177(2)
0.2259	0.01613	77.5(0.5)	-0.00756	177(2)

Table 4.1 (continued)

m_3	$\rho_{expt} - \rho_l$	$V_{3\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p,3\phi}$
/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})
		$T = 328.15$ K		
0.0240	0.00169	79.8(0.7)	-0.00127	176(3)
0.0438	0.00311	78.9(0.6)	-0.00154	185(2)
0.0673	0.00477	78.9(0.6)	-0.00226	184(2)
0.0886	0.00627	78.9(0.6)	-0.00297	183(2)
0.1105	0.00782	78.9(0.5)	-0.00374	182(2)
0.1334	0.00943	78.8(0.5)	-0.00446	183(2)
0.1564	0.01104	78.8(0.5)	-0.00510	184(2)
0.1794	0.01264	78.7(0.5)	-0.00589	184(2)
0.2026	0.01426	78.7(0.5)	-0.00677	182(2)
0.2259	0.01584	78.6(0.5)	-0.00752	183(2)

Table 4.2 Estimates of parameters to the Pitzer-ion interaction model equations, shown as equations (2.37) and (2.38), for aqueous solutions of CF_3SO_3H at $T = $ (288.15, 298.15, 313.15, and 328.15) K and $p = 0.1$ MPa

V_3^0 /(cm³·mol⁻¹)	$10^4(\beta^{(0)V})$ /(cm³·kg·mol⁻¹·J⁻¹)	$10^3(\beta^{(1)V})$ /(cm³·kg·mol⁻¹·J⁻¹)	C^V /(kg²·cm³·mol⁻³)	concentration range /(mol·kg⁻¹)
		$T = 288.15$ K		
74.61(0.01)	-0.7(0.6)	-1.9(0.1)	4.9(0.7)	0.0222-0.2259*
		$T = 298.15$ K		
75.40(0.06)	-0.8(0.2)	-1.0(0.1)	0.022(0.007)	0.0222-9.4636
75.00[j]	-1.113[j]	-0.6501[j]	0.03348[j]	
		$T = 313.15$ K		
76.71(0.05)	-0.7(0.2)	-1.1(0.1)	0.016(0.007)	0.0222-9.4636
76.60[j]	-0.8897[a]	-0.9100[j]	0.02297[j]	
		$T = 328.15$ K		
77.6(0.2)	-1.1(0.5)	-0.8(0.3)	0.03(0.02)	0.0222-9.4636
76.8[j]	-1.802[j]	-0.05681[j]	0.05630[j]	
C_{p3}^0 /(J·K⁻¹·mol⁻¹)	$10^5(\beta^{(0)J})$ /(kg·mol⁻¹·K⁻²)	$10^5(\beta^{(1)J})$ /(kg·mol⁻¹·K⁻²)	C^J /(J·kg²·K⁻¹·mol⁻³)	concentration range /(mol·kg⁻¹)
		$T = 288.15$ K		
152.3(0.1)	-19(1)	38(2)	-209(22)	0.0222-0.2259*
		$T = 298.15$ K		
155.9(0.6)	0.90(0.06)	4.6(0.4)	0.49(0.08)	0.0222-9.4636
153.10[j]	1.065[j]	3.210[j]	0.6650[j]	
		$T = 313.15$ K		
164.3(0.6)	0.89(0.06)	5.2(0.4)	0.54(0.08)	0.0222-9.4636
161.20[j]	1.031[j]	3.906[j]	0.7136[j]	
		$T = 328.15$ K		
163(3)	0.8(0.3)	4(2)	0.5(0.4)	0.0222-9.4636
152.90[j]	1.044[j]	2.125[j]	0.7832[j]	

[j]Xiao *et. al*, (2001)

*no values were reported by Xiao, *et al.*, (2001) at $T = 288.15$ K. Therefore, global fitting using equations (2.37) and (2.38) were performed using only values reported in this chapter.

Table 4.3 Estimates of parameters to equations (4.1) to (4.8) that model the temperature dependences of $V_{3\phi}$ and $C_{p,3\phi}$ values for aqueous solutions of CF_3SO_3H at $p = 0.1$ MPa

$V_{2\phi}$	
Parameter:	Value:
a_1 /(cm^3·mol^{-1})	67.8(2)
a_2 /(cm^3·mol^{-1}·K^{-1})	-291(29)
a_3 /(cm^3·K·mol^{-1})	4.0x10^{-2}(5x10^{-3})
a_4 /(cm^3·kg·mol^{-1}·J^{-1})	6x10^{-5}(2x10^{-5})
a_5 /(cm^3·K·mol^{-1}·J^{-1})	-4.5x10^{-7}(7x10^{-8})
a_6 /(cm^3·kg·mol^{-1}·J^{-1})	-1.06x10^{-3}(6x10^{-5})
a_7 /(J·kg·K^{-1}·mol^{-3})	2.0x10^{-2}(4x10^{-3})
Standard error /(cm^3·mol^{-1})	0.13
$C_{p,2\phi}$	
Parameter:	Value:
c_1 /(J·K^{-1}·mol^{-1})	262(30)
c_2 /(J·K·mol^{-1})	-1.8x10^5(2x10^4)
c_3 /(J·K^{-2}·mol^{-1})	-0.2(9x10^{-2})
c_4 /(kg·mol^{-1}·K^{-1})	-5x10^{-2}(1x10^{-2})
c_5 /(kg·mol^{-1}·K^{-2})	3.4x10^{-4}(7x10^{-5})
c_6 /(kg·mol^{-1}·K^{-3})	-6x10^{-7}(1x10^{-7})
c_7 /(kg·mol^{-1}·K^{-1})	-0.4(0.2)
c_8 /(kg·mol^{-1}·K^{-2})	2x10^{-3}(1x10^{-3})
c_9 /(kg·mol^{-1}·K^{-3})	-3x10^{-6}(2x10^{-6})
c_{10} /(J·kg·K^{-1}·mol^{-3})	3.3x10^{-1}(6x10^{-2})
Standard error /(J·K^{-1}·mol^{-1})	1.53

4.3 NaCF$_3$SO$_3$ in Aqueous Solution

4.3.1 Experimental

The preparation of $CF_3SO_3Na_{(aq)}$ (sodium triflate) followed the procedure outlined previously by Xiao *et al.* (1997b, 2001). A 0.35 mol·L^{-1} solution of $CF_3SO_3H_{(aq)}$ was prepared from 98% CF_3SO_3H obtained from the Aldrich Chemical Company and standardized as described above. An approximately 1.0 mol·L^{-1} solution of NaOH (standardized against potassium hydrogen phthalate, KHP) was prepared from a concentrated stock solution of $NaOH_{(aq)}$ from the Fisher Scientific Company (Catalog

No. SS22-7). The KHP was obtained from EM Science (0.995 mol fraction, Catalog No.

B10207-34) and was previously dried at $T = 383.15$ K for 1 hour before use. The density

of the standardized $NaOH_{(aq)}$ solution was measured using the Sodev O2D vibrating tube

densimeter. This density was subsequently used to calculate the exact mass of the

standardized base required to neutralize the standardized $CF_3SO_3H_{(aq)}$ solution and create

a $NaCF_3SO_{3(aq)}$ stock solution. The resulting aqueous stock solution of sodium triflate of

known concentration was diluted (by mass) as required to prepare solutions of aqueous

sodium triflate of various known concentrations. These solutions were subsequently

passed through the Picker system in order to measure their relative densities and relative

massic heat capacities.

4.3.2 Results and conclusions

Apparent molar volumes and apparent molar heat capacities for aqueous solutions

of $NaCF_3SO_3$ were calculated (using equations (2.19) and (2.20)) using the measured

relative density and heat capacity data, respectively, described above. Values for

$(\rho_{expt} - \rho_1)$, $V_{2\phi}$, $((c_{p,expt} \cdot \rho_{expt})/(c_{p1} \cdot \rho_1)) - 1$, and $C_{p,2\phi}$ for $NaCF_3SO_{3(aq)}$ solutions of known

concentration are reported at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and

$p = 0.1$ MPa in Table 4.4. The values reported in parentheses are the relative

uncertainties which have been calculated using the standard propagation of error

procedure described in Chapter 3.

The apparent molar volumes and heat capacities for aqueous solutions of

$NaCF_3SO_3$ were modeled using the same modified Pitzer-ion interaction equations that

were used in the modeling of the apparent molar properties of aqueous solutions of the
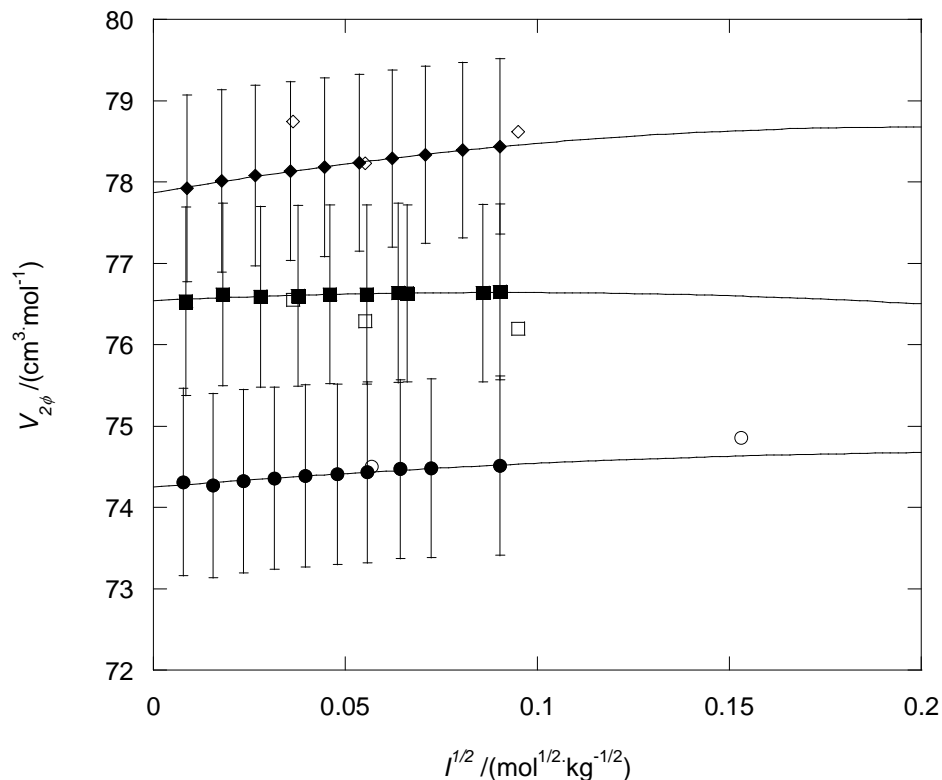
Figure 4.4 A comparison of the ionic strength dependence of $V_{2\phi}$ values calculated from equation (2.19) for $NaCF_3SO_{3(aq)}$ with the $V_{2\phi}$ values reported by Xiao and Tremaine (1997b): •, current study at $T = 298.15$ K; ○, Xiao and Tremaine (1997b) at $T = 298.15$ K; ■, current study at $T = 313.15$ K; □, Xiao and Tremaine (1997b) at $T = 313.15$ K; ◆, current study at $T = 328.15$ K; ◇, Xiao and Tremaine (1997b) at $T = 328.15$ K (the solid lines are for visualization purposes only).

parent acid. Due to a lower molality range studied for aqueous solutions of $NaCF_3SO_3$, the C^V and C^J terms of equations (2.37) and (2.38) were found to be unnecessary. Values for V_2^0, C_{p2}^0, $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ were obtained using least squares multiple regression analyses and have been reported in Table 4.5, where they have also been

compared to those values reported by Xiao *et al.* (2001). Figure 4.4 reports the dependence of $V_{2\phi}$ values on ionic strength at $T = (298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa for aqueous solutions of $NaCF_3SO_3$. Due to the large initial concentration of the $NaOH_{(aq)}$ (approximately 1.0 mol·L^{-1}) used in the preparation of the $NaCF_3SO_{3(aq)}$, the relative uncertainties associated with the $NaCF_3SO_{3(aq)}$ are significantly larger than those reported for the parent acid. However, the reported $V_{2\phi}$ values are in good agreement with those reported by Xiao and Tremaine (1997b).

The temperature dependences of the V_2^0, C_{p2}^0, $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ parameters were modeled using the equations:

$$V_2^0 = b_1 + \frac{b_2}{(T - \theta)} + b_3 \cdot T, \tag{4.9}$$

$$\beta^{(0)V} = \frac{b_4}{T} + b_5 + b_6 \cdot T, \tag{4.10}$$

$$\beta^{(1)V} = \frac{b_7}{T} + b_8 + b_9 \cdot T. \tag{4.11}$$

$$C_{p2}^0 = d_1 + d_2 \cdot T, \tag{4.12}$$

$$\beta^{(0)J} = \frac{d_3}{T} + d_4 + d_5 \cdot T, \tag{4.13}$$

$$\beta^{(1)J} = \frac{d_6}{T} + d_7 + d_8 \cdot T. \tag{4.14}$$

Estimated values of the fitting coefficients b_i ($i = 1$ to 9) and d_j ($j = 1$ to 8) were determined using regression analyses and have been reported in Table 4.6 along with their estimated standard errors. Figure 4.5 shows a comparison between $V_{2\phi}$ values at each concentration (those calculated using equation (2.19) and those calculated using equation (2.37)). The $V_{2\phi}$ values in equation (2.37) were determined using the
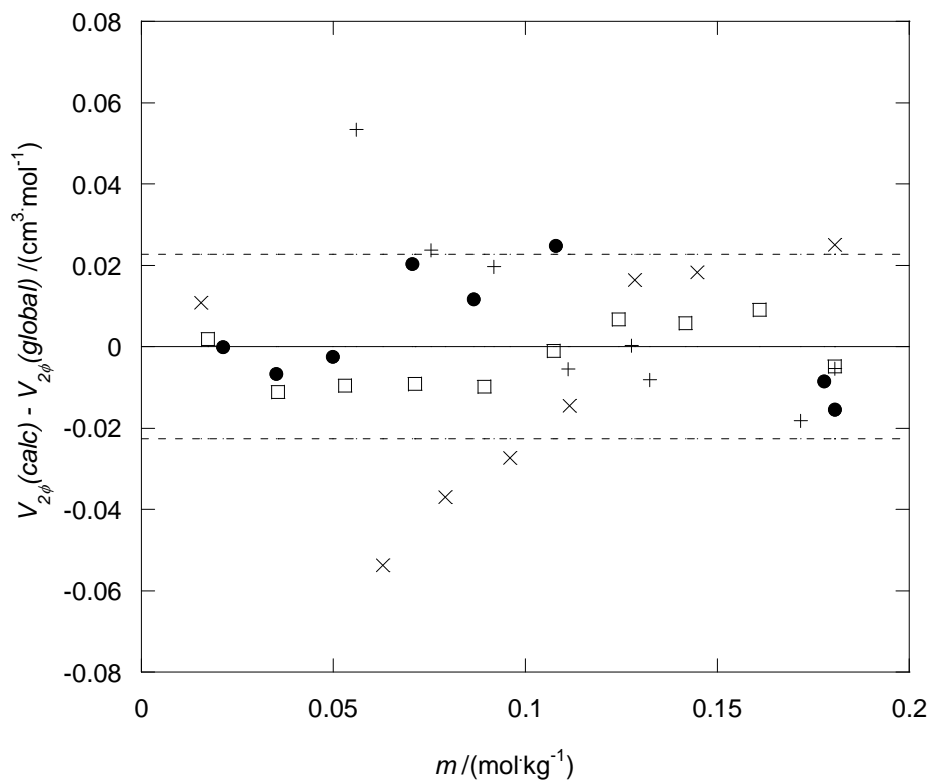
Figure 4.5 Comparison of $V_{2\phi}$ values (as a function of molality) calculated using equation (2.19) ($V_{2\phi}$(calc)) with those calculated using equation (2.37) and the fitting parameters to equations (4.9) to (4.11) ($V_{2\phi}$(global)) for $NaCF_3SO_{3(aq)}$ at: •, $T = 288.15$ K; ×, $T = 298.15$ K; +, $T = 313.15$ K; and □, $T = 328.15$ K; and $p = 0.1$ MPa (the dashed lines represent the standard error).

temperature dependent fitting coefficients of equations (4.9) to (4.11). A similar

comparison is shown in Figure 4.6 for $C_{p,2\phi}$ values calculated using equations (2.20) and

(2.38), where the calculated $C_{p,2\phi}$ values for equations (2.38) were determined using the

calculated fitting coefficients for equations (4.12) to (4.14). $V_{2\phi}$ and $C_{p,2\phi}$ values

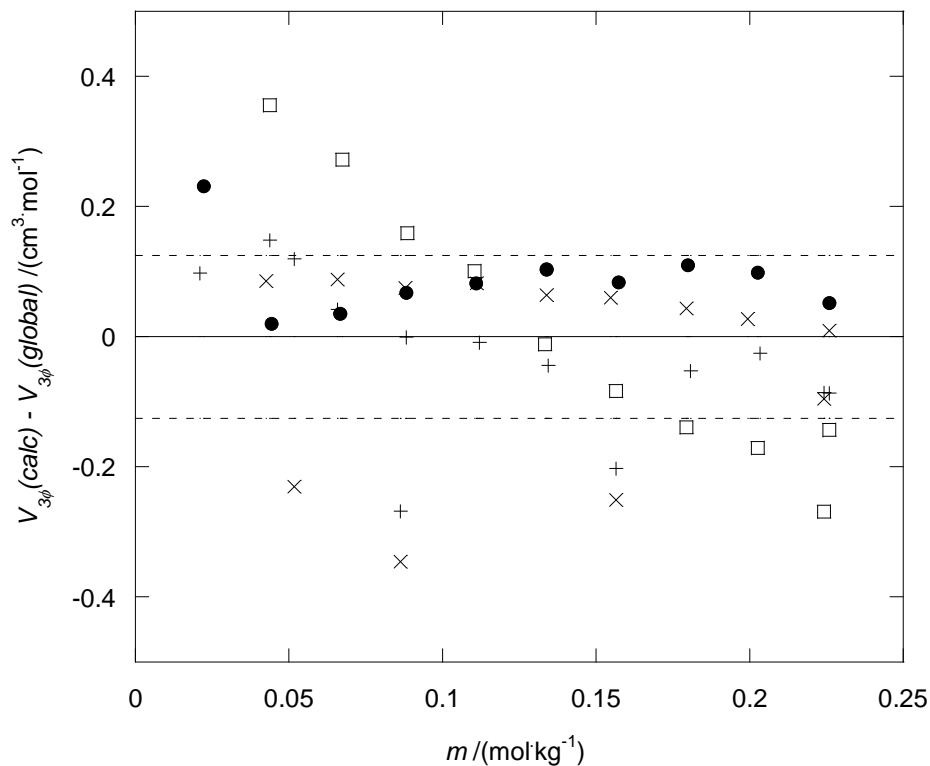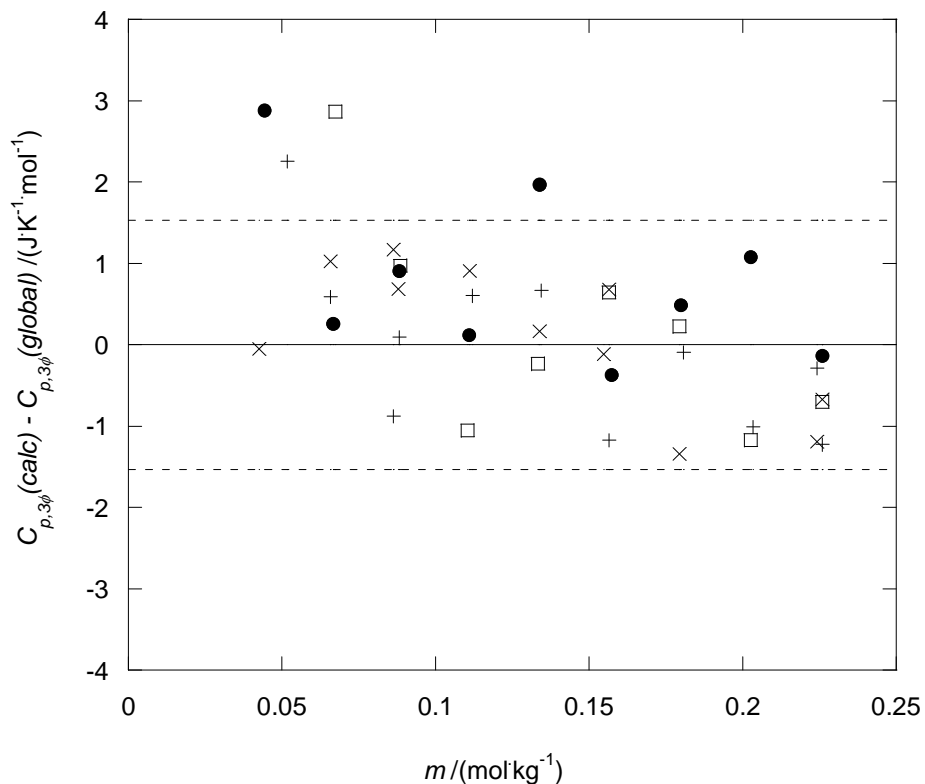calculated using equations (2.19) and (2.20) ($V_{2\phi}$(calc) and $C_{p,2\phi}$(calc)) indicate good
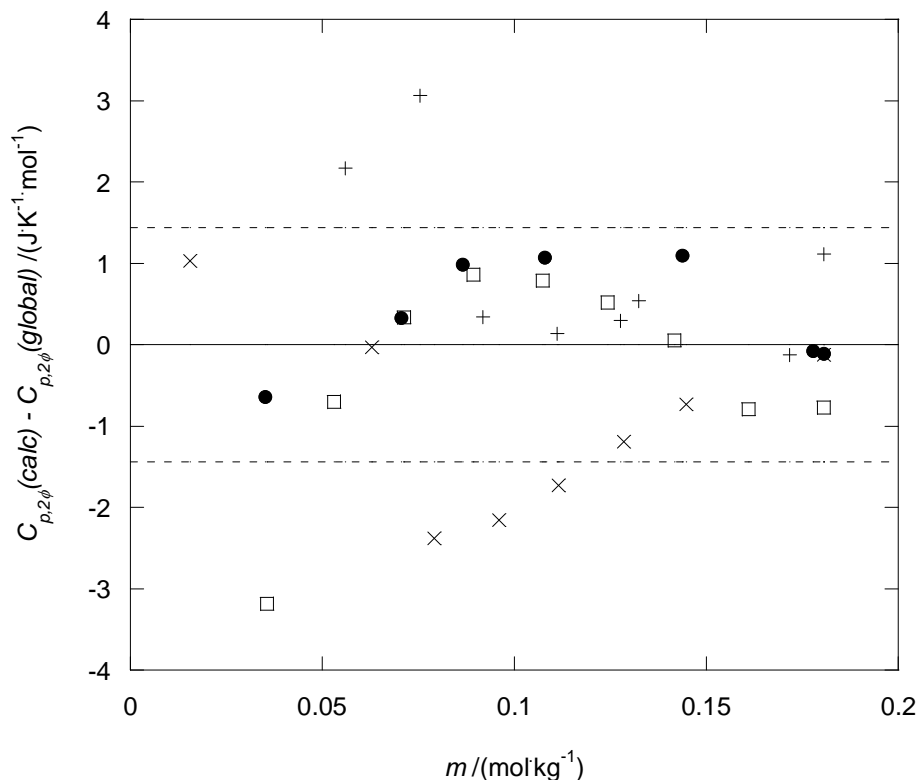
Figure 4.6 Comparison of $C_{p,2\phi}$ values (as a function of molality) calculated using equation (2.20) ($C_{p,2\phi}$(calc)) with those calculated using equations (2.38) and the fitting parameters to equations (4.12) to (4.14) ($C_{p,2\phi}$(global)) for NaCF$_3$SO$_{3(aq)}$ at: $\bullet$, T = 288.15 K; $\times$, T = 298.15 K; +, T = 313.15 K; and $\square$, T = 328.15 K; and p = 0.1 MPa (the dashed lines represent the standard error).

agreement when compared to those $V_{2\phi}$ and $C_{p,2\phi}$ values calculated using equations (2.37) and (2.38) and ($V_{2\phi}$(global) and $C_{p,2\phi}$(global)).

In order to further ensure that the properties of the parent acid are sufficient to be used in the subsequent study of the aqueous REE triflates, the properties of the parent acid must first be compared to those for aqueous sodium triflate. In the limit

$m_2 \rightarrow 0$ mol·kg^{-1}, the apparent molar volumes and heat capacities at infinite dilution of aqueous triflic acid solutions, V_2^0 and C_{p2}^0, respectively, are equal to the partial molar properties. Utilizing the convention that $Y_2^0(\text{H}^+; \text{aq}) = 0$, the single ion properties of the $\text{CF}_3\text{SO}_3^-{}_{(aq)}$ anion may be obtained directly from the properties of the parent acid:

$$Y_2^0(CF_3SO_3^-; aq) = Y_2^0(CF_3SO_3H; aq). \tag{4.15}$$

In addition, the single ion properties, $V_2^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ and $C_{p2}^0(\text{CF}_3\text{SO}_3^-; \text{aq})$, may be estimated using the $V_2^0(\text{Na}^+; \text{aq})$ and $C_{p2}^0(\text{Na}^+; \text{aq})$ values reported by Hovey *et al.* (1988) and the calculated values of V_2^0 and C_{p2}^0 for $\text{NaCF}_3\text{SO}_{3(aq)}$:

$$Y_2^0(CF_3SO_3^-; aq) = Y_2^0(NaCF_3SO_3; aq) - Y_2^0(Na^+; aq). \tag{4.16}$$

Values for $V_2^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ and $C_{p2}^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ calculated using equations (4.15) and (4.16) are reported in Table 4.7, as are those reported by Xiao *et al.* (2001). The $V_2^0(\text{CF}_3\text{SO}_3^-{}_{(aq)})$ and $C_{p2}^0(\text{CF}_3\text{SO}_3^-{}_{(aq)})$ values calculated in this study using both equations (4.15) and (4.16) are in close agreement. Values for $V_2^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ and $C_{p2}^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ calculated in this study using equations (4.15) and (4.16) are in good agreement when compared with those reported by Xiao *et al.* (2001) at all temperatures with the possible exception of values for $C_{p2}^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ at $T = 328.15$ K. Xiao *et al.* (2001) report maxima in their values for $C_{p2}^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ at $T = 313.15$ K which are not observed in this study. This comparison confirms that the $V_2^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ and $C_{p2}^0(\text{CF}_3\text{SO}_3^-; \text{aq})$ values obtained in this study from the parent acid are reasonable to use in combination with Young's rule in the calculation of apparent molar properties of the aqueous REE triflate salt solutions (presented next).

Table 4.4 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of $NaCF_3SO_3$ at known concentration at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa

m_2	$\rho_{expt} - \rho_l$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p,2\phi}$
/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})
		T = 288.15 K		
0.0212	0.00211	73(1)	-0.00064	175(7)
0.0352	0.00350	73(1)	-0.00103	180(6)
0.0499	0.00495	73(1)	-0.00145	180(6)
0.0706	0.00699	73(1)	-0.00202	183(6)
0.0865	0.00855	73(1)	-0.00247	185(6)
0.1080	0.01066	73(1)	-0.00299	187(6)
0.1253	0.01233	73(1)	-0.00348	189(6)
0.1437	0.01414	73(1)	-0.00391	190(6)
0.1778	0.01745	73(1)	-0.00474	192(6)
0.1805	0.01771	73(1)	-0.00483	193(6)
		T = 298.15 K		
0.0155	0.00152	74(1)	-0.00041	198(8)
0.0313	0.00305	74(1)	-0.00084	197(6)
0.0469	0.00457	74(1)	-0.00121	200(6)
0.0630	0.00612	74(1)	-0.00159	200(6)
0.0792	0.00768	74(1)	-0.00196	202(6)
0.0959	0.00929	74(1)	-0.00236	204(6)
0.1116	0.01080	74(1)	-0.00270	206(6)
0.1285	0.01242	74(1)	-0.00305	207(6)
0.1447	0.01396	74(1)	-0.00342	210(6)
0.1805	0.01736	75(1)	-0.00419	211(6)
		T = 313.15 K		
0.0171	0.00163	77(1)	-0.00040	217(7)
0.0362	0.00344	77(1)	-0.00068	223(6)
0.0560	0.00532	77(1)	-0.00126	222(6)
0.0754	0.00715	77(1)	-0.00170	222(6)
0.0919	0.00870	77(1)	-0.00200	224(6)
0.1111	0.01050	77(1)	-0.00236	225(6)
0.1277	0.01204	77(1)	-0.00273	226(6)
0.1324	0.01248	77(1)	-0.00282	227(6)
0.1718	0.01615	77(1)	-0.00361	230(5)
0.1805	0.01696	77(1)	-0.00378	230(5)

Table 4.4 (continued)

m_2	$\rho_{expt} - \rho_l$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p,2\phi}$
/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})
		$T = 328.15$ K		
0.0175	0.00164	78(1)	-0.00040	218(7)
0.0356	0.00333	78(1)	-0.00084	222(6)
0.0531	0.00495	78(1)	-0.00121	225(6)
0.0714	0.00665	78(1)	-0.00160	227(6)
0.0894	0.00831	78(1)	-0.00197	229(6)
0.1073	0.00996	78(1)	-0.00233	230(6)
0.1244	0.01152	78(1)	-0.00262	231(5)
0.1417	0.01310	78(1)	-0.00299	233(5)
0.1610	0.01486	78(1)	-0.00337	234(5)
0.1805	0.01662	78(1)	-0.00372	235(5)

Table 4.5 Estimates of parameters to the Pitzer-ion interaction model equations, shown
as equations (2.37) and (2.38), for aqueous solutions of NaCF$_3$SO$_3$ at
$T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa

V_2^0	$10^4(\beta^{(0)V})$	$10^3(\beta^{(1)V})$
/(cm^3·mol^{-1})	/(cm^3·kg·mol^{-1}·J^{-1})	/(cm^3·kg·mol^{-1}·J^{-1})
	$T = 288.15$ K	
72.35(0.03)	27(4)	-4.9(0.6)
	$T = 298.15$ K	
74.05(0.04)	17(6)	-3.3(0.9)
	$T = 313.15$ K	
76.30(0.02)	13(3)	-3.1(0.5)
	$T = 328.15$ K	
77.580(0.007)	17(1)	-3.2(0.2)
C_{p2}^0	$10^5(\beta^{(0)J})$	$10^5(\beta^{(1)J})$
/(J·K^{-1}·mol^{-1})	/(kg·mol^{-1}·K^{-2})	/(kg·mol^{-1}·K^{-2})
	$T = 288.15$ K	
172.6(0.5)	-10(3)	11.3(4)
	$T = 298.15$ K	
194.7(0.8)	-38(5)	54(8)
193.6[k]	-0.7408[k]	-3.194[k]
	$T = 313.15$ K	
213.6(0.6)	-13(3)	20(4)
206.3[k]	-2.288[k]	-3.908[k]
	$T = 328.15$ K	
211.97(0.06)	0.3(0.2)	-1.2(0.5)
202.1[k]	5.403[k]	-87.82[k]

[k]Xiao *et al*. (2001)

Table 4.6 Estimates of parameters to equations (4.9) to (4.14) that model the temperature dependences of $V_{2\phi}$ and $C_{p,2\phi}$ values for aqueous solutions of $NaCF_3SO_3$ at $p = 0.1$ MPa

$V_{2\phi}$	
Parameter:	Value:
b_1 /(cm^3·mol^{-1})	69(3)
b_2 /(cm^3·mol^{-1}·K^{-1})	-533(48)
b_3 /(cm^3·K·mol^{-1})	$4.1 \times 10^{-2}(8 \times 10^{-3})$
b_4 /(cm^3·kg·mol^{-1}·J^{-1}·K^{-1})	160(27)
b_5 /(cm^3·kg·mol^{-1}·J^{-1})	-1.0(0.2)
b_6 /(cm^3·K·mol^{-1}·J^{-1})	$1.7 \times 10^{-3}(3 \times 10^{-4})$
b_7 /(cm^3·kg·mol^{-1}·J^{-1}·K^{-1})	-281(50)
b_8 /(cm^3·kg·mol^{-1}·J^{-1})	1.8(0.3)
b_9 /(cm^3·K·mol^{-1}·J^{-1})	$-3.0 \times 10^{-3}(5 \times 10^{-4})$
Standard error /(cm^3·mol^{-1})	0.03
$C_{p,2\phi}$	
Parameter:	Value:
d_1 /(J·K^{-1}·mol^{-1})	-100(36)
d_2 /(J·K^{-2}·mol^{-1})	0.9(0.1)
d_3 /(kg·mol^{-1}·K^{-1})	-21(4)
d_4 /(kg·mol^{-1}·K^{-2})	$0.14(3 \times 10^{-2})$
d_5 /(kg·mol^{-1}·K^{-3})	$-2.2 \times 10^{-4}(4 \times 10^{-5})$
d_6 /(kg·mol^{-1}·K^{-1})	40(6)
d_7 /(kg·mol^{-1}·K^{-2})	-0.26(0.04)
d_8 /(kg·mol^{-1}·K^{-3})	$4.3 \times 10^{-4}(7 \times 10^{-5})$
Standard error /(J·K^{-1}·mol^{-1})	1.44

Table 4.7 Standard partial molar volumes and heat capacities for $CF_3SO_3^-{}_{(aq)}$ calculated from the apparent molar volumes and heat capacities of $CF_3SO_3H_{(aq)}$ reported in this study and $Na^+{}_{(aq)}$ values reported by Hovey *et al.* (1988); compared to those reported by Xiao *et al.* (2001)

T /(K)	$V_2^0(CF_3SO_3^-{}_{(aq)})^l$ /(cm^3·mol^{-1})	$V_2^0(CF_3SO_3^-{}_{(aq)})^m$ /(cm^3·mol^{-1})	$C_{p2}^0(CF_3SO_3^-{}_{(aq)})^l$ /(J·K^{-1}·mol^{-1})	$C_{p2}^0(CF_3SO_3^-{}_{(aq)})^m$ /(J·K^{-1}·mol^{-1})
288.15	74.32(0.01)		145.3(0.1)	
298.15	75.40(0.06)	75.0	156.5(0.6)	153.1
313.15	76.73(0.05)	76.6	165.1(0.6)	161.2
328.15	77.8(0.2)	76.8	168(3)	152.9
T /(K)	$V_2^0(CF_3SO_3^-{}_{(aq)})^n$ /(cm^3·mol^{-1})	$V_2^0(CF_3SO_3^-{}_{(aq)})^o$ /(cm^3·mol^{-1})	$V_2^0(Na^+{}_{(aq)})^p$ /(cm^3·mol^{-1})	
288.15	74.1(0.3)		-1.75(0.3)	
298.15	75.3(0.3)	74.7(0.8)	-1.27(0.3)	
313.15	76.7(0.3)	76.2(1.0)	-0.44(0.3)	
328.15	77.5(0.3)	77(1.5)	0.12(0.3)	
T /(K)	$C_{p2}^0(CF_3SO_3^-{}_{(aq)})^n$ /(J·K^{-1}·mol^{-1})	$C_{p2}^0(CF_3SO_3^-{}_{(aq)})^o$ /(J·K^{-1}·mol^{-1})	$C_{p2}^0(Na^+{}_{(aq)})^p$ /(J·K^{-1}·mol^{-1})	
288.15	141(1)		31.8(1.3)	
298.15	153(1)	151(2)	42.2(1.3)	
313.15	161(1)	154(7)	52.8(1.3)	
328.15	162(3)	153(1)	49.5(1.3)	

[l]Single ion values calculated and reported in the current study using equation (4.15)
[m]Single ion values calculated using equation (4.15) and reported in Xiao *et al.* (2001)
[n]Single ion values calculated and reported in the current study using $Na^+{}_{(aq)}$ single ion parameters from Hovey *et al.* (1988) and equation (4.16)
[o]Single ion values calculated using equation (4.16) reported in Xiao *et al.* (2001)
[p]Single ion values for $Na^+{}_{(aq)}$ reported in Hovey *et al.* (1988)

4.4 The REE Triflates in Aqueous Solution

4.4.1 Experimental

Preparation of acidified aqueous REE triflate salt solutions followed the procedure previously outlined by Spedding *et al.* (1966b) in which the REE oxides were dissolved in approximately 1.20 mol·L^{-1} triflic acid with stirring and warming at $T = 353$ K. $Gd_2O_{3(s)}$ (Gadolinium oxide, 0.999 mol fraction), $Dy_2O_{3(s)}$ (Dysprosium oxide, 0.999 mol fraction), $Nd_2O_{3(s)}$ (Neodymium oxide, 0.999 mol fraction), $Er_2O_{3(s)}$

(Erbium oxide, 0.999 mol fraction), $Yb_2O_{3(s)}$ (Ytterbium oxide, 0.999 mol fraction), and

$Y_2O_{3(s)}$ (Yttrium oxide, 0.9999 mol fraction) were obtained from the Aldrich Chemical

Company (Catalog Numbers 27581-3, 28926-4, 22865-6, 28924-8, 24699-9, and

20516-8, respectively). After the oxide appeared to be completely dissolved, a 10 mL

aliquot of each REE triflate stock solution was titrated with approximately 3.00 $mol \cdot L^{-1}$

triflic acid to identify an equivalence point pH (all of which were found to be above

pH = 3.0 and below pH = 3.4). The pH of the stock solution was brought below the

equivalence point pH by drop-wise addition of 6.0 $mol \cdot L^{-1}$ CF_3SO_3H. The resulting

solution was re-heated to approximately $T = 353$ K for several hours and allowed to cool.

This pH adjustment procedure was repeated until no change in pH was noted between

successive pH adjustment and heating cycles.

Titrimetric analyses were performed using ethylenediaminetetraacetic acid

(EDTA) to determine the concentration of the $REE_{(aq)}$, $R^{3+}_{(aq)}$, in each acidified REE

triflate stock solution. Xylenol orange was used as the endpoint indicator and an acetic

acid buffer was used to maintain a pH = 5.5. In all cases, at least three consecutive

titrations were performed in order to increase precision (less than 0.5 mol % deviation).

Stock solutions of EDTA were prepared from the disodium salt of EDTA

($Na_2EDTA \cdot 2H_2O$) that was obtained from BDH Chemicals (0.99 mol fraction, Catalog

No. JT8993-1). The disodium EDTA salt was oven-dried and prepared using the

procedure described by Skoog and West (1982), in which the EDTA was weighed to

$\pm$ 0.00001 g. The molalities of the excess acid in the acidified REE triflate stock salt

solutions were determined by titration against THAM. Samples of THAM used in each

acidimetric titration were weighed to $\pm$ 0.00001 g. Methyl red was used as the endpoint

indicator in these titrations. Diluted solutions of the acidified aqueous REE triflate salts were prepared by mass on the molality concentration scale by dilution of the standardized solutions using deionized, degassed water. The dilute solutions were stored in sealed volumetric glass flasks and their densities and massic heat capacities were measured within 24 hours of their preparation.

4.4.2 Results and conclusions

Apparent molar volumes and heat capacities for each of the acidified rare earth triflate salts were calculated using equations (4.17) and (4.18):

$$V_{\phi,\text{exp}t} = \left(\frac{(1 + m_2 \cdot M_2 + m_3 \cdot M_3)}{\rho_{\text{exp}t}} - \frac{(1/\rho_1)}{(m_2 + m_3)} \right) \tag{4.17}$$

$$C_{p\phi,\text{exp}t} = \left(\frac{(1 + m_2 \cdot M_2 + m_3 \cdot M_3) \cdot c_{p,\text{exp}t} - c_{p1}}{(m_2 + m_3)} \right), \tag{4.18}$$

where equations (4.17) and (4.18) are similar to equations (2.19) and (2.20), but for a system where more than one solute is present. These apparent molar properties were subjected to Young's rule to determine the apparent molar volumes and heat capacities of the aqueous REE triflate salt solutions. $(\rho_{\text{exp}t} - \rho_1)$, $V_{\phi,\text{exp}t}$, $V_{2\phi}$, $((c_{p,\text{exp}t} \cdot \rho_{\text{exp}t})/(c_{p1} \cdot \rho_1)) - 1$, $C_{p\phi,\text{exp}t}$, and $C_{p,2\phi}$ values are reported at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa for aqueous solutions of $Gd(CF_3SO_3)_3$ (Gadolinium triflate), $Dy(CF_3SO_3)_3$ (Dysprosium triflate), $Nd(CF_3SO_3)3$ (Neodymium triflate), $Er(CF_3SO_3)_3$ (Erbium triflate), $Yb(CF_3SO_3)_3$ (Ytterbium triflate), and $Y(CF_3SO_3)_3$ (Yttrium triflate) of known concentration in Tables 4.8 to 4.13, respectively. The values in parentheses are the estimated uncertainties that have been calculated using the standard propagation of error method:

$$\left(\delta V_{\phi,\exp t}\right)^2 = \left(\frac{M_2}{\rho_{\exp t}\cdot\left(m_2+m_3\right)} - \frac{\left(1+m_2\cdot M_2+m_3\cdot M_3\right)/\rho_{\exp t}-1/\rho_1}{\left(m_2+m_3\right)^2}\right)^2\cdot\delta m_2^{\,2}$$

$$+ \left(\frac{M_3}{\rho_{\exp t}\cdot\left(m_2+m_3\right)} - \frac{\left(1+m_2\cdot M_2+m_3\cdot M_3\right)/\rho_{\exp t}-1/\rho_1}{\left(m_2+m_3\right)^2}\right)^2\cdot\delta m_3^{\,2}$$

$$+ \left(\frac{1+m_2\cdot M_2+m_3\cdot M_3}{\rho_{\exp t}^{\,2}\cdot\left(m_2+m_3\right)}\right)^2\cdot\delta\rho_{\exp t}^{\,2} \qquad (4.19)$$

$$\left(\delta C_{p\phi,\exp t}\right)^2 = \left(\frac{M_2\cdot c_{p,\exp t}}{\left(m_2+m_3\right)} - \frac{\left(1+m_2\cdot M_2+m_3\cdot M_3\right)\cdot c_{p,\exp t}-c_{p1}}{\left(m_2+m_3\right)^2}\right)^2\cdot\delta m_2^{\,2}$$

$$+ \left(\frac{M_3\cdot c_{p,\exp t}}{\left(m_2+m_3\right)} - \frac{\left(1+m_2\cdot M_2+m_3\cdot M_3\right)\cdot c_{p,\exp t}-c_{p1}}{\left(m_2+m_3\right)^2}\right)^2\cdot\delta m_3^{\,2}$$

$$+ \left(\frac{1+m_2\cdot M_2+m_3\cdot M_3}{\left(m_2+m_3\right)}\right)^2\cdot\delta c_{p,\exp t}^{\,2}, \qquad (4.20)$$

where equations (4.19) and (4.20) follow the same form as those of equations (3.5) and (3.12), but coincide with equations (4.17) and (4.18).

The apparent molar volumes and heat capacities of aqueous solutions of the REE triflate salts were modeled using modified Pitzer-ion interaction equations (Pitzer, 1991; Hakin *et al.*, 2003a, 2003b, 2004a, 2005; Marriott *et al.*, 2001). These Pitzer equations have been previously reported (for a general electrolyte) as equations (2.37) and (2.38) and were found to successfully model the concentration dependences of $V_{2\phi}$ and $C_{p,2\phi}$ values at all the investigated temperatures. Estimated values of V_2^0, C_{p2}^0, $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ were obtained using least squares multiple regression analyses and are reported in Table 4.14, where they have also been compared with those values previously reported by Xiao *et al.* (1996a). Figures 4.7 and 4.8 show the dependences of $V_{2\phi}$ and $C_{p,2\phi}$ on
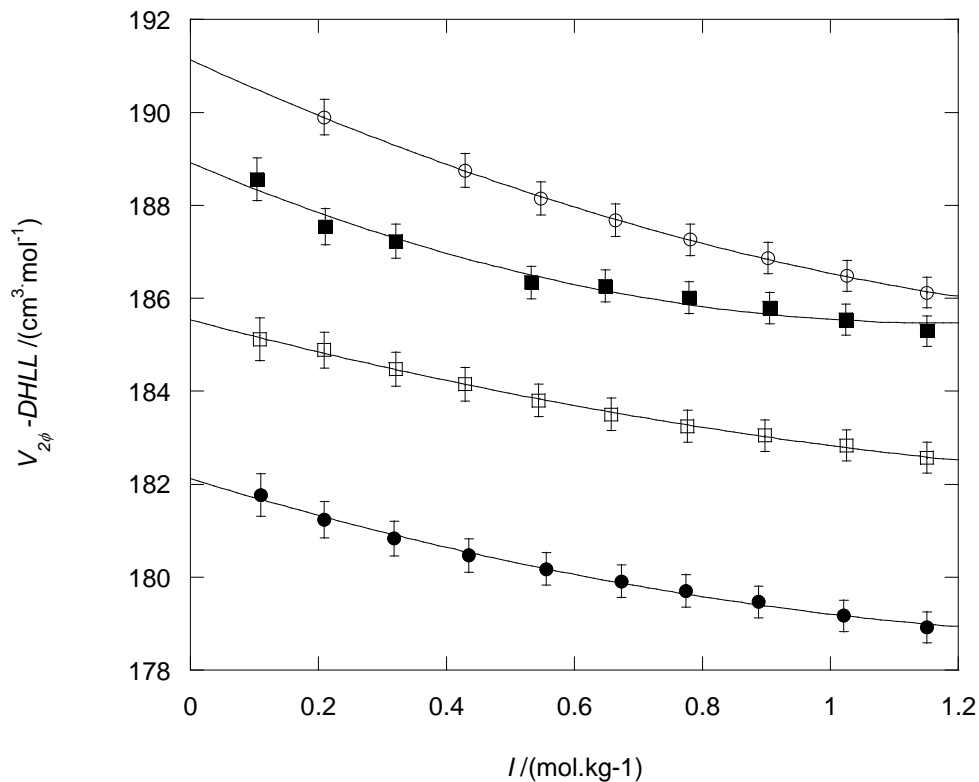
Figure 4.7 Trends in apparent molar volumes, $V_{2\phi}$ - *DHLL*, for Gd(CF$_3$SO$_3$)$_{3(aq)}$ at $T = (288.15, 198.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa as a function of ionic strength at: ●, $T = 288.15$ K; □, $T = 298.15$ K; ■, $T = 313.15$ K; and ○, $T = 328.15$ K (the solid lines are for visualization purposes only).

ionic strength at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa for aqueous acidified Gd(CF$_3$SO$_3$)$_3$ solutions. As can be seen, the temperature dependence on the $C_{p,2\phi}$ values for Gd(CF$_3$SO$_3$)$_{3(aq)}$ is more pronounced than that observed for the corresponding $V_{2\phi}$ values. This trend is also consistent for all aqueous REE systems investigated.

A primary concern in the calculation of partial molar properties of aqueous REE
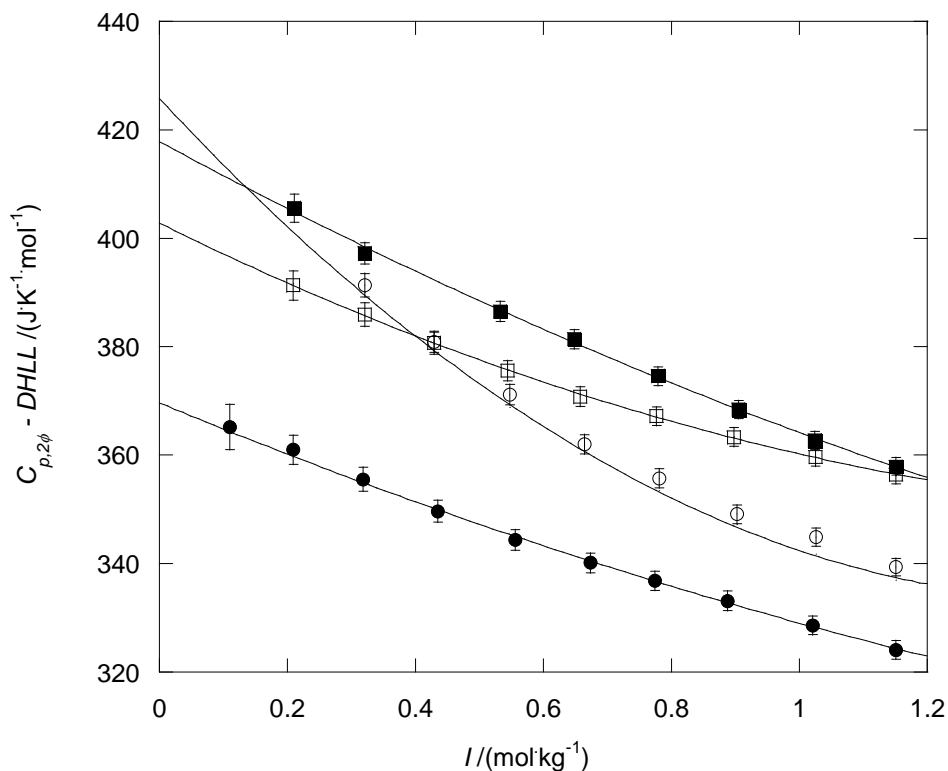
Figure 4.8 Trends in apparent molar heat capacities, $C_{p,2\phi}$ - *DHLL*, for Gd(CF$_3$SO$_3$)$_{3(aq)}$ at T = (288.15, 198.15, 313.15, and 328.15) K and p = 0.1 MPa as a function of ionic strength at: ●, T = 288.15 K; □, T = 298.15 K; ■, T = 313.15 K; and ○, T = 328.15 K (the solid lines are for visualization lines only).

salt solutions at infinite dilution is the degree of complex formation between the R^{3+}

cation and the counter ion used in the salt. Previous studies (Marriott *et al.*, 2001;

Rard *et al.*, 1977, 1979, 1981, 1982) have shown that mean molal activity coefficients for

aqueous REE salts solutions and water activity trends differ as a function of molality for

aqueous solutions of the REE chlorides, nitrates, and perchlorates. Such differences are

believed to be the result of various degrees of speciation. In previous studies (Hakin *et al.,* 2005; Marriott *et al.,* 2001) the concentration dependences of apparent molar

71
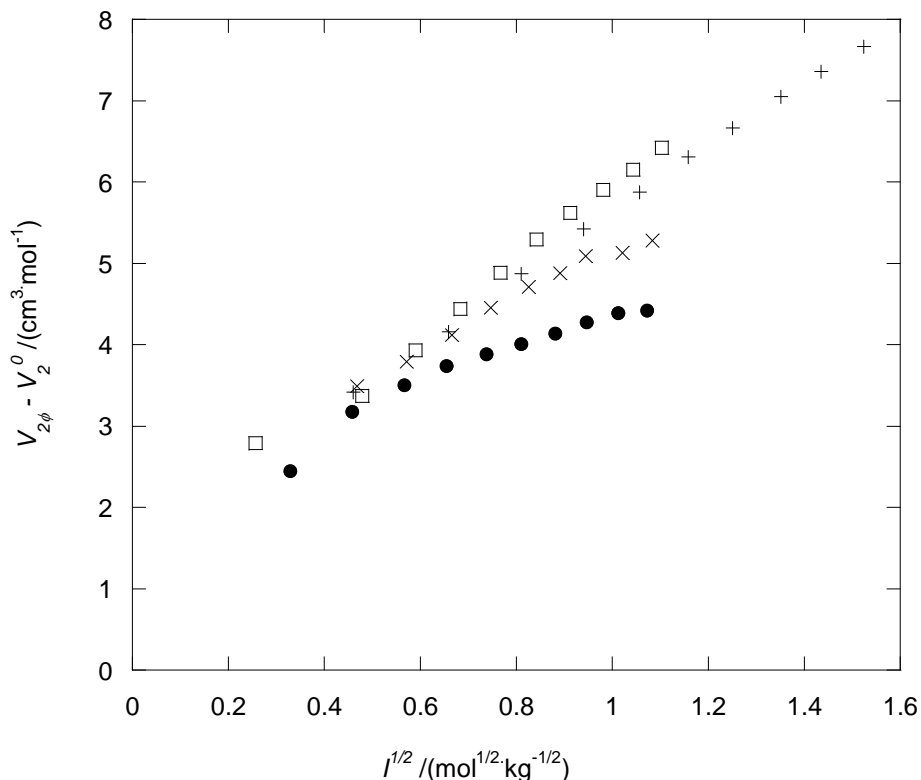
Figure 4.9 $V_{2\phi}$ - V_2^0 against $I^{1/2}$ at $T = 298.15$ K and $p = 0.1$ MPa for aqueous solutions of: •, Gd(CF$_3$SO$_3$)$_3$ (this study); ×, Gd(ClO$_4$)$_3$ (Hakin *et al.*, 2004b); +, GdCl$_3$ (Hakin *et al.*, 2003b); and □, Gd(NO$_3$)$_3$ (Hakin, *et al.*, 2005).

volumes and heat capacities, $V_{2\phi}$ - V_2^0 and $C_{p,2\phi}$ - C_{p2}^0, respectively, have been used as an indication of complex formation within aqueous REE salt solutions. As such, Figures 4.9 and 4.10 compare $V_{2\phi}$ - V_2^0 and $C_{p,2\phi}$ - C_{p2}^0 values for Gd(CF$_3$SO$_3$)$_{3(aq)}$ (this study), Gd(ClO$_4$)$_{3(aq)}$, (Hakin *et al.,* 2004b), GdCl$_{3(aq)}$ (Hakin *et al.,* 2003b), and Gd(NO$_3$)$_{3(aq)}$ (Hakin *et al.,* 2005) at $T = 298.15$ K and $p = 0.1$ MPa against $I^{1/2}$. The trends in Figures 4.9 and 4.10 indicate that the CF$_3$SO$_3^-$$_{(aq)}$ anion is less prone to speciation with R^{3+}$_{(aq)}$ than

Figure 4.10 $C_{p,2\phi}$ - Cp_2^0 against $I^{1/2}$ at $T = 298.15$ K and $p = 0.1$ MPa for aqueous solutions of: •, Gd(CF$_3$SO$_3$)$_3$ (this study); ×, Gd(ClO$_4$)$_3$ (Hakin *et al.*, 2004b); +, GdCl$_3$ (Hakin *et al.*, 2003b); and □ , Gd(NO$_3$)$_3$ (Hakin *et al.*, 2005).

the ClO$_4^-$ $_{(aq)}$, Cl$^-$ $_{(aq)}$, and NO$_3^-$ $_{(aq)}$ anions at $T = 298.15$ K. $V_{2\phi}$ - V_2^0 and $C_{p,2\phi}$ - C_{p2}^0 values

for all the systems investigated at the temperatures of interest show similar behavior.

Such trends add support to the contention that the CF$_3$SO$_3^-$ $_{(aq)}$ anion engages in speciation

with R^{3+} $_{(aq)}$ to a limited degree.   Therefore, the triflate salts are good candidates for

determining reliable single ion values for aqueous trivalent REE cations over the

temperature range $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa.

The values for the apparent molar volumes and apparent molar heat capacities at infinite dilution reported in Table 4.14 can be used to calculate the single ion contributions of the trivalent REE metal cations within the aqueous salt solutions investigated. Using the previously identified convention that $Y_2^0(H^+; aq) = 0$ (equation (4.15)), the single ion volumes and heat capacities of the aqueous trivalent REE cations, $Y_2^0(R^{3+}; aq)$ have been calculated using equation (4.21) at each investigated temperature:

$$Y_2^0(R^{3+}; aq) = Y_2^0(R(CF_3SO_3)_3; aq) - 3 \cdot \{Y_2^0(CF_3SO_3^-; aq)\},\tag{4.21}$$

The calculated single ion values are compared with values previously derived from the REE sulfates, chlorides, nitrates, and perchlorates (Hakin *et al.*, 2003a, 2003b, 2004b, 2005; Marriott *et al.*, 2001). These single ion values have also been compared with values reported by Xiao *et al.* (1997a, 1996b, 2001) and are shown in Table 4.15.

The single ion volumes and heat capacities calculated in this study and reported in Table 4.15 shows a high degree of consistency with previous studies. This consistency may be verified by looking at the temperature dependences of calculated values of $V_2^0(CF_3SO_3^-)$ - $V_2^0(ClO_4^-)$ and $C_{p2}^0(CF_3SO_3^-)$ - $C_{p2}^0(ClO_4^-)$ for aqueous solutions obtained from the parent acids in comparison with those calculated for pairs of REE salts containing a common cation, shown in Figures 4.11 and 4.12. For example, with respect to the parent acids:

$$V_2^0(CF_3SO_3^-) - V_2^0(ClO_4^-) = V_2^0(CF_3SO_3H) - V_2^0(HClO_4),\tag{4.22}$$

whereas for the gadolinium salts:

Figure 4.11 The temperature dependences of $V_2^0(CF_3SO_3^-) - V_2^0(ClO_4^-)$ values for the REE systems: ●, $CF_3SO_3H_{(aq)}$ (current study) and $HClO_{4(aq)}$ (Hovey, 1988); □ , $Gd(CF_3SO_3)_{3(aq)}$ (current study) and $Gd(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2004b); ■ , $Dy(CF_3SO_3)_{3(aq)}$ (current study) and $Dy(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2003a); ○, $Yb(CF_3SO_3)_{3(aq)}$ (current study) and $Yb(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2003a); and ▲ , $Y(CF_3SO_3)_{3(aq)}$ (current study) and $Y(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2003a) (the solid line is for visualization purposes only).

Figure 4.12 The temperature dependence of $C_{p2}^{0}(CF_3SO_3^-) - C_{p2}^{0}(ClO_4^-)$ values for the REE systems: ●, $CF_3SO_3H_{(aq)}$ (current study) and $HClO_{4(aq)}$ (Hovey, 1988); □ , $Gd(CF_3SO_3)_{3(aq)}$ (current study) and $Gd(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2004b); ■ , $Dy(CF_3SO_3)_{3(aq)}$ (current study) and $Dy(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2003a); ○, $Yb(CF_3SO_3)_{3(aq)}$ (current study) and $Yb(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2003a); and ▲, $Y(CF_3SO_3)_{3(aq)}$ (current study) and $Y(ClO_4)_{3(aq)}$ (Hakin *et al.*, 2003a) (the solid line is for visualization purposes only).

$$V_2^0(CF_3SO_3^-) - V_2^0(ClO_4^-) =$$

$$\frac{V_2^0(Gd(CF_3SO_3)_3) - V_2^0(Gd(ClO_4)_3)}{3}. \tag{4.23}$$
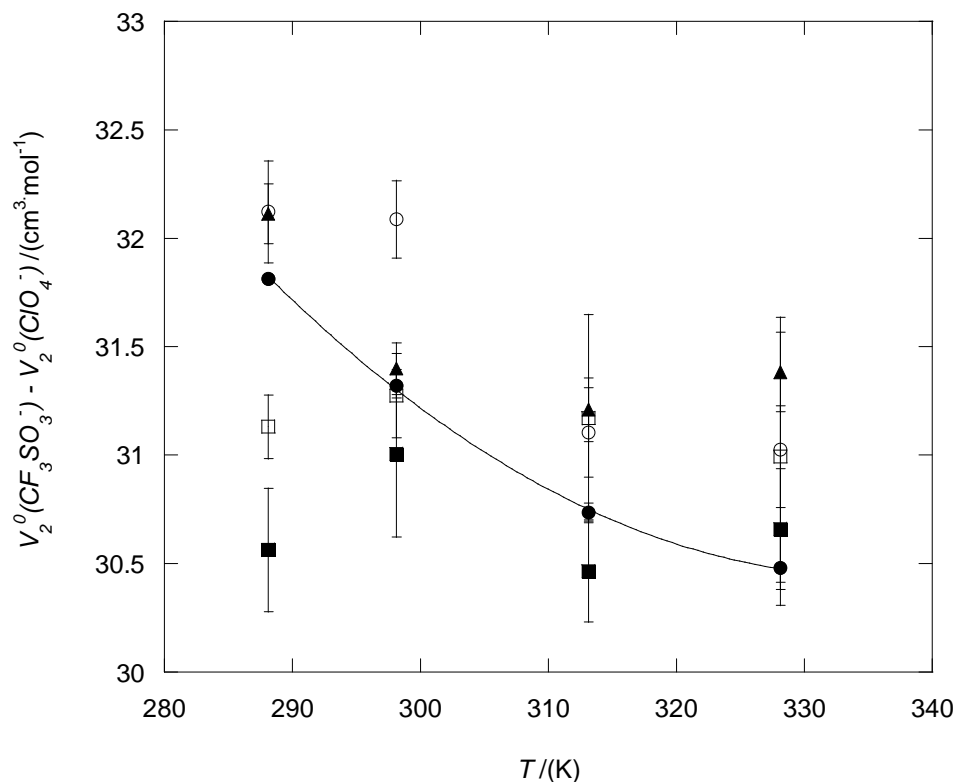
With the exception of $Dy^{3+}_{(aq)}$ and $Gd^{3+}_{(aq)}$ at $T = 288.15$ K, it appears that the single ion

properties obtained from the study of the trivalent REE perchlorates (Hakin *et al.*, 2003a,

76

2004b) are in better agreement with the REE triflates presented in the current study than those obtained using chloride (Hakin *et al.*, 2003b), nitrate (Hakin *et al.*, 2005), and sulfate (Marriott *et al.*, 2001) as the counter ion. These various levels of agreement observed in Table 4.15 are consistent with the apparent degrees of speciation present within the salts (as described above and presented in Figures 4.9 and 4.10). Also, the single ion values previously obtained by Hakin *et al.* (2003b) for the aqueous REE perchlorates are in closer agreement with the REE triflate salt calculated values obtained in this study than the perchlorate derived values previously reported by Xiao and Tremaine (1997b, 1996b).

The $V_{2\phi}$ values for $Gd(CF_3SO_3)_{3(aq)}$ and $CF_3SO_3H_{(aq)}$ reported by Xiao and Tremaine (1997b and 2001, respectively) at $T = 298.15$ K have been used in the manner presented in equation (4.21) to produce a singe ion volume for $Gd^{3+}_{(aq)}$ that has been reported in Table 4.15. This single ion value for $Gd^{3+}_{(aq)}$ is significantly higher than those reported in this thesis and in the past (Hakin *et al.*, 2003a, 2003b, 2004a, 2005; Marriott *et al.*, 2001). It is speculated that the results reported for $Gd(CF_3SO_3)_{3(aq)}$ by Xiao and Tremaine (1996a) could be in question.

From the compilation of the single ion values for the aqueous R^{3+} ions in past studies, it can be seen that there is a high degree of internal consistency for the aqueous R^{3+} ions derived in this study. Given the identified lack of speciation within aqueous REE triflate salt solutions, it is suggested that these systems are capable of providing precise values for the single ion volumes and heat capacities for aqueous REE trivalent metal cations. Therefore, it is suggested that the single ion values derived in this chapter from the aqueous REE triflate salts should be recommended for use.

Table 4.8 Calculated of relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of Gd(CF$_3$SO$_3$)$_3$ at known concentration at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt}\cdot\rho_{expt})}{c_{pl}\cdot\rho_l}-1$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
			T = 288.15 K				
0.0182	0.00101	0.00768	180.5(0.5)	184.6(0.5)	-0.00158	389(4)	415(4)
0.0349	0.00194	0.01468	180.8(0.4)	184.9(0.4)	-0.00296	396(3)	420(3)
0.0531	0.00295	0.02226	181.2(0.4)	185.2(0.4)	-0.00444	401(2)	426(2)
0.0725	0.00403	0.03027	181.4(0.4)	185.3(0.4)	-0.00600	405(2)	430(2)
0.0927	0.00515	0.03853	181.6(0.4)	185.5(0.4)	-0.00759	408(2)	432(2)
0.1122	0.00623	0.04646	181.8(0.4)	185.6(0.4)	-0.00907	410(2)	434(2)
0.1290	0.00716	0.05324	182.0(0.4)	185.7(0.4)	-0.01041	412(2)	436(2)
0.1479	0.00821	0.06081	182.1(0.3)	185.8(0.3)	-0.01186	413(2)	437(2)
0.1702	0.00945	0.06967	182.2(0.3)	185.8(0.3)	-0.01356	414(2)	437(2)
0.1919	0.01065	0.07823	182.2(0.3)	185.8(0.3)	-0.01515	415(2)	437(2)
			T = 298.15 K				
0.0179	0.00099	0.00749	184.1(0.5)	188.2(0.5)	-0.00151	410(4)	435(4)
0.0349	0.00194	0.01454	184.9(0.4)	188.9(0.4)	-0.00272	442(3)	466(3)
0.0535	0.00297	0.02218	185.3(0.4)	189.2(0.4)	-0.00409	448(2)	472(2)
0.0715	0.00397	0.02951	185.6(0.4)	189.5(0.4)	-0.00541	449(2)	473(2)
0.0907	0.00504	0.03729	185.8(0.4)	189.6(0.4)	-0.00678	453(2)	477(2)
0.1096	0.00608	0.04486	185.9(0.4)	189.7(0.4)	-0.00808	456(2)	479(2)
0.1295	0.00719	0.05280	186.1(0.3)	189.9(0.4)	-0.00940	459(2)	482(2)
0.1496	0.00830	0.06075	186.3(0.3)	190.0(0.3)	-0.01085	462(2)	484(2)
0.1709	0.00949	0.06910	186.5(0.3)	190.1(0.3)	-0.01228	464(2)	487(2)
0.1919	0.01065	0.07728	186.6(0.3)	190.1(0.3)	-0.01366	466(2)	488(2)
			T = 313.15 K				
0.0174	0.00096	0.00717	188.7(0.5)	192.8(0.5)	-0.00136	465(4)	490(4)
0.0352	0.00195	0.01448	188.2(0.4)	192.2(0.4)	-0.00263	471(3)	492(3)
0.0535	0.00297	0.02193	188.8(0.4)	192.8(0.4)	-0.00392	471(2)	496(2)
0.0713	0.00396	0.02905	189.6(0.4)	193.5(0.4)	-0.00519	473(2)	498(2)
0.0888	0.00493	0.03610	189.2(0.4)	193.0(0.4)	-0.00637	477(2)	501(2)
0.1081	0.00600	0.04375	189.7(0.4)	193.5(0.4)	-0.00770	480(2)	503(2)
0.1298	0.00721	0.05230	190.0(0.3)	193.7(0.3)	-0.00916	483(2)	506(2)
0.1509	0.00838	0.06050	190.3(0.3)	193.9(0.3)	-0.01061	485(2)	508(2)
0.1707	0.00948	0.06819	190.4(0.3)	194.0(0.3)	-0.01196	487(2)	509(2)
0.1919	0.01065	0.07630	190.6(0.3)	194.1(0.3)	-0.01336	489(2)	511(2)

Table 4.8 (continued)

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
				T = 328.15 K			
0.0177	0.00098	0.00723	191.8(0.5)	195.8(0.5)	-0.00150	432(4)	458(5)
0.0349	0.00194	0.01420	191.8(0.4)	195.8(0.4)	-0.00258	476(3)	502(4)
0.0536	0.00297	0.02170	192.0(0.4)	195.9(0.4)	-0.00398	474(2)	499(4)
0.0715	0.00397	0.02886	192.1(0.4)	196.0(0.4)	-0.00524	476(2)	502(4)
0.0913	0.00507	0.03669	192.3(0.4)	196.1(0.4)	-0.00668	478(2)	504(4)
0.1108	0.00615	0.04435	192.5(0.4)	196.2(0.4)	-0.00808	481(2)	504(4)
0.1302	0.00723	0.05191	192.6(0.4)	196.3(0.4)	-0.00938	481(2)	506(4)
0.1504	0.00835	0.05972	192.6(0.4)	196.3(0.4)	-0.01075	483(2)	508(4)
0.1709	0.00949	0.06762	192.9(0.3)	196.4(0.4)	-0.01212	486(2)	511(4)
0.1919	0.01065	0.07556	193.0(0.3)	196.4(0.4)	-0.01351	489(2)	512(4)

Table 4.9 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of $Dy(CF_3SO_3)_3$ at known concentration at $T = (288.15, 298.15, 313.15, \text{and } 328.15)$ K and $p = 0.1$ MPa

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt}\cdot\rho_{expt})}{c_{p1}\cdot\rho_l}-1$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg^{-1})	/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})	/(J·K^{-1}·mol^{-1})
				$T = 288.15$ K			
0.0148	0.00539	0.00673	154.2(0.6)	181.4(0.6)	-0.00141	247(5)	419(5)
0.0277	0.01008	0.01254	154.6(0.6)	181.4(0.6)	-0.00262	247(4)	418(4)
0.0433	0.01576	0.01952	155.2(0.5)	181.7(0.5)	-0.00405	256(3)	424(3)
0.0583	0.02125	0.02623	155.7(0.5)	181.6(0.5)	-0.00538	258(3)	424(3)
0.0734	0.02674	0.03290	156.2(0.5)	181.9(0.5)	-0.00663	266(3)	430(3)
0.0906	0.03302	0.04046	156.7(0.5)	182.0(0.5)	-0.00816	272(3)	434(3)
0.1034	0.03767	0.04603	157.1(0.5)	182.1(0.5)	-0.00919	276(3)	436(3)
0.1193	0.04346	0.05292	157.5(0.5)	182.2(0.5)	-0.01062	281(3)	439(3)
0.1416	0.05158	0.06196	161.8(0.5)	186.1(0.5)	-0.01223	303(3)	459(3)
0.1928	0.07023	0.08402	160.1(0.5)	183.3(0.5)	-0.01652	298 (2)	448(2)
				$T = 298.15$ K			
0.0172	0.00628	0.00769	161.0(0.6)	187.6(0.6)	-0.00150	299(5)	467(5)
0.0354	0.01290	0.01579	160.4(0.5)	186.8(0.5)	-0.00300	312(3)	476(3)
0.0531	0.01936	0.02350	162.8(0.5)	188.8(0.5)	-0.00445	319(3)	481(3)
0.0718	0.02617	0.03162	163.6(0.5)	189.1(0.5)	-0.00598	328(3)	488(3)
0.0908	0.03306	0.03979	164.0(0.5)	189.1(0.5)	-0.00746	333(3)	491(3)
0.1102	0.04014	0.04808	164.6(0.5)	189.3(0.5)	-0.00895	339(3)	494(3)
0.1297	0.04725	0.05638	164.9(0.5)	189.2(0.5)	-0.01041	345(3)	498(3)
0.1492	0.05437	0.06459	165.4(0.5)	189.3(0.5)	-0.01192	347(2)	498(2)
0.1704	0.06210	0.07344	165.9(0.5)	189.3(0.5)	-0.01360	351(2)	499(2)
0.1928	0.07023	0.08268	166.3(0.5)	189.3(0.5)	-0.01504	355(2)	502(2)
				$T = 313.15$ K			
0.0179	0.00652	0.00791	164.3(0.6)	190.9(0.6)	-0.00153	331(4)	495(5)
0.0347	0.01266	0.01525	166.2(0.5)	192.4(0.5)	-0.00279	347(3)	508(3)
0.0532	0.01940	0.02325	167.0(0.5)	192.6(0.5)	-0.00425	348(3)	507(3)
0.0708	0.02579	0.03079	167.5(0.5)	192.8(0.5)	-0.00558	353(3)	510(3)
0.0907	0.03305	0.03927	168.2(0.5)	193.0(0.5)	-0.00712	356(3)	514(3)
0.1106	0.04028	0.04764	168.8(0.5)	193.1(0.5)	-0.00860	363(3)	515(3)
0.1295	0.04718	0.05555	169.3(0.5)	193.3(0.5)	-0.01008	365(2)	514(3)
0.1497	0.05452	0.06391	169.8(0.5)	193.3(0.5)	-0.01151	368(2)	515(3)
0.1722	0.06273	0.07318	170.3(0.5)	193.4(0.5)	-0.01363	373(2)	517(2)
0.1928	0.07023	0.08151	170.9(0.5)	193.6(0.5)	-0.01462	376(2)	518(2)

Table 4.9 (continued)

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt})-1}{c_{p1} \cdot \rho_l}$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
			$T = 328.15$ K				
0.0167	0.00607	0.00729	167.3(0.6)	193.9(0.6)	-0.00147	319(5)	482(6)
0.0355	0.01293	0.01542	168.8(0.5)	194.9(0.6)	-0.00303	339(3)	498(5)
0.0531	0.01934	0.02297	169.4(0.5)	195.0(0.6)	-0.00439	346(3)	503(4)
0.0707	0.02576	0.03044	170.3(0.5)	195.5(0.5)	-0.00576	352(3)	507(4)
0.0909	0.03311	0.03893	170.9(0.5)	195.7(0.5)	-0.00733	357(3)	509(4)
0.1106	0.04029	0.04716	171.4(0.5)	195.7(0.5)	-0.00886	360(3)	509(4)
0.1279	0.04658	0.05433	171.8(0.5)	195.7(0.5)	-0.01018	364(2)	512(4)
0.1506	0.05485	0.06361	172.6(0.5)	196.1(0.5)	-0.01192	366(2)	511(4)
0.1693	0.06169	0.07125	173.0(0.5)	196.1(0.5)	-0.01335	370(2)	513(4)
0.1928	0.07023	0.08072	173.4(0.4)	196.0(0.5)	-0.01502	373(2)	513(4)

Table 4.10 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of $Nd(CF_3SO_3)_3$ at known concentration at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa

m_2	m_3	$\rho_{expt} - \rho_1$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt}\cdot\rho_{expt})-1}{c_{p1}\cdot\rho_1}$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
				T = 288.15 K			
0.0176	0.00060	0.00721	179.4(0.8)	181.9(0.8)	-0.00160	362(5)	379(5)
0.0344	0.00117	0.01405	179.9(0.7)	182.4(0.7)	-0.00311	368(4)	384(4)
0.0524	0.00178	0.02135	180.2(0.7)	182.6(0.7)	-0.00465	374(4)	390(4)
0.0708	0.00240	0.02871	180.4(0.7)	182.9(0.7)	-0.00620	379(4)	395(4)
0.0884	0.00300	0.03575	180.6(0.7)	183.0(0.7)	-0.00761	383(4)	399(4)
0.1082	0.00367	0.04356	180.8(0.7)	183.2(0.7)	-0.00927	387(4)	402(4)
0.1276	0.00433	0.05118	181.0(0.7)	183.3(0.7)	-0.01087	388(3)	403(3)
0.1474	0.00500	0.05889	181.1(0.7)	183.4(0.7)	-0.01242	392(3)	406(3)
0.1672	0.00567	0.06653	181.2(0.7)	183.4(0.7)	-0.01390	395(3)	410(3)
0.1886	0.00640	0.07478	181.2(0.6)	183.4(0.6)	-0.01556	397(3)	412(3)
				T = 298.15 K			
0.0172	0.00058	0.00699	182.8(0.8)	185.4(0.8)	-0.00149	394(5)	410(5)
0.0346	0.00117	0.01402	183.2(0.7)	185.7(0.7)	-0.00285	407(4)	423(4)
0.0528	0.00179	0.02128	183.6(0.7)	186.1(0.7)	-0.00427	414(4)	429(4)
0.0705	0.00239	0.02831	183.9(0.7)	186.3(0.7)	-0.00571	421(4)	436(4)
0.0897	0.00304	0.03586	184.2(0.7)	186.6(0.7)	-0.00713	426(4)	441(4)
0.1083	0.00367	0.04317	184.3(0.7)	186.6(0.7)	-0.00846	431(3)	446(3)
0.1276	0.00433	0.05062	184.6(0.7)	186.9(0.7)	-0.00998	432(3)	446(3)
0.1474	0.00500	0.05826	184.8(0.7)	187.0(0.7)	-0.01137	435(3)	450(3)
0.1609	0.00546	0.06364	183.5(0.7)	185.7(0.7)	-0.01240	430(3)	444(3)
0.1886	0.00640	0.07390	185.3(0.6)	187.5(0.6)	-0.01434	440(3)	454(3)
				T = 313.15 K			
0.0171	0.00058	0.00688	186.3(0.8)	188.8(0.8)	-0.00137	432(5)	448(5)
0.0345	0.00117	0.01378	187.3(0.7)	189.7(0.7)	-0.00269	443(4)	458(4)
0.0524	0.00178	0.02087	187.8(0.7)	190.3(0.7)	-0.00402	452(4)	467(4)
0.0699	0.00237	0.02771	188.3(0.7)	190.6(0.7)	-0.00528	458(4)	473(4)
0.0895	0.00304	0.03532	188.6(0.7)	190.9(0.7)	-0.00665	463(3)	478(3)
0.1084	0.00367	0.04259	188.8(0.7)	191.1(0.7)	-0.00804	465(3)	479(3)
0.1278	0.00434	0.05005	188.9(0.7)	191.2(0.7)	-0.00934	467(3)	482(3)
0.1474	0.00500	0.05748	189.1(0.7)	191.3(0.7)	-0.01076	467(3)	481(3)
0.1668	0.00566	0.06479	189.2(0.6)	191.4(0.6)	-0.01212	468(3)	482(3)
0.1886	0.00640	0.07298	189.2(0.6)	191.4(0.6)	-0.01354	471(3)	484(3)

Table 4.10 (continued)

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt}\cdot\rho_{expt})}{c_{p1}\cdot\rho_l}-1$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
				$T = 328.15$ K			
0.0170	0.00058	0.00676	189.3(0.8)	191.7(0.8)	-0.00134	445(5)	460(6)
0.0352	0.00119	0.01392	190.3(0.7)	192.7(0.7)	-0.00269	459(4)	474(5)
0.0528	0.00179	0.02080	190.7(0.7)	193.2(0.7)	-0.00396	465(4)	479(5)
0.0693	0.00235	0.02719	191.2(0.7)	193.6(0.7)	-0.00519	468(4)	483(5)
0.0892	0.00302	0.03483	191.3(0.7)	193.6(0.7)	-0.00658	471(3)	486(5)
0.1078	0.00366	0.04192	191.7(0.7)	194.0(0.7)	-0.00792	474(3)	488(5)
0.1276	0.00433	0.04943	191.8(0.7)	194.1(0.7)	-0.00933	474(3)	489(5)
0.1479	0.00501	0.05703	191.9(0.7)	194.2(0.7)	-0.01072	476(3)	490(5)
0.1673	0.00567	0.06427	192.0(0.6)	194.2(0.7)	-0.01196	480(3)	494(4)
0.1886	0.00640	0.07216	192.2(0.6)	194.4(0.7)	-0.01344	481(3)	494(4)

Table 4.11 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of $Er(CF_3SO_3)_3$ at known concentration at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
				T = 288.15 K			
0.0200	0.00120	0.00869	177.5(0.8)	181.9(0.8)	-0.00164	394(5)	422(5)
0.0389	0.00234	0.01685	178.1(0.8)	182.5(0.8)	-0.00311	404(4)	431(4)
0.0583	0.00350	0.02512	178.7(0.8)	183.0(0.8)	-0.00449	415(4)	442(4)
0.0789	0.00474	0.03385	179.0(0.8)	183.2(0.8)	-0.00603	421(4)	447(4)
0.0991	0.00596	0.04235	179.3(0.8)	183.5(0.8)	-0.00749	424(4)	451(4)
0.1198	0.00720	0.05097	179.6(0.8)	183.7(0.8)	-0.00901	426(4)	452(4)
0.1408	0.00846	0.05965	179.9(0.7)	183.9(0.7)	-0.01050	429(4)	455(4)
0.1612	0.00969	0.06802	180.1(0.7)	184.0(0.7)	-0.01192	431(4)	457(4)
0.1864	0.01120	0.07827	180.3(0.7)	184.1(0.7)	-0.01356	436(4)	461(4)
0.2092	0.01257	0.08744	180.5(0.7)	184.3(0.7)	-0.01511	438(4)	462(4)
				T = 298.15 K			
0.0208	0.00124	0.00894	181.4(0.8)	185.8(0.8)	-0.00158	434(5)	461(5)
0.0380	0.00226	0.01629	181.9(0.8)	186.2(0.8)	-0.00274	446(4)	472(4)
0.0577	0.00344	0.02464	182.3(0.8)	186.5(0.8)	-0.00415	453(4)	479(4)
0.0779	0.00464	0.03313	182.5(0.8)	186.7(0.8)	-0.00551	458(4)	484(4)
0.0975	0.00581	0.04129	182.8(0.8)	186.9(0.8)	-0.00692	460(4)	485(4)
0.0991	0.00590	0.04192	182.8(0.8)	186.9(0.8)	-0.00693	461(4)	486(4)
0.1192	0.00711	0.05025	183.1(0.7)	187.1(0.8)	-0.00829	463(4)	488(4)
0.1406	0.00838	0.05897	183.3(0.7)	187.3(0.7)	-0.00965	467(4)	491(4)
0.1852	0.01104	0.07705	183.5(0.7)	187.3(0.7)	-0.01256	468(4)	492(4)
0.2092	0.01247	0.08672	183.3(0.7)	187.0(0.7)	-0.01393	469(4)	493(4)
				T = 313.15 K			
0.0186	0.00112	0.00793	184.6(0.8)	189.0(0.8)	-0.00137	452(5)	479(5)
0.0379	0.00228	0.01607	185.5(0.8)	189.7(0.8)	-0.00268	468(4)	494(4)
0.0571	0.00343	0.02412	185.9(0.8)	190.1(0.8)	-0.00395	476(4)	501(4)
0.0776	0.00466	0.03263	186.2(0.8)	190.3(0.8)	-0.00531	479(4)	504(4)
0.0953	0.00572	0.03988	186.6(0.8)	190.6(0.8)	-0.00646	482(4)	507(4)
0.1186	0.00713	0.04941	186.9(0.7)	190.9(0.8)	-0.00787	489(4)	513(4)
0.1408	0.00846	0.05835	187.2(0.7)	191.2(0.7)	-0.00926	491(4)	515(4)
0.1632	0.00981	0.06734	187.4(0.7)	191.2(0.7)	-0.01066	493(4)	517(4)
0.1864	0.01120	0.07656	187.6(0.7)	191.4(0.7)	-0.01212	494(3)	517(4)
0.2092	0.01257	0.08551	187.9(0.7)	191.6(0.7)	-0.01347	496(3)	520(3)

Table 4.11 (continued)

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt})}{c_{pl} \cdot \rho_l} - 1$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg^{-1})	/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})	/(J·K^{-1}·mol^{-1})
				T = 328.15 K			
0.0190	0.00114	0.00800	187.6(0.8)	192.0(0.9)	-0.00141	458(5)	484(6)
0.0380	0.00229	0.01599	187.8(0.8)	192.1(0.8)	-0.00277	464(4)	490(5)
0.0570	0.00342	0.02381	188.8(0.8)	192.9(0.8)	-0.00405	475(4)	500(5)
0.0773	0.00465	0.03216	189.1(0.8)	193.2(0.8)	-0.00535	481(4)	506(5)
0.0982	0.00590	0.04068	189.4(0.8)	193.4(0.8)	-0.00678	484(4)	508(5)
0.1191	0.00716	0.04909	189.7(0.8)	193.7(0.8)	-0.00814	487(4)	511(5)
0.1406	0.00845	0.05767	189.9(0.7)	193.8(0.8)	-0.00943	492(4)	516(5)
0.1633	0.00981	0.06668	190.2(0.7)	194.0(0.8)	-0.01093	493(4)	516(5)
0.1837	0.01104	0.07470	190.4(0.7)	194.1(0.7)	-0.01224	495(3)	517(5)
0.2092	0.01257	0.08462	190.6(0.7)	194.3(0.7)	-0.01372	498(3)	521(5)

Table 4.12 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of $Yb(CF_3SO_3)_3$ at known concentration at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt}\cdot\rho_{expt})-1}{c_{p1}\cdot\rho_l}$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
			T = 288.15 K				
0.0203	0.01388	0.00987	132.6(0.6)	182.5(0.6)	-0.00204	134(5)	447(5)
0.0389	0.02661	0.01882	134.1(0.6)	183.0(0.6)	-0.00386	143(3)	451(3)
0.0615	0.04205	0.02955	135.7(0.6)	183.6(0.6)	-0.00589	157(3)	458(3)
0.0813	0.05553	0.03881	136.8(0.6)	183.9(0.6)	-0.00780	162(3)	459(3)
0.1060	0.07241	0.05030	138.3(0.6)	184.1(0.6)	-0.00997	173(3)	464(3)
0.1268	0.08664	0.05987	139.4(0.6)	184.3(0.6)	-0.01225	168(3)	453(3)
0.1510	0.10322	0.07097	140.2(0.5)	184.1(0.5)	-0.01388	189(3)	469(3)
0.1750	0.11959	0.08168	141.6(0.5)	184.6(0.5)	-0.01589	195(3)	474(3)
0.1992	0.13614	0.09245	142.7(0.5)	184.8(0.5)	-0.01795	202(3)	475(3)
0.2246	0.15347	0.10358	143.9(0.5)	185.0(0.5)	-0.02004	209(3)	477(3)
			T = 298.15 K				
0.0205	0.01399	0.00984	136.9(0.6)	187.0(0.6)	-0.00184	187(5)	498(5)
0.0408	0.02789	0.01951	138.6(0.6)	187.7(0.6)	-0.00368	195(3)	500(3)
0.0608	0.04156	0.02889	140.1(0.6)	188.2(0.6)	-0.00533	207(3)	506(3)
0.0827	0.05651	0.03904	141.7(0.6)	188.8(0.6)	-0.00723	218(3)	512(3)
0.1040	0.07108	0.04882	142.9(0.6)	189.1(0.6)	-0.00889	228(3)	517(3)
0.1259	0.08606	0.05878	144.1(0.5)	189.3(0.6)	-0.01065	237(3)	521(3)
0.1511	0.10328	0.07011	145.3(0.5)	189.4(0.5)	-0.01268	243(3)	522(3)
0.1726	0.11793	0.07963	146.3(0.5)	189.6(0.5)	-0.01437	249(3)	523(3)
0.2004	0.13692	0.09184	147.4(0.5)	189.6(0.5)	-0.01646	257(3)	526(3)
0.2246	0.15347	0.10234	148.4(0.5)	189.8(0.5)	-0.01828	263(3)	527(3)
			T = 313.15 K				
0.0200	0.01368	0.00949	142.3(0.6)	192.0(0.6)	-0.00181	207(5)	513(5)
0.0403	0.02753	0.01904	142.4(0.6)	191.1(0.6)	-0.00338	230(3)	529(3)
0.0615	0.04200	0.02885	144.1(0.6)	191.7(0.6)	-0.00517	235(3)	528(3)
0.0835	0.05709	0.03898	145.5(0.6)	192.0(0.6)	-0.00698	244(3)	531(3)
0.1038	0.07093	0.04818	146.5(0.6)	192.2(0.6)	-0.00853	253(3)	535(3)
0.1266	0.08651	0.05843	147.6(0.5)	192.3(0.5)	-0.01039	259(3)	536(3)
0.1503	0.10270	0.06895	148.7(0.5)	192.4(0.5)	-0.01223	265(3)	537(3)
0.1738	0.11879	0.07931	149.7(0.5)	192.5(0.5)	-0.01404	271(3)	538(3)
0.1996	0.13637	0.09049	150.8(0.5)	192.6(0.5)	-0.01604	276(3)	537(3)
0.2246	0.15347	0.10123	151.8(0.5)	192.6(0.5)	-0.01779	282(3)	539(3)

Table 4.12 (continued)

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{c_{p,expt} \cdot \rho_{expt}}{c_{pl} \cdot \rho_l} - 1$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
			$T = 328.15$ K				
0.0192	0.01313	0.00906	142.5(0.6)	192.1(0.7)	-0.00177	217(5)	519(6)
0.0399	0.02724	0.01862	145.6(0.6)	194.1(0.6)	-0.00352	221(3)	517(5)
0.0612	0.04184	0.02844	146.9(0.6)	194.3(0.6)	-0.00495	233(3)	523(4)
0.0812	0.05552	0.03751	148.4(0.6)	194.9(0.6)	-0.00696	243(3)	530(4)
0.1024	0.06997	0.04702	149.4(0.6)	195.0(0.6)	-0.00866	250(3)	529(4)
0.1246	0.08517	0.05690	150.6(0.5)	195.2(0.6)	-0.01057	256(3)	530(4)
0.1486	0.10155	0.06742	151.9(0.5)	195.5(0.6)	-0.01228	266(3)	535(4)
0.1751	0.11969	0.07896	153.0(0.5)	195.5(0.6)	-0.01451	271(3)	535(4)
0.1938	0.13242	0.08694	153.9(0.5)	195.7(0.6)	-0.01577	276(3)	535(4)
0.2246	0.15347	0.10000	155.2(0.5)	195.8(0.5)	-0.01820	282(3)	536(4)

Table 4.13 Calculated relative densities, relative massic heat capacities, apparent molar volumes, and apparent molar heat capacities of aqueous solutions of $Y(CF_3SO_3)_3$ at known concentration at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt}\cdot\rho_{expt})}{c_{p1}\cdot\rho_l}-1$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg⁻¹)	/(mol·kg⁻¹)	/(g·cm⁻³)	/(cm³·mol⁻¹)	/(cm³·mol⁻¹)		/(J·K⁻¹·mol⁻¹)	/(J·K⁻¹·mol⁻¹)
			T = 288.15 K				
0.0194	0.00061	0.00684	181.7(0.4)	184.1(0.4)	-0.00157	415(4)	430(4)
0.0391	0.00122	0.01372	182.3(0.3)	184.8(0.3)	-0.00312	424(2)	439(2)
0.0608	0.00190	0.02125	182.6(0.3)	184.9(0.3)	-0.00473	431(2)	445(2)
0.0803	0.00252	0.02795	182.9(0.3)	185.1(0.3)	-0.00616	436(2)	450(2)
0.1013	0.00317	0.03511	183.0(0.3)	185.2(0.3)	-0.00765	440(1)	454(1)
0.1224	0.00383	0.04223	183.2(0.3)	185.4(0.3)	-0.00922	442(1)	456(1)
0.1422	0.00445	0.04887	183.4(0.3)	185.5(0.3)	-0.01055	445(1)	459(1)
0.1633	0.00512	0.05590	183.5(0.2)	185.6(0.2)	-0.01200	447(1)	461(1)
0.1863	0.00584	0.06348	183.6(0.2)	185.7(0.2)	-0.01349	451(1)	465(1)
0.2119	0.00664	0.07185	183.7(0.2)	185.8(0.2)	-0.01522	453(1)	466(1)
			T = 298.15 K				
0.0193	0.00060	0.00674	184.7(0.4)	187.0(0.4)	-0.00146	448(4)	463(4)
0.0386	0.00121	0.01342	185.3(0.3)	187.6(0.3)	-0.00281	461(2)	476(2)
0.0588	0.00184	0.02035	185.7(0.3)	187.9(0.3)	-0.00423	466(2)	480(2)
0.0786	0.00246	0.02709	186.0(0.3)	188.2(0.3)	-0.00558	471(2)	485(2)
0.0999	0.00313	0.03427	186.3(0.3)	188.5(0.3)	-0.00702	474(1)	488(2)
0.1216	0.00381	0.04153	186.5(0.3)	188.6(0.3)	-0.00847	476(1)	490(2)
0.1433	0.00449	0.04870	186.7(0.2)	188.9(0.3)	-0.00986	480(1)	493(1)
0.1652	0.00517	0.05589	186.9(0.2)	189.0(0.2)	-0.01122	483(1)	496(1)
0.1880	0.00589	0.06333	186.9(0.2)	189.0(0.2)	-0.01269	484(1)	497(1)
0.2119	0.00664	0.07103	187.2(0.2)	189.3(0.2)	-0.01408	488(1)	501(1)
			T = 313.15 K				
0.0194	0.00061	0.00671	188.6(0.4)	190.6(0.4)	-0.00138	482(4)	496(4)
0.0388	0.00122	0.01332	189.3(0.3)	191.6(0.3)	-0.00268	491(2)	505(2)
0.0590	0.00185	0.02015	189.4(0.3)	191.6(0.3)	-0.00410	490(2)	502(2)
0.0793	0.00248	0.02694	190.0(0.3)	192.2(0.3)	-0.00539	496(2)	510(2)
0.1010	0.00316	0.03416	190.2(0.3)	192.3(0.3)	-0.00680	498(1)	512(2)
0.1222	0.00383	0.04115	190.4(0.3)	192.5(0.3)	-0.00812	502(1)	516(2)
0.1430	0.00448	0.04795	190.5(0.2)	192.6(0.3)	-0.00944	504(1)	517(1)
0.1654	0.00518	0.05520	190.7(0.2)	192.8(0.2)	-0.01087	505(1)	518(1)
0.1883	0.00590	0.06254	190.9(0.2)	192.9(0.2)	-0.01224	507(1)	520(1)
0.2119	0.00664	0.07010	190.8(0.2)	192.9(0.2)	-0.01373	507(1)	519(1)

Table 4.13 (continued)

m_2	m_3	$\rho_{expt} - \rho_l$	$V_{\phi,expt}$	$V_{2\phi}$	$\dfrac{(c_{p,expt} \cdot \rho_{expt}) - 1}{c_{pl} \cdot \rho_l}$	$C_{p\phi,expt}$	$C_{p,2\phi}$
/(mol·kg^{-1})	/(mol·kg^{-1})	/(g·cm^{-3})	/(cm^3·mol^{-1})	/(cm^3·mol^{-1})		/(J·K^{-1}·mol^{-1})	/(J·K^{-1}·mol^{-1})
			$T = 328.15$ K				
0.0196	0.00061	0.00670	192.1(0.4)	194.3(0.4)	-0.00142	492(4)	506.3(5)
0.0388	0.00121	0.01319	193.0(0.3)	195.3(0.3)	-0.00275	502(2)	516.1(4)
0.0583	0.00183	0.01974	193.5(0.3)	195.7(0.3)	-0.00404	506(2)	519.4(4)
0.0790	0.00247	0.02658	194.0(0.3)	196.1(0.3)	-0.00546	512(2)	525.2(4)
0.1001	0.00313	0.03351	194.3(0.3)	196.4(0.3)	-0.00688	513(1)	526.8(3)
0.1210	0.00379	0.04034	194.5(0.2)	196.5(0.3)	-0.00829	514(1)	527.3(3)
0.1419	0.00444	0.04708	194.7(0.2)	196.7(0.3)	-0.00962	517(1)	530.0(3)
0.1655	0.00518	0.05465	194.8(0.2)	196.8(0.3)	-0.01104	521(1)	534.0(3)
0.1816	0.00569	0.05980	194.8(0.2)	196.8(0.3)	-0.01208	521(1)	533.9(3)
0.2119	0.00664	0.06934	195.0(0.2)	197.0(0.3)	-0.01396	523(1)	535.6(3)

Table 4.14 Estimates of parameters to the Pitzer-ion interaction model equations, shown as equations (2.37) and (2.38), for aqueous solutions of $Gd(CF_3SO_3)_3$, $Dy(CF_3SO_3)_3$, $Nd(CF_3SO_3)_3$, $Er(CF_3SO_3)_3$, $Yb(CF_3SO_3)_3$, and $Y(CF_3SO_3)_3$ at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa

REE salt	V_2^0 /(cm^3·mol^{-1})	$10^4(\beta^{(0)V})$ /(cm^3·kg·mol^{-1}·J^{-1})	$10^3(\beta^{(1)V})$ /(cm^3·kg·mol^{-1}·J^{-1})
	$T = 288.15$ K		
$Gd(CF_3SO_3)_{3(aq)}$	182.42(0.07)	-2.9(0.8)	-3.5(0.3)
$Dy(CF_3SO_3)_{3(aq)}$	179.83(0.09)	13(1)	-9.1(0.5)
$Nd(CF_3SO_3)_{3(aq)}$	179.77(0.07)	-2.8(0.9)	-3.1(0.4)
$Er(CF_3SO_3)_{3(aq)}$	179.41(0.08)	-3.1(0.8)	-1.7(0.4)
$Yb(CF_3SO_3)_{3(aq)}$	179.94(0.08)	-3.1(0.8)	-1.6(0.4)
$Y(CF_3SO_3)_{3(aq)}$	181.78(0.04)	-2.9(0.4)	-2.9(0.2)
	$T = 298.15$ K		
$Gd(CF_3SO_3)_{3(aq)}$	185.77(0.09)	-5(1)	-2.4(0.4)
	189.57[q]		-2.166[q]
$Dy(CF_3SO_3)_{3(aq)}$	185.4(0.1)	-8(1)	-1.7(0.5)
$Nd(CF_3SO_3)_{3(aq)}$	183.2(0.1)	4(1)	-5.7(0.5)
$Er(CF_3SO_3)_{3(aq)}$	183.2(0.2)	-6(2)	-2.2(0.8)
$Yb(CF_3SO_3)_{3(aq)}$	183.5(0.1)	-8.4(0.8)	1.2(0.4)
$Y(CF_3SO_3)_{3(aq)}$	184.52(0.08)	-1.5(0.8)	-3.2(0.4)
	$T = 313.15$ K		
$Gd(CF_3SO_3)_{3(aq)}$	190.4(0.5)	10(5)	-9(2)
$Dy(CF_3SO_3)_{3(aq)}$	189.2(0.2)	-2(1)	-4.6(0.6)
$Nd(CF_3SO_3)_{3(aq)}$	185.68(0.02)	-9.8(0.3)	-0.2(0.1)
$Er(CF_3SO_3)_{3(aq)}$	186.18(0.09)	-1.5(0.9)	-3.7(0.4)
$Yb(CF_3SO_3)_{3(aq)}$	187.1(0.2)	-8(1)	-0.9(0.6)
$Y(CF_3SO_3)_{3(aq)}$	188.1(0.1)	-2(1)	-3.9(0.5)
	$T = 328.15$ K		
$Gd(CF_3SO_3)_{3(aq)}$	193.4(0.2)	4(2)	-9.6(0.8)
$Dy(CF_3SO_3)_{3(aq)}$	190.8(0.2)	-6(2)	-3.6(0.7)
$Nd(CF_3SO_3)_{3(aq)}$	188.4(0.1)	-7(1)	-2.4(0.6)
$Er(CF_3SO_3)_{3(aq)}$	187.7(0.3)	-6(2)	-2(1)
$Yb(CF_3SO_3)_{3(aq)}$	189.5(0.5)	-5(3)	-3(2)
$Y(CF_3SO_3)_{3(aq)}$	190.71(0.06)	-6.9(0.6)	-2.2(0.3)

Table 4.14 (continued)

REE salt	C_{p2}^{0} /(J·K^{-1}·mol^{-1})	$10^5(\beta^{(0)J})$ /(kg·mol^{-1}·K^{-2})	$10^5(\beta^{(1)J})$ /(kg·mol^{-1}·K^{-2})
	$T = 288.15$ K		
Gd(CF$_3$SO$_3$)$_{3(aq)}$	378.0(0.8)	2.3(0.3)	17(1)
Dy(CF$_3$SO$_3$)$_{3(aq)}$	386(4)	3(2)	-36(6)
Nd(CF$_3$SO$_3$)$_{3(aq)}$	343(1)	-0.7(0.6)	23(3)
Er(CF$_3$SO$_3$)$_{3(aq)}$	380(2)	2.8(0.8)	5(4)
Yb(CF$_3$SO$_3$)$_{3(aq)}$	412(3)	-1.4(0.9)	28(4)
Y(CF$_3$SO$_3$)$_{3(aq)}$	392.2(0.9)	0.4(0.3)	17(1)
	$T = 298.15$ K		
Gd(CF$_3$SO$_3$)$_{3(aq)}$	421(2)	-0.6(0.5)	31(3)
Dy(CF$_3$SO$_3$)$_{3(aq)}$	417(5)	-3(1)	-9(6)
Nd(CF$_3$SO$_3$)$_{3(aq)}$	365(2)	2.4(0.6)	9(3)
Er(CF$_3$SO$_3$)$_{3(aq)}$	415(1)	3.8(0.5)	9(2)
Yb(CF$_3$SO$_3$)$_{3(aq)}$	439(2)	2.9(0.6)	9(3)
Y(CF$_3$SO$_3$)$_{3(aq)}$	421(2)	1.1(0.7)	19(3)
	$T = 313.15$ K		
Gd(CF$_3$SO$_3$)$_{3(aq)}$	449(2)	1.7(0.8)	-41(3)
Dy(CF$_3$SO$_3$)$_{3(aq)}$	447(5)	-2(1)	-23(6)
Nd(CF$_3$SO$_3$)$_{3(aq)}$	395(2)	4.3(0.7)	9(3)
Er(CF$_3$SO$_3$)$_{3(aq)}$	429(2)	2.8(0.6)	14(3)
Yb(CF$_3$SO$_3$)$_{3(aq)}$	455(4)	3.9(0.6)	12(4)
Y(CF$_3$SO$_3$)$_{3(aq)}$	448(2)	1.5(0.5)	26(2)
	$T = 328.15$ K		
Gd(CF$_3$SO$_3$)$_{3(aq)}$	448(3)	-1.0(0.5)	43(3)
Dy(CF$_3$SO$_3$)$_{3(aq)}$	430(2)	-3.9(0.7)	-17(3)
Nd(CF$_3$SO$_3$)$_{3(aq)}$	410(2)	2.2(0.6)	23(3)
Er(CF$_3$SO$_3$)$_{3(aq)}$	421(4)	2.9(0.8)	16(4)
Yb(CF$_3$SO$_3$)$_{3(aq)}$	452(5)	2.6(0.9)	22(5)
Y(CF$_3$SO$_3$)$_{3(aq)}$	456(2)	0.8(0.5)	30(2)

[q]Xiao and Tremaine (1996a)

Table 4.15 A comparison of literature and calculated $V_2^0(R^{3+}; aq)$ and $C_{p2}^0(R^{3+}; aq)$ values for $R^{3+}_{(aq)} = (Gd^{3+}, Dy^{3+}, Nd^{3+}, Er^{3+}, Yb^{3+},$ and $Y^{3+})$ at $T = (288.15, 298.15, 313.15,$ and 328.15) K and $p = 0.1$ MPa

$V_2^0(R^{3+}; aq) /(cm^3 \cdot mol^{-1})$					
$Gd^{3+}_{(aq)}$	$Dy^{3+}_{(aq)}$	$Nd^{3+}_{(aq)}$	$Er^{3+}_{(aq)}$	$Yb^{3+}_{(aq)}$	$Y^{3+}_{(aq)}$
		$T = 288.15$ K			
-40.54(0.07)[r]	-43.13(0.09)[r]	-43.18(0.08)[r]	-43.55(0.08)[r]	-43.01(0.08)[r]	-41.18(0.05)[r]
-38.49(0.37)[s]	-39.8(0.8)[u]			-44.4(0.8)[u]	-41.4(0.4)[t]
-39.8(0.4)[t]	-39.4(0.4)[v]			-43.9(0.4)[v]	-41.4(0.8)[u]
-39.7(0.8)[u]					-42.1(0.4)[v]
		$T = 298.15$ K			
-40.5(0.1)[r]	-40.8(0.2)[r]	-43.0(0.1)[r]	-43.1(0.2)[r]	-42.7(0.2)[r]	-41.7(0.1)[r]
-40.31(0.39)[s]	-40.5(0.8)[u]	-43.49(0.3)[w]	-42.98(0.3)[w]	-44.1(0.8)[u]	-41.7(0.4)[t]
-40.8(0.4)[t]	-39.9(0.5)[v]	-43.6[x]	-42.6[x]	-45.0(0.4)[v]	-42.2(0.8)[u]
-40.0(0.8)[u]	-40.7(0.3)[w]			-44.42(0.3)[w]	-41.9(0.4)[v]
-40.49(0.3)[w]				-44.2[x]	-40.21[w]
-41.21[y]					
-36.72(0.70)[z]					
		$T = 313.15$ K			
-39.8(0.5)[r]	-41.0(0.2)[r]	-44.5(0.1)[r]	-44.0(0.1)[r]	-43.1(0.2)[r]	-42.1(0.1)[r]
-41.13(0.38)[s]	-41.7(0.8)[u]	-45.1[x]	-44.3[x]	-45.3(0.8)[u]	-42.7(0.4)[t]
-41.9(0.4)[t]	-40.2(0.4)[v]			-44.2(0.4)[v]	-42.6(0.8)[u]
-41.3(0.8)[u]				-45.6[x]	-43.5(0.4)[v]
-42.38[y]					
		$T = 328.15$ K			
-40.1(0.3)[r]	-42.7(0.4)[r]	-45.1(0.4)[r]	-45.8(0.5)[r]	-44.0(0.6)[r]	-42.8(0.4)[r]
-41.65(0.38)[s]	-44.4(0.8)[u]	-45.6[x]	-44.3[x]	-47.5(0.8)[u]	-43.4(0.5)[t]
-42.4(0.5)[t]	-43.3(0.4)[v]			-45.6(0.5)[v]	-43.0(0.8)[u]
-43.2(0.8)[u]				-45.9[x]	-45.5(0.4)[v]
-42.13[y]					

Table 4.15 (continued)

$C_{p2}^0(R^{3+}; aq) / (J \cdot K^{-1} \cdot mol^{-1})$

$Gd^{3+}_{(aq)}$	$Dy^{3+}_{(aq)}$	$Nd^{3+}_{(aq)}$	$Er^{3+}_{(aq)}$	$Yb^{3+}_{(aq)}$	$Y^{3+}_{(aq)}$
		T = 288.15 K			
-58.1(0.8)[r]	-50(4)[r]	-93(1)[r]	-56(2)[r]	-24(3)[r]	-43.9(0.9)[r]
-74.8(3.7)[s]	-45.4(8.4)[u]			-42.9(8.0)[u]	-57(4)[t]
-58(4)[t]	-75(6)[v]			-24(5)[v]	-71.0(8.4)[u]
-82.0(7.5)[u]					-44(4)[v]
		T = 298.15 K			
-48(2)[r]	-53(5)[r]	-105(2)[r]	-54(2)[r]	-30(3)[r]	-49(2)[r]
-64.8(4.6)[s]	-50.0(8.4)[u]	-104.1(5)[w]	-60.6(5)[w]	-43.5(8.0)[u]	-57(4)[t]
-70(4)[t]	-55(5)[v]	-111.9[x]	-68.3[x]	-64(4)[v]	-68.4(7.6)[u]
-95.3(7.5)[u]	-69.6(10)[w]			-57.2(5)[w]	-65(4)[v]
-67.7(5)[w]					-70[w]
-73.6[y]					
		T = 313.15 K			
-46(2)[r]	-48(5)[r]	-100(2)[r]	-66(2)[r]	-40(4)[r]	-48(2)[r]
-81.5(3.6)[s]	-59.2(8.4)[u]	-96.0[x]	-71.0[x]	-46.3(8.7)[u]	-78(4)[t]
-76(4)[t]	-73(4)[v]			-61(4)[v]	-64.5(7.6)[u]
-94.3(7.8)[u]				-63.4[x]	-76(4)[v]
-87.5[y]					
		T = 328.15 K			
-58(6)[r]	-76(6)[r]	-97(6)[r]	-85(7)[r]	-54(7)[r]	-96(6)[r]
-66.0(5.8)[j]	-79.5(8.1)[u]	-111.1[x]	-91.4[x]	-54.1(8.7)[u]	-79(4)[t]
-78(5)[t]	-75(6)[v]			-50(4)[v]	-75.7(8.3)[u]
-71.1(7.5)[u]				-64.3[x]	-81(7)[v]
-87.7[y]					

[r] Current study
[s] Hakin, *et al.* (2004b)
[t] Hakin, *et al.* (2005)
[u] Hakin, *et al.* (2003b)
[v] Hakin, *et al.* (2003a)
[w] Marriott, *et al.* (2001)
[x] Xiao and Tremaine (1997a)
[y] Xiao and Tremaine (1996b)
[z] Xiao *et al.* (1996a, 2001)

5) A THERMOCHEMICAL STUDY OF AQUEOUS SOLUTIONS OF SELECTED REE TRIFLATES OVER AN EXTENDED SURFACE OF TEMPERATURE AND PRESSURE

5.1 Introduction

Despite the significant amount of previous work on aqueous REE salt solutions at near ambient temperatures and ambient pressure (Hakin *et al.*, 2003a, 2003b, 2004b, 2005; Marriott *et al.*, 2001; Spedding *et al.*, 1966a, 1966b, 1975a, 1975b, 1979; Xiao *et al.,* 1996a, 1996b, 1997a; and those presented in Chapter 4), few studies have been conducted at temperatures and pressures removed from these conditions. Hakin *et al.* (2004a) focused on the volumetric study of $Yb(ClO_4)_{3(aq)}$ at $T = (323.15, 348.15, 373.15, 398.15,$ and $423.15)$ K and $p = (10.00, 20.00,$ and $30.00)$ MPa. In addition, Xiao *et al.* (1996a, 1999) conducted a volumetric study of aqueous solutions of the REE triflates $(Gd(CF_3SO_3)_{3(aq)}$ and $La(CF_3SO_3)_{3(aq)})$ at temperatures above those achievable by the Picker system described in Chapter 3.

Many processes commonly used to extract the REEs from their native ores occur at temperatures and pressures that are far removed from ambient (or near ambient) conditions. One such example is the extraction of lanthanum, cerium, and neodymium from monazite sand, which requires temperatures in the range 413 K to 483 K (Sabot and Maestro, 1995). In addition, the common uses for the REEs described in Chapter 4 do not always exist at near ambient conditions. Therefore, fundamental thermodynamic data for the aqueous REE metal ions are also important at temperatures and pressures far removed from ambient.

5.2 Trifluoromethanesulfonic Acid in Aqueous Solution

Trifluoromethanesulfonic acid (triflic acid, CF_3SO_3H) was obtained from Aldrich Chemical Company (98%, Catalog No. 15853-4). The acid was diluted and standardized using the methods described in Chapter 4.

Relative densities were measured using the high temperature and pressure vibrating tube densimeter described in Chapter 3. Apparent molar volumes, $V_{3\phi}$, for triflic acid were calculated using the relative solution densities, ρ_{expt}, using equation (2.19).

In Chapter 4, the need for thermodynamic data for aqueous triflic acid over an extended range of ionic strength was discussed. Since there have been no reported thermodynamic studies of $CF_3SO_3H_{(aq)}$ at elevated temperatures and pressures, the maximum concentration of the acid used in the measurements described in this chapter was significantly higher ($c = 1.22$ mol·L^{-1}) than the concentration used in the studies reported in Chapter 4.

Values for $(\rho_{expt} - \rho_l)$ and $V_{3\phi}$ for aqueous triflic acid solutions of known concentration are reported in Table 5.1 along with their relative uncertainties at each temperature and pressure of interest. The relative uncertainties were calculated using the procedure described in Chapter 3. The Pitzer-ion equation (equation (2.37)) was used to model the concentration dependences of the calculated apparent molar volumes of aqueous triflic acid solutions at each investigated temperature in order to determine the apparent molar volumes at infinite dilution, V_3^0, for triflic acid at each temperature and pressure of interest.

Values for the Debye-Hückel limiting slope, A_V, were determined using the full
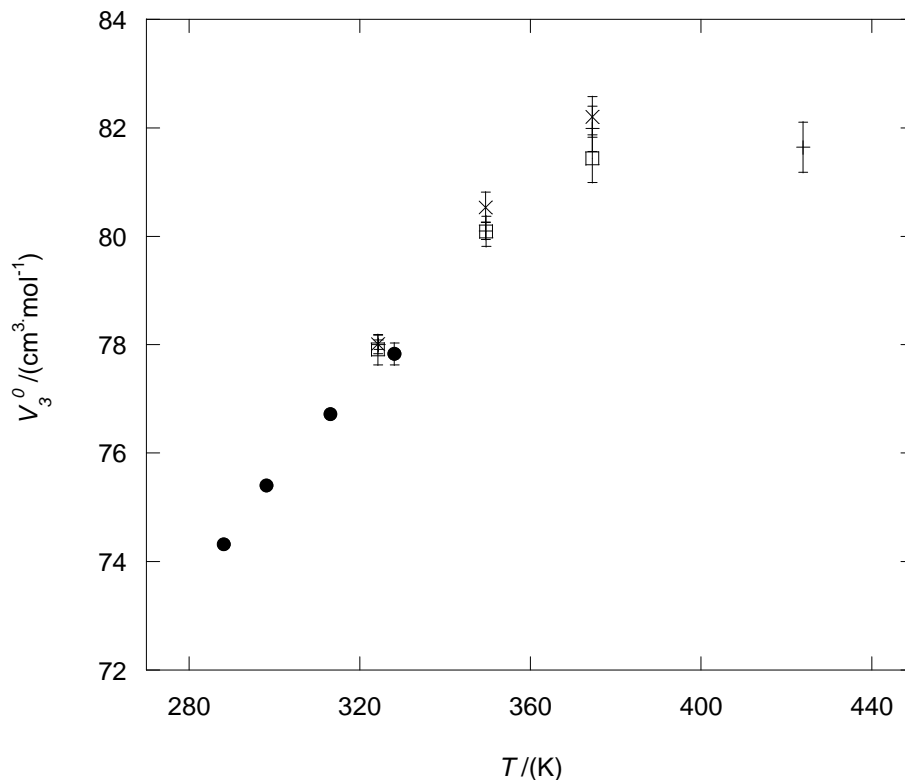
Figure 5.1 The temperature dependences of V_3^0 values for aqueous solutions of CF_3SO_3H, calculated, using equations (2.19) and (2.37), at each experimental pressure of interest: $\bullet$, $p = 0.1$ MPa; $\times$, $p = 5.00$ MPa; $+$, $p = 10.00$ MPa; and $\square$, $p = 15.00$ MPa.

compilation of A_V values reported by Archer and Wang (1990). Values for V_3^0 and the parameters $\beta^{(0)V}$, $\beta^{(1)V}$, and C^V were determined using least squares multiple regression analyses. These values, along with their estimated uncertainties, are reported in Table 5.2. Figure 5.1 shows the V_3^0 values for $CF_3SO_3H_{(aq)}$ as a function of temperature for each investigated pressure, as well as those V_3^0 values reported in Chapter 4 (Table 4.2) at ambient pressure.

The temperature and pressure dependences of the fitting parameters were also
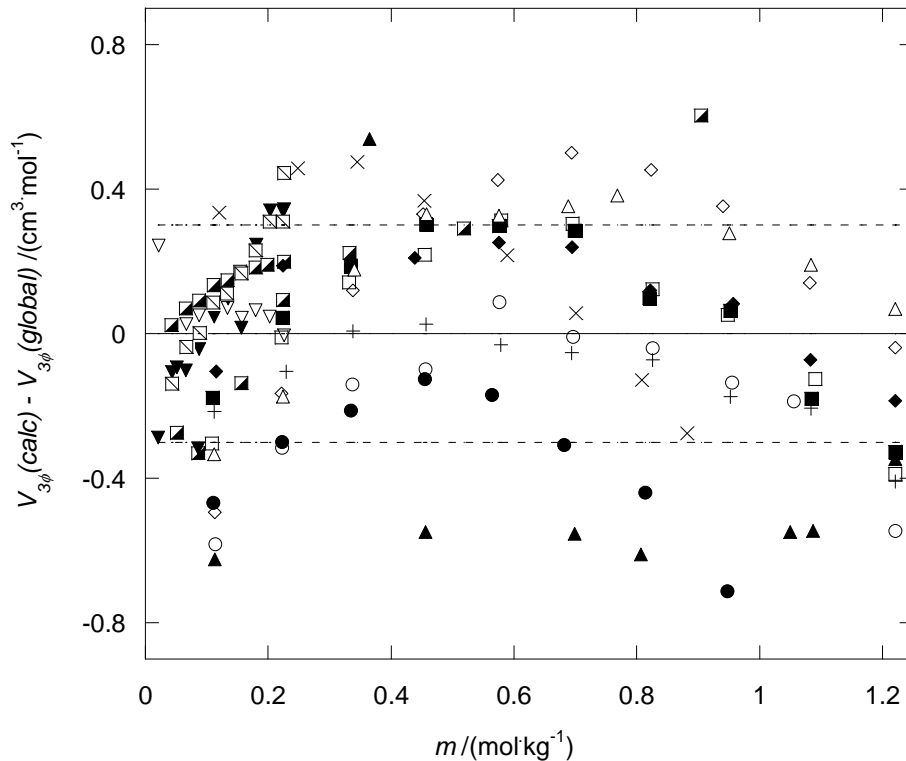
Figure 5.2 Comparison of $V_{3\phi}$ values (as a function of molality) calculated using equation (2.19) ($V_{3\phi}$(calc)) with those calculated using equations (2.37) and (5.1) to (5.4) for $CF_3SO_3H_{(aq)}$ ($V_{3\phi}$(global)) over the temperature and pressure surface of interest: $\triangledown$, $T = 288.15$ K, $p = 0.1$ MPa; ◩, $T = 298.15$ K, $p = 0.1$ MPa; ▼, $T = 313.15$ K, $p = 0.1$ MPa; ◪, $T = 328.15$ K, $p = 0.1$ MPa; ●, $T = 323.15$ K, $p = 5.00$ MPa; ×, $T = 323.15$ K, $p = 10.00$ MPa; +, $T = 323.15$ K, $p = 15.00$ MPa; □ , $T = 348.15$ K, $p = 5.00$ MPa; ◇,$T = 348.15$ K, $p = 10.00$ MPa; ■, $T = 348.15$ K, $p = 15.00$ MPa; △ , $T = 373.15$ K, $p = 5.00$ MPa; ▲, $T = 373.15$ K, $p = 10.00$ MPa; ◌, $T = 373.15$ K, $p = 15.00$ MPa; and ◆, $T = 423.15$ K, $p = 10.00$ MPa (the dashed lines represent the standard error).

investigated. Such dependences were found to be well modeled by equations of the form:

$$V_3^0 = f_1 + f_2 \cdot \beta \cdot (T - T_m) + f_3 \cdot \beta \cdot (T - T_m)^2, \tag{5.1}$$

$$\beta^{(0)V} = f_4 + f_5 \cdot (T - T_m)^2 + f_6 \cdot (p - p_m) \cdot (T - T_m), \tag{5.2}$$

$$\beta^{(1)V} = f_7 + f_8 \cdot (T - T_m) + f_9 \cdot (T - T_m)^2 + f_{10} \cdot (p - p_m) \cdot (T - T_m), \qquad (5.3)$$

$$C^V = f_{11} + f_{12} \cdot (T - T_m) + f_{13} \cdot (T - T_m)^2. \qquad (5.4)$$

The forms of these global fit equations are based on those reported by Simonson *et al.* (1994) where p_m is the mid-point pressure of study ($p_m = 7.5$ MPa), T_m is the mid-point temperature of study ($T_m = 355.15$ K), and β is the isothermal compressibility coefficient of water (Archer, 1992) that has been calculated using Hill's (1990) equation of state for water. Estimated values of the fitting coefficients f_1 to f_{13} were obtained using a regression analysis and are reported in Table 5.3, along with their estimated standard errors. A comparison of $V_{3\phi}$ values for aqueous solutions of CF_3SO_3H calculated using equation (2.19) ($V_{3\phi}$(calc)) and those calculated using equation (2.37), $V_{3\phi}$(global), is shown in Figure 5.2, where $V_{3\phi}$(global) at each concentration was calculated using the fitting coefficients for equations (5.1) to (5.4). The comparison indicates good agreement between the $V_{3\phi}$ values calculated using equation (2.19) and those $V_{3\phi}$ values calculated using equations (2.37) and (5.1) to (5.4).

Table 5.1 Calculated relative densities and apparent molar volumes of aqueous solutions of CF_3SO_3H of known concentration at $T = $ (323.15, 348.15, 373.15, and 423.15) K and $p = $ (5.00, 10.00, and 15.00) MPa

T /(K)	p /(MPa)	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{3\phi}$ /(cm^3·mol^{-1})
		$T = $ 323.15 K, $p = $ 5.00 MPa		
324.30	5.004	0.1104	0.00794	78(1)
324.29	5.006	0.1104	0.00791	78(1)
324.31	5.005	0.2226	0.01590	77(2)
324.31	5.009	0.2226	0.01556	79(2)
324.31	5.004	0.3342	0.02373	77.3(0.4)
324.31	5.008	0.3342	0.02377	77.2(0.4)
324.31	5.010	0.4554	0.03221	76.94(----)
324.30	5.014	0.5645	0.03976	76.7(0.2)
324.31	5.017	0.5645	0.03979	76.6(0.2)
324.30	5.006	0.6813	0.04785	76.3(0.2)
324.31	5.011	0.6813	0.04786	76.3(0.2)
324.30	5.004	0.8139	0.05690	75.9(0.2)
324.30	5.004	0.8139	0.05693	75.9(0.2)
324.30	5.005	0.9473	0.06607	75.4(0.1)
324.30	5.011	0.9473	0.06605	75.4(0.1)
324.29	5.007	1.0764	0.07484	75.0(0.1)
324.30	5.005	1.0764	0.07481	75.0(0.2)
324.31	5.008	1.2204	0.08468	74.4(0.2)
324.31	5.005	1.2204	0.08455	74.5(0.2)
		$T = $ 323.15 K, $p = $ 10.00 MPa		
324.45	10.009	0.1196	0.00851	78.34(----)
324.45	10.011	0.2481	0.01746	78(1)
324.45	10.011	0.2481	0.01768	78(1)
324.45	10.009	0.3446	0.02433	77.7(0.4)
324.45	10.009	0.3446	0.02436	77.6(0.3)
324.45	10.007	0.4544	0.03230	76.6(0.6)
324.46	10.009	0.4544	0.03204	77.2(0.6)
324.46	10.006	0.5887	0.04117	77.0(0.8)
324.45	10.011	0.5887	0.04163	76.3(0.8)
324.46	10.009	0.7007	0.04937	75.9(0.6)
324.46	10.007	0.7007	0.04899	76.5(0.6)
324.46	10.009	0.8079	0.05617	76(1)
324.46	10.007	0.8079	0.05703	75(1)
324.42	10.009	0.8819	0.06182	75.4(0.4)
324.41	10.009	0.8819	0.06162	75.6(0.4)
324.40	10.014	0.9019	0.06628	71.8(0.5)
324.40	10.006	0.9019	0.06584	72.3(0.5)
324.40	10.006	1.2204	0.08485	74(1)
324.39	10.006	1.2204	0.08326	76(1)

Table 5.1 (continued)

T /(K)	p /(MPa)	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{3\phi}$ /(cm^3·mol^{-1})
$T = 323.15$ K, $p = 15.00$ MPa				
324.27	15.013	0.1120	0.00804	78(1)
324.27	15.013	0.1120	0.00805	78(1)
324.27	15.014	0.2297	0.01645	77.2(0.6)
324.27	15.014	0.2297	0.01637	77.6(0.6)
324.26	15.016	0.3383	0.02416	76.8(0.4)
324.26	15.014	0.3383	0.02409	77.0(0.4)
324.27	15.013	0.4569	0.03249	76.5(0.3)
324.27	15.014	0.4569	0.03247	76.6(0.8)
324.27	15.013	0.5785	0.04094	76.2(0.8)
324.26	15.014	0.5785	0.04109	76.0(0.3)
324.27	15.016	0.6932	0.04919	75.4(0.4)
324.27	15.009	0.6932	0.04898	75.7(0.3)
324.27	15.011	0.8256	0.05805	75.4(0.2)
324.27	15.013	0.8256	0.05811	75.3(0.2)
324.26	15.013	0.9523	0.06670	75.1(0.2)
324.27	15.009	0.9523	0.06685	74.9(0.2)
324.27	15.011	1.0835	0.07561	74.7(0.1)
324.27	15.013	1.0835	0.07566	74.6(0.2)
324.27	15.013	1.2204	0.08492	74.2(0.1)
324.27	15.013	1.2204	0.08504	74.1(0.1)
$T = 348.15$ K, $p = 5.00$ MPa				
349.55	5.010	0.1086	0.00755	80(1)
349.54	5.006	0.1086	0.00758	80(1)
349.55	5.005	0.2213	0.01536	79.7(0.5)
349.55	5.008	0.2213	0.01536	79.7(0.6)
349.55	5.004	0.3320	0.02297	79.3(0.4)
349.55	5.008	0.3320	0.02298	79.3(0.3)
349.55	5.014	0.4551	0.03138	78.9(0.3)
349.55	5.010	0.4551	0.03139	78.8(0.3)
349.54	5.006	0.5787	0.03971	78.5(0.2)
349.54	5.005	0.5787	0.03969	78.6(0.2)
349.54	5.005	0.6952	0.04751	78.2(0.2)
349.55	5.003	0.6952	0.04750	78.2(0.2)
349.54	5.008	0.8258	0.05631	77.7(0.2)
349.52	5.004	0.8258	0.05628	77.8(0.2)
349.54	5.006	0.9483	0.06430	77.5(0.1)
349.55	5.006	0.9483	0.06436	77.4(0.2)
349.50	5.009	1.0902	0.07362	77.1(0.1)
349.49	5.012	1.0902	0.07364	77.1(0.2)
349.49	5.008	1.2204	0.08218	76.6(0.1)
349.49	5.005	1.2204	0.08227	76.6(0.1)

Table 5.1 (continued)

T /(K)	p /(MPa)	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{3\phi}$ /(cm^3·mol^{-1})
		$T = 348.15$ K, $p = 10.00$ MPa		
349.46	10.007	0.1127	0.00783	80(38)
349.46	10.009	0.1127	0.00787	80(38)
349.46	10.009	0.2215	0.01547	79.2(0.5)
349.46	10.008	0.2215	0.01540	79.5(0.6)
349.45	10.007	0.3377	0.02346	78.9(0.5)
349.46	10.007	0.3377	0.02348	78.9(0.5)
349.46	10.007	0.4525	0.03126	78.7(0.3)
349.46	10.007	0.4525	0.03131	78.6(0.3)
349.52	10.011	0.5745	0.03963	78.2(0.2)
349.46	10.006	0.5745	0.03955	78.3(0.3)
349.46	10.006	0.6940	0.04751	78.1(0.3)
349.47	10.011	0.6940	0.04765	77.9(0.3)
349.46	10.006	0.8229	0.05606	77.8(0.2)
349.47	10.009	0.8229	0.05617	77.6(0.2)
349.47	10.012	0.9402	0.06378	77.5(0.3)
349.47	10.014	0.9402	0.06397	77.3(0.3)
349.46	10.011	1.0815	0.07309	77.0(0.3)
349.46	10.009	1.0815	0.07335	76.8(0.3)
349.47	10.007	1.2204	0.08207	76.7(0.3)
349.47	10.007	1.2204	0.08246	76.4(0.3)
		$T = 348.15$ K, $p = 15.00$ MPa		
349.60	15.040	0.1095	0.00772	79(1)
349.60	15.034	0.1095	0.00767	80(1)
349.60	15.020	0.2233	0.01562	79.0(0.5)
349.60	15.020	0.2233	0.01558	79.2(0.6)
349.59	15.024	0.3348	0.02322	79.1(0.8)
349.60	15.034	0.3348	0.02344	78.4(0.8)
349.61	15.037	0.4564	0.03177	78.1(0.4)
349.60	15.034	0.4564	0.03161	78.5(0.4)
349.59	15.023	0.5757	0.03970	78.2(0.3)
349.60	15.025	0.5757	0.03985	77.9(0.4)
349.61	15.035	0.6993	0.04835	77.3(0.4)
349.61	15.039	0.6993	0.04811	77.7(0.4)
349.59	15.037	0.8206	0.05620	77.4(0.4)
349.59	15.042	0.8206	0.05649	77.0(0.4)
349.59	15.040	0.9523	0.06523	76.7(0.1)
349.60	15.040	0.9523	0.06523	76.7(0.1)
349.58	15.032	1.0847	0.07412	76.2(0.2)
349.59	15.045	1.0847	0.07411	76.2(0.2)
349.58	15.034	1.2204	0.08307	75.8(0.1)
349.59	15.028	1.2204	0.08298	75.9(0.1)

Table 5.1 (continued)

T /(K)	p /(MPa)	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{3\phi}$ /(cm^3·mol^{-1})
$T = 373.15$ K, $p = 5.00$ MPa
374.52	5.005	0.1121	0.00761	82(1)
374.53	5.012	0.1121	0.00768	81(1)
374.53	5.008	0.2238	0.01523	81.2(0.5)
374.54	5.006	0.2238	0.01524	81.2(0.5)
374.54	5.005	0.3406	0.02306	81.0(0.4)
374.54	5.003	0.3406	0.02308	80.9(0.3)
374.54	5.004	0.4577	0.03093	80.4(0.3)
374.54	5.005	0.4577	0.03084	80.6(0.3)
374.54	5.004	0.5757	0.03871	80.1(0.2)
374.53	5.004	0.5757	0.03880	80.0(0.3)
374.53	5.004	0.6890	0.04621	79.7(0.2)
374.53	5.003	0.6890	0.04623	79.7(0.2)
374.53	5.005	0.7682	0.05135	79.5(0.2)
374.53	5.004	0.7682	0.05141	79.5(0.2)
374.51	5.007	0.9507	0.06322	79.0(0.1)
374.52	5.006	0.9507	0.06330	78.9(0.1)
374.51	5.007	1.0834	0.07185	78.5(0.2)
374.50	5.005	1.0834	0.07171	78.6(0.3)
374.51	5.003	1.2204	0.08048	78.2(0.1)
374.50	5.005	1.2204	0.08052	78.2(0.1)
$T = 373.15$ K, $p = 10.00$ MPa
374.47	10.035	0.1127	0.00773	81(1)
374.47	10.040	0.1127	0.00778	81(1)
374.50	10.043	0.2409	0.01665	80.0(0.5)
374.49	10.033	0.2409	0.01659	80.2(0.6)
374.49	10.033	0.3646	0.02530	79(1)
374.49	10.035	0.3646	0.02495	80(1)
374.49	10.038	0.4558	0.03167	78.4(0.9)
374.50	10.040	0.4558	0.03129	79.3(0.9)
374.49	10.038	0.5856	0.04020	78.5(0.4)
374.49	10.035	0.5856	0.04045	78.1(0.5)
374.49	10.035	0.6987	0.04818	78(1)
374.48	10.033	0.6987	0.04766	78.4(0.8)
374.49	10.035	0.8069	0.05487	78.1(0.6)
374.48	10.042	0.8069	0.05537	77.4(0.6)
374.48	10.048	1.0493	0.07058	77.6(0.4)
374.48	10.038	1.0493	0.07105	77.1(0.4)
374.45	10.035	1.0871	0.07299	77.6(0.5)
374.44	10.040	1.0871	0.07348	77.1(0.5)
374.43	10.033	1.2204	0.08119	77.6(0.4)
374.43	10.035	1.2204	0.08172	77.1(0.4)

Table 5.1 (continued)

T /(K)	p /(MPa)	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{3\phi}$ /(cm^3·mol^{-1})
		$T = 373.15$ K, $p = 15.00$ MPa		
374.55	15.020	0.1137	0.00787	81(1)
374.54	15.020	0.1137	0.00785	81(1)
374.54	15.025	0.2220	0.01529	80.3(0.5)
374.54	15.018	0.2220	0.01531	80.2(0.5)
374.54	15.006	0.3371	0.02307	80.1(0.7)
374.53	15.011	0.3371	0.02323	79.6(0.6)
374.54	15.023	0.4558	0.03131	79.2(0.4)
374.53	15.020	0.4558	0.03116	79.6(0.4)
374.53	15.016	0.5767	0.03916	79.4(0.6)
374.55	15.022	0.5767	0.03944	78.9(0.6)
374.54	15.024	0.6961	0.04712	79.0(0.7)
374.54	15.027	0.6961	0.04751	78.4(0.7)
374.54	15.020	0.8259	0.05581	78.4(0.2)
374.53	15.025	0.8259	0.05593	78.3(0.2)
374.49	15.011	0.9554	0.06446	77.9(0.3)
374.53	15.015	0.9554	0.06423	78.1(0.3)
374.53	15.008	1.0559	0.07083	77.8(0.1)
374.54	15.018	1.0559	0.07082	77.8(0.2)
374.55	15.018	1.2204	0.08146	77.3(0.2)
374.54	15.024	1.2204	0.08166	77.2(0.2)
		$T = 423.15$ K, $p = 10.00$ MPa		
423.88	10.023	0.1154	0.00774	83(1)
423.90	10.028	0.1154	0.00777	83(1)
423.91	10.033	0.2241	0.01493	83.0(0.5)
423.89	10.030	0.2241	0.01489	83.3(0.6)
423.91	10.029	0.3462	0.02267	83.7(0.5)
423.90	10.031	0.3462	0.02276	83.4(0.4)
423.96	10.032	0.4390	0.02893	82.7(0.4)
423.91	10.034	0.4390	0.02901	82.4(0.4)
423.90	10.033	0.5755	0.03782	82.1(0.2)
423.92	10.033	0.5755	0.03780	82.1(0.2)
423.90	10.036	0.6949	0.04544	81.8(0.3)
423.90	10.027	0.6949	0.04556	81.6(0.2)
423.87	10.031	0.8224	0.05377	81.1(0.3)
423.89	10.029	0.8224	0.05367	81.3(0.3)
423.89	10.024	0.9565	0.06217	80.9(0.2)
423.91	10.029	0.9565	0.06232	80.7(0.2)
423.90	10.022	1.0829	0.07040	80.2(0.2)
423.88	10.027	1.0829	0.07025	80.4(0.2)
423.88	10.028	1.2204	0.07891	79.9(0.2)
423.90	10.021	1.2204	0.07911	79.7(0.2)

Table 5.2 Estimates of the parameters to the Pitzer-ion interaction equation, shown as equation (2.37), for aqueous solutions of CF_3SO_3H at $T = (323.15, 348.15, 373.15,$ and $423.15)$ K and $p = (5.00, 10.00,$ and $15.00)$ MPa

T /(K)	p /(MPa)	V_3^0 /(cm³·mol⁻¹)	$10^4(\beta^{(0)V})$ /(kg·mol⁻¹·MPa⁻¹)	$10^3(\beta^{(1)V})$ /(kg·mol⁻¹·MPa⁻¹)	C^V /(mol²·kg⁻²)
324.30	5.01	78.0(0.2)	-6.3(0.6)	-0.8(0.1)	-0.4(0.2)
324.44	10.01	78.00(0.09)	-12.2(0.3)	-0.13(0.07)	0.96(0.08)
324.27	15.01	77.9(0.3)	-9(1)	-0.7(0.2)	0.5(0.3)
349.53	5.01	80.5(0.3)	-8.0(0.9)	-1.1(0.2)	0.3(0.2)
349.47	10.01	80.1(0.2)	-5.7(0.5)	-1.2(0.1)	-0.4(0.1)
349.60	15.03	80.1(0.3)	-9.3(0.9)	-1.0(0.2)	0.6(0.3)
374.53	5.005	82.2(0.4)	-10(1)	-1.3(0.2)	0.8(0.4)
374.48	10.04	82.0(0.4)	-14(1)	-1.3(0.3)	2.8(0.4)
374.54	15.02	81.4(0.4)	-8(1)	-1.6(0.3)	0.5(0.4)
423.90	10.03	81.6(0.5)	-14(1)	-0.7(0.3)	1.5(0.4)

Table 5.3 Estimated parameters for equations (5.1) to (5.4) that model the temperature and pressure dependences of $V_{3\phi}$ values for aqueous solutions of CF_3SO_3H at $T = (288.15, 298.15, 313.15, 323.15, 328.15, 348.15, 373.15,$ and $423.15)$ K and $p = (0.1, 5.00, 10.00,$ and $15.00)$ MPa

$V_{3\phi}$ Parameter:	Value:
f_1 /(cm³·mol⁻¹)	64(2)
f_2 /(cm³·MPa·mol⁻¹·K⁻¹)	$3.7 \times 10^4 (4 \times 10^3)$
f_3 /(cm³·MPa·mol⁻¹·K⁻²)	59(8)
f_4 /(cm³·kg·mol⁻¹·J⁻¹)	-2.4(0.2)
f_5 /(cm³·kg·mol⁻¹·J⁻¹·K⁻²)	$1.0 \times 10^{-4} (4 \times 10^{-5})$
f_6 /(cm³·kg·mol⁻¹·J⁻¹·K⁻¹·MPa⁻¹)	$-1.3 \times 10^{-7} (2 \times 10^{-8})$
f_7 /(cm³·kg·mol⁻¹·J⁻¹)	$7 \times 10^{-7} (1 \times 10^{-7})$
f_8 /(cm³·kg·mol⁻¹·J⁻¹·K⁻¹)	$-4.6 \times 10^{-3} (2 \times 10^{-4})$
f_9 /(cm³·kg·mol⁻¹·J⁻¹·K⁻²)	$-2.5 \times 10^{-5} (1 \times 10^{-6})$
f_{10} /(cm³·kg·mol⁻¹·J⁻¹·K⁻¹·MPa⁻¹)	$6.2 \times 10^{-7} (8 \times 10^{-8})$
f_{11} /(kg·mol⁻¹)	$-1.4 \times 10^{-6} (5 \times 10^{-7})$
f_{12} /(kg·mol⁻¹·K⁻¹)	-0.07(0.02)
f_{13} /(kg·mol⁻¹·K⁻²)	$2.4 \times 10^{-5} (6 \times 10^{-6})$
Standard error /(cm³·mol⁻¹)	0.30

5.3 The REE Triflates in Aqueous Solution

The preparation and standardization of acidified aqueous REE triflate salt solutions followed the procedure previously outlined by both Spedding *et al.* (1966b) and Chapter 4. Relative densities for each of the acidified REE triflate salt solutions ($Gd(CF_3SO_3)_{3(aq)}$, $Nd(CF_3SO_3)_{3(aq)}$, and $Yb(CF_3SO_3)_{3(aq)}$) were measured using the high temperature and pressure vibrating tube densimeter described in Chapter 3.

Apparent molar volumes for each of the acidified REE salt solutions were calculated using equation (4.17). The resulting apparent molar volumes were subjected to Young's rule to determine the apparent molar volumes of the aqueous REE triflate salt solutions. The values for $(\rho_{expt}-\rho_l)$, $V_{\phi,expt}$, and $V_{2\phi}$ are reported at $T = (323.15, 298.15, 348.15,$ and $373.15)$ K and $p = (5.0, 10.0,$ and $15.0)$ MPa for aqueous solutions of $Gd(CF_3SO_3)_3$, $Nd(CF_3SO_3)_3$, and $Yb(CF_3SO_3)_3$ of known concentration in Tables 5.4, 5.5, and 5.6, respectively. Values for $(\rho_{expt} - \rho_l)$, $V_{\phi,expt}$, and $V_{2\phi}$ are also reported for aqueous solutions of $Gd(CF_3SO_3)_3$ of known concentration at $T = 423.15$ K and $p = 10.0$ MPa in Table 5.4. The values reported in the tables in parentheses are the relative uncertainties which were calculated using the procedure described in Chapter 3.

The reported apparent molar volumes of each of the aqueous REE triflate salt solutions were also modeled using the modified Pitzer-ion interaction equation for a 3:1 electrolyte (equation (2.37)). The Pitzer equation was found to successfully model the concentration dependences of the $V_{2\phi}$ values for each aqueous REE triflate salt system at each investigated temperature and pressure combination. Estimates of values for the V_2^0, $\beta^{(0)V}$, $\beta^{(1)V}$, and $\beta^{(1)J}$ parameters were obtained by regression analysis for each aqueous REE triflate salt and are reported, along with their standard errors, in Tables 5.7 to 5.9.
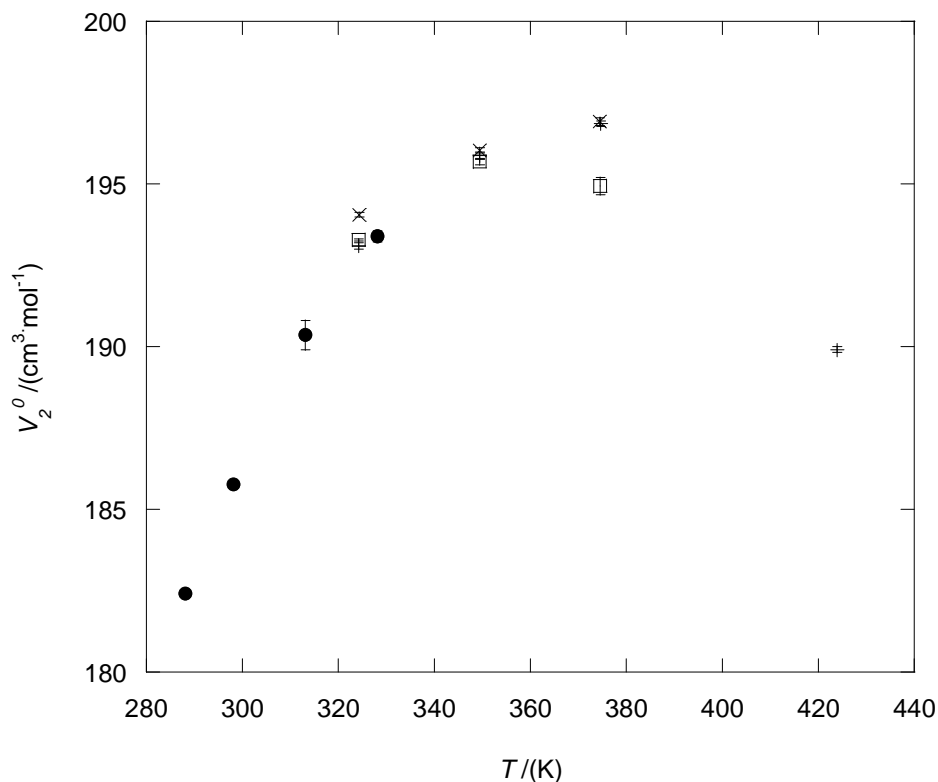
Figure 5.3 Values of V_2^0 for aqueous solutions of Gd(CF$_3$SO$_3$)$_3$, calculated from equation (2.37), and plotted as a function of temperature over the pressure surface of interest: •, $p = 0.1$ MPa; ×, $p = 5.00$ MPa; +, $p = 10.00$ MPa; and □ , $p = 15.00$ MPa.

Figure 5.3 shows the V_2^0 values as a function of temperature for Gd(CF$_3$SO$_3$)$_{3(aq)}$, calculated using equation (2.37). This figure indicates that there is a maximum in V_2^0 values at approximately $T = 348.15$ K. This curvature is typical of electrolyte systems in aqueous solutions. This trend was also shown above in Figure 5.2 for CF$_3$SO$_3$H$_{(aq)}$.

Single ion volumes were calculated for each REE, V_2^0(R^{3+}; aq) using equation (2.37) and have been compared with those previously reported (Hakin *et al.*, 2004b). These comparisons are shown in Table 5.10. As can be seen, the V_2^0(Yb^{3+}; aq) values obtained in this study appear to be consistent with those derived from the perchlorate salt

106

system (Hakin *et al.*, 2004a). Since there have been so few studies with respect to the calculation of $V_2^0(R^{3+}; aq)$ values for the REEs at temperatures and pressures removed from ambient (or near ambient), it is recommended that the values presented in this chapter for $Gd^{3+}_{(aq)}$, $Nd^{3+}_{(aq)}$, and $Yb^{3+}_{(aq)}$ should be adopted for use.

Table 5.4 The relative densities and apparent molar volumes of aqueous solutions of Gd(CF$_3$SO$_3$)$_3$ of known concentration at T = (323.15, 348.15, 373.15, and 423.15) K and p = (5.00, 10.00, and 15.00) MPa

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			T = 323.15 K, p = 5.00 MPa			
324.30	5.009	0.0177	0.00043	0.00721	194(14)	197(14)
324.30	5.008	0.0177	0.00043	0.00748	179(14)	182(14)
324.30	5.008	0.0359	0.00088	0.01452	194.6(0.6)	197.6(0.7)
324.30	5.008	0.0359	0.00088	0.01447	195.9(0.6)	198.9(0.7)
324.30	5.011	0.0534	0.00130	0.02142	197.1(0.2)	200.1(0.3)
324.30	5.006	0.0534	0.00130	0.02153	195.1(0.1)	198.0(0.2)
324.29	5.009	0.0726	0.00177	0.02913	195(1)	198(1)
324.28	5.003	0.0726	0.00177	0.02907	196(1)	199(1)
324.28	5.003	0.0912	0.00223	0.03646	195.5(0.7)	198.5(0.7)
324.28	5.003	0.0912	0.00223	0.03638	196.3(0.7)	199.3(0.7)
324.27	5.005	0.1077	0.00263	0.04287	195.8(0.6)	198.7(0.6)
324.28	5.002	0.1077	0.00263	0.04279	196.4(0.6)	199.4(0.6)
324.29	5.008	0.1313	0.00321	0.05205	195.9(0.7)	198.8(0.7)
324.28	5.004	0.1313	0.00321	0.05193	196.8(0.7)	199.8(0.7)
324.28	5.008	0.1475	0.00360	0.05823	196.1(0.4)	199.0(0.4)
324.28	5.007	0.1475	0.00360	0.05816	196.5(0.4)	199.5(0.4)
324.28	5.006	0.1703	0.00416	0.06687	196.6(0.4)	199.6(0.4)
324.28	5.006	0.1703	0.00416	0.06686	196.7(0.4)	199.6(0.4)
324.28	5.005	0.1929	0.00471	0.07541	197(1)	199(1)
324.28	5.004	0.1929	0.00471	0.07540	197(1)	199(1)

Table 5.4 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg⁻¹)	m_3 /(mol·kg⁻¹)	$\rho_{expt} - \rho_l$ /(g·cm⁻³)	$V_{\phi,expt}$ /(cm³·mol⁻¹)	$V_{2\phi}$ /(cm³·mol⁻¹)
			T = 323.15 K, p = 10.00 MPa			
324.27	10.016	0.0195	0.00048	0.00787	198(4)	201(4)
324.27	10.004	0.0195	0.00048	0.00795	194(4)	196(4)
324.22	10.017	0.0351	0.00086	0.01425	194(2)	197(2)
324.22	10.014	0.0351	0.00086	0.01425	194(2)	197(2)
324.22	10.014	0.0539	0.00132	0.02178	194.5(0.2)	197.2(0.2)
324.22	10.016	0.0539	0.00132	0.02177	194.5(0.1)	197.3(0.2)
324.22	10.017	0.0710	0.00173	0.02852	196(1)	198(1)
324.22	10.017	0.0710	0.00173	0.02858	195(1)	198(1)
324.23	10.014	0.0912	0.00222	0.03651	195.1(0.3)	197.8(0.3)
324.23	10.017	0.0912	0.00222	0.03654	194.8(0.3)	197.6(0.3)
324.23	10.018	0.1106	0.00270	0.04414	195(2)	198(2)
324.23	10.016	0.1106	0.00270	0.04414	195(2)	198(2)
324.22	10.016	0.1283	0.00313	0.05109	195(2)	198(2)
324.22	10.016	0.1283	0.00313	0.05107	195(2)	198(2)
324.22	10.017	0.1487	0.00363	0.05896	195(1)	197(1)
324.22	10.016	0.1487	0.00363	0.05894	195(1)	198(1)
324.22	10.019	0.1714	0.00418	0.06762	195(1)	198(1)
324.22	10.017	0.1714	0.00418	0.06773	194(1)	197(1)
324.22	10.016	0.1929	0.00471	0.07588	194.7(0.2)	197.4(0.2)
324.22	10.017	0.1929	0.00471	0.07592	194.5(0.2)	197.3(0.2)
			T = 323.15 K, p = 15.00 MPa			
324.28	15.004	0.0178	0.00043	0.00727	193.8(0.3)	196.6(0.4)
324.28	15.001	0.0178	0.00043	0.00726	193.9(0.3)	196.7(0.4)
324.28	15.001	0.0356	0.00087	0.01445	195.0(0.6)	197.8(0.7)
324.28	15.001	0.0356	0.00087	0.01446	194.6(0.6)	197.3(0.7)
324.28	15.001	0.0534	0.00130	0.02154	195.2(0.2)	198.0(0.3)
324.27	15.003	0.0534	0.00130	0.02153	195.5(0.1)	198.3(0.3)
324.27	15.001	0.0726	0.00177	0.02916	196.0(0.2)	198.7(0.4)
324.28	15.001	0.0726	0.00177	0.02918	195.7(0.2)	198.5(0.4)
324.27	15.003	0.0909	0.00222	0.03637	196.21(0.09)	199.0(0.3)
324.28	15.001	0.0909	0.00222	0.03637	196.20(0.09)	199.0(0.3)
324.29	15.001	0.1105	0.00270	0.04396	196.6(0.4)	199.4(0.5)
324.28	15.004	0.1105	0.00270	0.04398	196.4(0.4)	199.2(0.5)
324.28	15.001	0.1293	0.00315	0.05124	196.8(0.3)	199.6(0.4)
324.28	15.003	0.1293	0.00315	0.05125	196.7(0.3)	199.4(0.4)
324.28	15.001	0.1496	0.00365	0.05907	196.9(0.8)	199.7(0.9)
324.28	15.003	0.1496	0.00365	0.05907	196.9(0.8)	199.7(0.9)
324.28	15.001	0.1709	0.00417	0.06717	197.0(0.6)	199.8(0.7)
324.27	15.008	0.1709	0.00417	0.06712	197.3(0.4)	200.1(0.5)
324.28	15.008	0.1929	0.00471	0.07550	197.0(0.6)	199.8(0.7)
324.28	15.003	0.1929	0.00471	0.07540	197.5(0.6)	200.3(0.7)

Table 5.4 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 5.00$ MPa			
349.54	5.006	0.0177	0.00043	0.00710	198(1)	200(1)
349.54	5.005	0.0177	0.00043	0.00711	197(1)	199(1)
349.53	5.008	0.0358	0.00087	0.01427	198(2)	200(2)
349.53	5.007	0.0358	0.00087	0.01428	197(2)	200(2)
349.52	5.008	0.0545	0.00133	0.02167	197.8(0.2)	200.5(0.3)
349.52	5.007	0.0545	0.00133	0.02169	197.3(0.1)	200.0(0.3)
349.52	5.005	0.0715	0.00174	0.02834	197.5(0.2)	200.2(0.4)
349.52	5.004	0.0715	0.00174	0.02833	197.7(0.2)	200.4(0.4)
349.53	5.004	0.0916	0.00223	0.03615	197.6(0.7)	200.3(0.7)
349.52	5.004	0.0916	0.00223	0.03613	197.8(0.7)	200.5(0.7)
349.52	5.006	0.1085	0.00265	0.04268	197.9(0.9)	200.6(0.9)
349.53	5.006	0.1085	0.00265	0.04270	197.7(0.9)	200.5(0.9)
349.53	5.007	0.1277	0.00312	0.04983	199(2)	202(2)
349.53	5.008	0.1277	0.00312	0.05002	198(2)	201(2)
349.53	5.005	0.1502	0.00366	0.05858	198(1)	201(1)
349.53	5.005	0.1502	0.00366	0.05856	198(1)	200(1)
349.53	5.003	0.1706	0.00416	0.06616	199(1)	201(1)
349.53	5.005	0.1706	0.00416	0.06627	198(1)	201(1)
349.49	5.007	0.1929	0.00471	0.07463	198.1(0.9)	200.9(0.9)
349.49	5.007	0.1929	0.00471	0.07456	198.4(0.9)	201.2(0.9)
			$T = 348.15$ K, $p = 10.00$ MPa			
349.44	10.004	0.0178	0.00043	0.00716	196.1(0.6)	198.9(0.6)
349.43	10.004	0.0178	0.00043	0.00715	196.4(0.6)	199.1(0.6)
349.44	10.009	0.0355	0.00087	0.01425	196.0(0.9)	198.7(0.9)
349.43	10.009	0.0355	0.00087	0.01422	196.8(0.9)	199.5(0.9)
349.44	10.006	0.0535	0.00131	0.02136	196.6(0.2)	199.4(0.2)
349.44	10.006	0.0535	0.00131	0.02137	196.4(0.1)	199.1(0.2)
349.44	10.006	0.0716	0.00175	0.02846	196.7(0.3)	199.4(0.4)
349.44	10.004	0.0716	0.00175	0.02848	196.5(0.3)	199.2(0.4)
349.43	10.004	0.0911	0.00222	0.03609	196.8(0.2)	199.5(0.2)
349.44	10.004	0.0911	0.00222	0.03608	196.9(0.2)	199.6(0.2)
349.44	10.004	0.1107	0.00270	0.04367	196.8(0.3)	199.5(0.4)
349.44	10.004	0.1107	0.00270	0.04364	197.1(0.3)	199.8(0.4)
349.44	10.004	0.1298	0.00317	0.05082	199(2)	201(2)
349.44	10.006	0.1298	0.00317	0.05103	197(2)	200(2)
349.44	10.004	0.1501	0.00366	0.05869	198(1)	200(1)
349.44	10.004	0.1501	0.00366	0.05882	197(1)	199(1)
349.43	10.004	0.1677	0.00409	0.06542	197.1(0.6)	199.9(0.7)
349.44	10.006	0.1677	0.00409	0.06532	197.8(0.6)	200.5(0.7)
349.42	10.006	0.1929	0.00471	0.07467	198(1)	201(1)
349.42	10.004	0.1929	0.00471	0.07486	197(1)	200(1)

Table 5.4 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 15.00$ MPa			
349.58	15.034	0.0188	0.00046	0.00760	194(3)	197(3)
349.59	15.030	0.0188	0.00046	0.00756	196(3)	199(3)
349.59	15.035	0.0348	0.00085	0.01403	194.3(0.2)	197.0(0.5)
349.60	15.035	0.0348	0.00085	0.01403	194.3(0.2)	197.0(0.5)
349.60	15.037	0.0534	0.00130	0.02132	196.8(0.2)	192(2)
349.57	15.030	0.0534	0.00130	0.02138	195.6(0.1)	198(2)
349.52	15.042	0.0723	0.00176	0.02882	196(1)	199(1)
349.53	15.039	0.0723	0.00176	0.02876	197(1)	200(1)
349.52	15.037	0.0908	0.00222	0.03599	196.9(0.8)	199.6(0.9)
349.51	15.035	0.0908	0.00222	0.03599	196.9(0.8)	199.6(0.9)
349.52	15.040	0.1104	0.00269	0.04366	196.4(0.8)	199.1(0.9)
349.51	15.039	0.1104	0.00269	0.04360	196.9(0.8)	199.6(0.9)
349.49	15.039	0.1301	0.00318	0.05125	196.6(0.7)	199.3(0.8)
349.50	15.034	0.1301	0.00318	0.05118	197.2(0.7)	199.9(0.8)
349.46	15.035	0.1510	0.00368	0.05917	196.9(0.6)	199.7(0.7)
349.45	15.025	0.1510	0.00368	0.05920	196.7(0.6)	199.4(0.7)
349.45	15.024	0.1716	0.00419	0.06707	196.6(0.7)	199.3(0.8)
349.44	15.023	0.1716	0.00419	0.06695	197.3(0.7)	200.0(0.8)
349.45	15.020	0.1929	0.00471	0.07493	197.4(0.6)	200.1(0.7)
349.45	15.018	0.1929	0.00471	0.07500	197.0(0.6)	199.7(0.7)
			$T = 373.15$ K, $p = 5.00$ MPa			
374.48	5.032	0.0213	0.00052	0.00842	198(1)	201(1)
374.47	5.029	0.0213	0.00052	0.00843	197(1)	200(1)
374.48	5.028	0.0352	0.00086	0.01394	197(4)	200(4)
374.48	5.030	0.0352	0.00086	0.01406	194(4)	196(4)
374.47	5.029	0.0535	0.00131	0.02111	196.9(0.2)	199.6(0.4)
374.48	5.028	0.0535	0.00131	0.02118	195.7(0.1)	198.3(0.4)
374.48	5.026	0.0734	0.00179	0.02891	196.4(0.5)	199.0(0.6)
374.47	5.026	0.0734	0.00179	0.02888	196.8(0.5)	199.5(0.6)
374.48	5.030	0.0920	0.00224	0.03607	196.6(0.6)	199.2(0.7)
374.48	5.024	0.0920	0.00224	0.03608	196.5(0.6)	199.1(0.7)
374.48	5.026	0.1102	0.00269	0.04307	196.7(0.3)	199.3(0.5)
374.48	5.028	0.1102	0.00269	0.04309	196.5(0.3)	199.1(0.5)
374.48	5.029	0.1299	0.00317	0.05056	196.9(0.8)	199.5(0.9)
374.48	5.028	0.1299	0.00317	0.05064	196.2(0.8)	198.8(0.9)
374.48	5.027	0.1525	0.00372	0.05913	197(1)	199(1)
374.48	5.033	0.1525	0.00372	0.05912	198(1)	199(1)
374.49	5.030	0.1710	0.00417	0.06608	196.8(0.4)	199.4(0.6)
374.48	5.016	0.1710	0.00417	0.06614	196.4(0.4)	199.0(0.6)
374.48	5.028	0.1929	0.00471	0.07421	196.9(0.4)	199.5(0.5)
374.48	5.029	0.1929	0.00471	0.07426	196.7(0.4)	199.3(0.5)

Table 5.4 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 373.15$ K, $p = 10.00$ MPa			
374.64	10.006	0.0195	0.00048	0.00773	198.3(0.5)	200.9(0.6)
374.64	10.004	0.0195	0.00048	0.00772	198.6(0.5)	201.3(0.6)
374.64	10.006	0.0350	0.00086	0.01383	198.9(0.9)	202(1)
374.64	10.007	0.0350	0.00086	0.01386	198.2(0.9)	201(1)
374.64	10.006	0.0532	0.00130	0.02101	197.6(0.2)	200.2(0.5)
374.64	10.006	0.0532	0.00130	0.02094	198.9(0.1)	201.6(0.4)
374.64	10.003	0.0716	0.00175	0.02808	198.8(0.2)	201.4(0.5)
374.64	10.006	0.0716	0.00175	0.02807	198.9(0.2)	201.6(0.5)
374.64	10.007	0.0883	0.00215	0.03441	199.9(0.9)	203(1)
374.63	10.004	0.0883	0.00215	0.03448	199.0(0.9)	202(1)
374.64	10.007	0.1088	0.00266	0.04233	199.2(0.2)	201.9(0.5)
374.64	10.006	0.1088	0.00266	0.04233	199.2(0.2)	201.9(0.5)
374.63	10.007	0.1309	0.00320	0.05071	199.3(0.1)	202.0(0.4)
374.63	10.007	0.1309	0.00320	0.05069	199.4(0.1)	202.1(0.4)
374.63	10.004	0.1498	0.00366	0.05777	199.7(0.2)	202.4(0.5)
374.63	10.004	0.1498	0.00366	0.05779	199.5(0.2)	202.2(0.5)
374.63	10.007	0.1710	0.00417	0.06570	199.6(0.2)	202.3(0.5)
374.63	10.006	0.1710	0.00417	0.06569	199.7(0.2)	202.4(0.5)
374.62	10.006	0.1929	0.00471	0.07373	199.99(0.05)	202.7(0.4)
374.63	10.006	0.1929	0.00471	0.07373	200.00(0.05)	202.7(0.4)
			$T = 373.15$ K, $p = 15.00$ MPa			
374.54	15.020	0.0175	0.00043	0.00698	197(1)	200(1)
374.55	15.018	0.0175	0.00043	0.00699	197(1)	199(1)
374.54	15.018	0.0358	0.00087	0.01413	199(1)	202(1)
374.55	15.024	0.0358	0.00087	0.01416	198(1)	201(1)
374.54	15.027	0.0537	0.00131	0.02111	199.6(0.2)	202.3(0.5)
374.54	15.022	0.0537	0.00131	0.02116	198.6(0.1)	201.2(0.5)
374.54	15.022	0.0717	0.00175	0.02809	200(1)	203(1)
374.54	15.024	0.0717	0.00175	0.02817	199(1)	201(1)
374.55	15.022	0.0908	0.00222	0.03554	199(1)	201(1)
374.54	15.020	0.0908	0.00222	0.03545	200(1)	203(1)
374.53	15.020	0.1109	0.00271	0.04310	200(1)	203(1)
374.53	15.022	0.1109	0.00271	0.04322	199(1)	202(1)
374.54	15.025	0.1306	0.00319	0.05071	199(1)	202(1)
374.54	15.016	0.1306	0.00319	0.05058	200(1)	203(1)
374.52	15.024	0.1509	0.00368	0.05831	199(1)	202(1)
374.53	15.016	0.1509	0.00368	0.05818	200(1)	203(1)
374.55	15.006	0.1709	0.00417	0.06565	200(1)	203(1)
374.53	15.015	0.1709	0.00417	0.06583	199(1)	202(1)
374.53	15.011	0.1929	0.00471	0.07382	200.0(0.6)	202.7(0.8)
374.55	15.008	0.1929	0.00471	0.07394	199.3(0.6)	202.0(0.8)

Table 5.4 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 423.15$ K, $p = 10.00$ MPa			
423.91	10.026	0.0176	0.00043	0.00686	195(1)	197(1)
423.89	10.031	0.0176	0.00043	0.00685	195(1)	198(1)
423.88	10.016	0.0364	0.00089	0.01412	196.6(0.6)	198.7(0.7)
423.89	10.032	0.0364	0.00089	0.01414	195.9(0.6)	198.1(0.7)
423.86	10.025	0.0539	0.00132	0.02081	197.0(0.2)	199.2(0.5)
423.88	10.029	0.0539	0.00132	0.02084	196.4(0.1)	198.5(0.5)
423.89	10.031	0.0725	0.00177	0.02787	197.1(0.5)	199.2(0.6)
423.87	10.030	0.0725	0.00177	0.02787	197.0(0.5)	199.1(0.6)
423.88	10.027	0.0909	0.00222	0.03481	197.7(0.9)	200(1)
423.89	10.032	0.0909	0.00222	0.03487	196.9(0.9)	199(1)
423.89	10.028	0.1105	0.00270	0.04218	197.5(0.6)	199.6(0.8)
423.86	10.030	0.1105	0.00270	0.04218	197.5(0.6)	199.7(0.8)
423.86	10.030	0.1304	0.00318	0.04952	198(1)	200(1)
423.85	10.037	0.1304	0.00318	0.04962	197(1)	199(1)
423.86	10.031	0.1508	0.00368	0.05705	198.2(0.4)	200.3(0.6)
423.86	10.026	0.1508	0.00368	0.05710	197.8(0.4)	199.9(0.6)
423.85	10.025	0.1712	0.00418	0.06454	198.3(0.6)	200.5(0.7)
423.84	10.016	0.1712	0.00418	0.06459	198.0(0.5)	200.1(0.6)
423.85	10.012	0.1929	0.00471	0.07233	199(1)	201(1)
423.85	10.026	0.1929	0.00471	0.07251	198(1)	200(1)

Table 5.5 The relative densities and apparent molar volumes of aqueous solutions of $Nd(CF_3SO_3)_3$ of known concentration at $T = (323.15, 348.15,$ and $373.15)$ K and $p = (5.00, 10.00,$ and $15.00)$ MPa

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
$T = 323.15$ K, $p = 5.00$ MPa						
324.26	5.026	0.0194	0.00122	0.00781	186(1)	192(1)
324.27	5.028	0.0194	0.00122	0.00778	187(1)	194(1)
324.26	5.029	0.0378	0.00237	0.01507	187.2(0.5)	193.8(0.6)
324.27	5.028	0.0378	0.00237	0.01509	186.6(0.5)	193.2(0.6)
324.26	5.028	0.0560	0.00352	0.02230	187.1(0.2)	193.7(0.3)
324.26	5.028	0.0560	0.00352	0.02226	187.7(0.1)	194.3(0.2)
324.26	5.028	0.0760	0.00477	0.03011	187.3(0.6)	193.9(0.7)
324.26	5.033	0.0760	0.00477	0.03006	187.9(0.6)	194.5(0.7)
324.26	5.032	0.0955	0.00600	0.03769	187.7(0.5)	194.3(0.5)
324.26	5.031	0.0955	0.00600	0.03765	188.1(0.5)	194.8(0.5)
324.26	5.029	0.1158	0.00727	0.04547	188.0(0.2)	194.6(0.3)
324.26	5.030	0.1158	0.00727	0.04545	188.2(0.2)	194.8(0.3)
324.25	5.030	0.1364	0.00857	0.05332	188.3(0.4)	195.0(0.4)
324.26	5.026	0.1364	0.00857	0.05338	187.9(0.4)	194.6(0.4)
324.26	5.030	0.1572	0.00988	0.06121	188.3(0.3)	195.0(0.3)
324.25	5.031	0.1572	0.00988	0.06125	188.0(0.3)	194.7(0.3)
324.26	5.032	0.1794	0.01127	0.06958	188.4(0.3)	195.0(0.4)
324.25	5.032	0.1794	0.01127	0.06960	188.3(0.3)	194.9(0.4)
324.26	5.034	0.2022	0.01271	0.07801	188.8(0.4)	195.5(0.4)
324.26	5.034	0.2022	0.01271	0.07809	188.5(0.4)	195.1(0.4)

Table 5.5 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 323.15$ K, $p = 10.00$ MPa			
324.28	10.004	0.0207	0.00130	0.00828	188(1)	194(1)
324.28	10.004	0.0207	0.00130	0.00829	187(1)	194(1)
324.29	10.006	0.0378	0.00237	0.01505	188.5(0.7)	195.2(0.7)
324.28	10.006	0.0378	0.00237	0.01507	188.0(0.7)	194.7(0.7)
324.29	10.005	0.0582	0.00366	0.02310	188.5(0.2)	195.2(0.2)
324.29	10.004	0.0582	0.00366	0.02308	188.8(0.1)	195.5(0.2)
324.29	10.006	0.0761	0.00478	0.03004	189.3(0.6)	196.0(0.6)
324.29	10.007	0.0761	0.00478	0.03007	188.9(0.6)	195.6(0.6)
324.30	10.007	0.0754	0.00474	0.02978	189.2(0.3)	195.9(0.4)
324.30	10.006	0.0754	0.00474	0.02981	188.9(0.3)	195.6(0.4)
324.29	10.006	0.1162	0.00730	0.04552	189.4(0.5)	196.1(0.5)
324.29	10.007	0.1162	0.00730	0.04546	189.9(0.5)	196.7(0.5)
324.29	10.004	0.1377	0.00865	0.05378	189.1(0.5)	195.8(0.5)
324.29	10.006	0.1377	0.00865	0.05371	189.6(0.5)	196.3(0.5)
324.29	10.006	0.1579	0.00992	0.06125	190(2)	197(2)
324.28	10.006	0.1579	0.00992	0.06134	190(2)	197(2)
324.25	10.006	0.1789	0.01124	0.06906	190.6(0.9)	197.4(0.9)
324.25	10.006	0.1789	0.01124	0.06919	189.9(0.9)	196.6(0.9)
324.22	10.006	0.2022	0.01271	0.07771	191(1)	198(1)
324.22	10.004	0.2022	0.01271	0.07784	190(1)	197(1)
			$T = 323.15$ K, $p = 15.00$ MPa			
324.29	15.030	0.0194	0.00122	0.00781	186(2)	193(2)
324.29	15.029	0.0194	0.00122	0.00777	188(2)	195(2)
324.29	15.027	0.0378	0.00237	0.01502	190(3)	196(3)
324.29	15.023	0.0378	0.00237	0.01511	187(3)	194(3)
324.29	15.030	0.0560	0.00352	0.02231	187.8(0.2)	194.5(0.3)
324.28	15.032	0.0560	0.00352	0.02234	187.3(0.1)	194.0(0.3)
324.29	15.024	0.0760	0.00477	0.03011	188.2(0.6)	194.8(0.7)
324.28	15.023	0.0760	0.00477	0.03013	187.9(0.6)	194.6(0.7)
324.28	15.018	0.0955	0.00600	0.03770	188.4(0.6)	195.1(0.7)
324.27	15.023	0.0955	0.00600	0.03772	188.3(0.6)	194.9(0.7)
324.27	15.030	0.1158	0.00727	0.04550	189(1)	195(1)
324.27	15.035	0.1158	0.00727	0.04550	189(1)	195(1)
324.26	15.034	0.1364	0.00857	0.05344	188.4(0.9)	195.1(0.9)
324.26	15.030	0.1364	0.00857	0.05332	189.2(0.9)	196.0(0.9)
324.26	15.018	0.1572	0.00988	0.06124	189.0(0.6)	195.7(0.7)
324.27	15.020	0.1572	0.00988	0.06122	189.1(0.6)	195.8(0.7)
324.27	15.032	0.1794	0.01127	0.06962	189.0(0.3)	195.7(0.4)
324.27	15.032	0.1794	0.01127	0.06956	189.3(0.3)	196.0(0.4)
324.27	15.021	0.2022	0.01271	0.07803	189.6(0.7)	196.3(0.8)
324.26	15.015	0.2022	0.01271	0.07818	188.9(0.7)	195.5(0.8)

Table 5.5 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 5.00$ MPa			
349.56	5.031	0.0186	0.00117	0.00755	170.4(0.5)	197.2(0.6)
349.57	5.028	0.0186	0.00117	0.00757	168.8(0.5)	195.1(0.6)
349.57	5.027	0.0372	0.00234	0.01463	190.6(0.7)	197.2(0.8)
349.57	5.027	0.0372	0.00234	0.01465	190.1(0.7)	196.6(0.8)
349.55	5.030	0.0561	0.00352	0.02198	190.3(0.2)	196.8(0.3)
349.56	5.027	0.0561	0.00352	0.02197	190.4(0.1)	197.0(0.3)
349.56	5.031	0.0748	0.00470	0.02920	190.5(0.1)	197.0(0.3)
349.56	5.032	0.0748	0.00470	0.02921	190.4(0.1)	197.0(0.3)
349.56	5.031	0.0954	0.00600	0.03711	190.6(0.4)	197.2(0.5)
349.56	5.031	0.0954	0.00600	0.03712	190.5(0.4)	197.0(0.5)
349.56	5.030	0.1159	0.00728	0.04489	190.6(0.3)	197.2(0.4)
349.55	5.030	0.1159	0.00728	0.04489	190.7(0.3)	197.2(0.4)
349.55	5.032	0.1357	0.00853	0.05226	191.5(0.5)	198.1(0.6)
349.55	5.029	0.1357	0.00853	0.05233	191.0(0.5)	197.6(0.6)
349.55	5.029	0.1581	0.00993	0.06072	190.9(0.5)	197.5(0.5)
349.55	5.029	0.1581	0.00993	0.06070	191.1(0.5)	197.6(0.5)
349.56	5.032	0.1785	0.01122	0.06824	191.3(0.6)	197.9(0.7)
349.55	5.033	0.1785	0.01122	0.06834	190.7(0.6)	197.2(0.7)
349.56	5.032	0.2022	0.01271	0.07701	191.2(0.5)	197.7(0.6)
349.56	5.035	0.2022	0.01271	0.07692	191.6(0.5)	198.2(0.6)
			$T = 348.15$ K, $p = 10.00$ MPa			
349.52	10.006	0.0175	0.00110	0.00689	191(2)	197(2)
349.53	10.006	0.0175	0.00110	0.00690	191(2)	197(2)
349.54	10.004	0.0361	0.00227	0.01420	191(2)	197(2)
349.54	10.006	0.0361	0.00227	0.01414	192(2)	199(2)
349.55	10.007	0.0538	0.00338	0.02114	190.2(0.2)	196.8(0.2)
349.56	10.006	0.0538	0.00338	0.02111	190.8(0.1)	197.4(0.2)
349.56	10.004	0.0736	0.00462	0.02875	190.8(0.2)	197.4(0.3)
349.56	10.007	0.0736	0.00462	0.02874	191.0(0.2)	197.6(0.3)
349.55	10.007	0.0958	0.00602	0.03725	191.1(0.3)	197.7(0.3)
349.56	10.004	0.0958	0.00602	0.03724	191.2(0.3)	197.8(0.3)
349.56	10.004	0.1147	0.00721	0.04443	191.21(0.07)	197.8(0.2)
349.56	10.006	0.1147	0.00721	0.04443	191.23(0.07)	197.9(0.2)
349.56	10.006	0.1347	0.00846	0.05196	191.3(0.1)	198.0(0.2)
349.56	10.004	0.1347	0.00846	0.05197	191.3(0.1)	197.9(0.2)
349.56	10.006	0.1572	0.00988	0.06040	191.4(0.4)	198.0(0.4)
349.56	10.007	0.1572	0.00988	0.06037	191.6(0.4)	198.2(0.4)
349.51	10.011	0.1793	0.01127	0.06855	191.7(0.2)	198.3(0.3)
349.50	10.009	0.1793	0.01127	0.06858	191.5(0.2)	198.2(0.3)
349.49	10.004	0.2022	0.01271	0.07692	192.0(0.7)	198.7(0.7)
349.49	10.006	0.2022	0.01271	0.07706	191.3(0.7)	197.9(0.7)

Table 5.5 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 15.00$ MPa			
349.54	15.039	0.0187	0.00117	0.00739	190(1)	196(1)
349.54	15.045	0.0187	0.00117	0.00740	189(1)	195(1)
349.55	15.049	0.0369	0.00232	0.01458	189.4(0.6)	195.9(0.7)
349.56	15.044	0.0369	0.00232	0.01460	188.8(0.6)	195.3(0.7)
349.55	15.040	0.0558	0.00351	0.02198	189.2(0.2)	195.7(0.3)
349.55	15.018	0.0558	0.00351	0.02196	189.4(0.1)	196.0(0.3)
349.54	15.025	0.0747	0.00470	0.02932	189.5(0.1)	196.1(0.3)
349.53	15.029	0.0747	0.00470	0.02931	189.6(0.1)	196.1(0.3)
349.53	15.029	0.0951	0.00598	0.03713	190.0(0.5)	196.6(0.6)
349.54	15.039	0.0951	0.00598	0.03717	189.6(0.5)	196.1(0.6)
349.53	15.037	0.1147	0.00721	0.04461	189.9(0.6)	196.5(0.7)
349.54	15.039	0.1147	0.00721	0.04454	190.5(0.6)	197.1(0.7)
349.54	15.040	0.1361	0.00855	0.05262	190.9(0.5)	197.5(0.6)
349.54	15.034	0.1361	0.00855	0.05268	190.4(0.5)	196.9(0.6)
349.54	15.039	0.1579	0.00992	0.06080	191.0(0.7)	197.6(0.7)
349.54	15.030	0.1579	0.00992	0.06086	190.6(0.7)	197.2(0.7)
349.55	15.029	0.1794	0.01127	0.06858	192.2(0.4)	198.9(0.5)
349.54	15.027	0.1794	0.01127	0.06862	192.0(0.4)	198.7(0.5)
349.50	15.022	0.2022	0.01271	0.07704	191.8(0.7)	198.5(0.7)
349.45	15.035	0.2022	0.01271	0.07708	191.7(0.7)	198.3(0.7)
			$T = 373.15$ K, $p = 5.00$ MPa			
374.60	5.019	0.0191	0.00120	0.00738	194.8(0.3)	201.5(0.4)
374.59	5.020	0.0191	0.00120	0.00737	195.6(0.3)	202.3(0.4)
374.59	5.018	0.0369	0.00232	0.01434	191(4)	198(4)
374.58	5.019	0.0369	0.00232	0.01422	195(4)	201(4)
374.57	5.017	0.0557	0.00350	0.02142	194.4(0.2)	201.0(0.3)
374.58	5.018	0.0557	0.00350	0.02151	192.8(0.1)	199.3(0.3)
374.58	5.021	0.0752	0.00473	0.02882	194(2)	201(2)
374.58	5.020	0.0752	0.00473	0.02865	197(2)	204(2)
374.58	5.021	0.0951	0.00597	0.03629	194(1)	201(1)
374.58	5.022	0.0951	0.00597	0.03636	194(1)	200(1)
374.57	5.020	0.1149	0.00722	0.04372	194.3(0.7)	200.9(0.8)
374.58	5.019	0.1149	0.00722	0.04374	194.2(0.7)	200.7(0.8)
374.57	5.018	0.1359	0.00854	0.05158	193.86(----)	200.38(----)
374.57	5.018	0.1587	0.00997	0.05958	196(2)	203(2)
374.57	5.019	0.1587	0.00997	0.05986	195(2)	201(2)
374.57	5.018	0.1790	0.01125	0.06740	193.8(0.6)	200.3(0.7)
374.57	5.018	0.1790	0.01125	0.06739	193.9(0.6)	200.4(0.7)
374.58	5.018	0.2022	0.01271	0.07579	194.0(0.4)	200.5(0.5)
374.59	5.021	0.2022	0.01271	0.07573	194.3(0.4)	200.8(0.5)

Table 5.5 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 373.15$ K, $p = 10.00$ MPa			
374.32	10.037	0.0358	0.00225	0.01386	193(1)	200(1)
374.31	10.040	0.0358	0.00225	0.01389	192(1)	199(1)
374.31	10.037	0.0548	0.00344	0.02115	193.3(0.2)	199.8(0.5)
374.32	10.038	0.0548	0.00344	0.02127	191.0(0.1)	197.4(0.4)
374.31	10.035	0.0722	0.00453	0.02789	191.6(0.3)	198.1(0.5)
374.31	10.037	0.0722	0.00453	0.02791	191.3(0.3)	197.7(0.5)
374.32	10.038	0.0929	0.00584	0.03579	191.5(0.4)	197.9(0.6)
374.34	10.040	0.0929	0.00584	0.03579	191.6(0.4)	198.0(0.6)
374.31	10.037	0.1151	0.00723	0.04414	191.7(0.3)	198.1(0.5)
374.32	10.037	0.1151	0.00723	0.04411	191.9(0.3)	198.3(0.5)
374.34	10.040	0.1342	0.00843	0.05126	191.8(0.3)	198.2(0.5)
374.34	10.037	0.1342	0.00843	0.05123	192.0(0.3)	198.4(0.5)
374.33	10.038	0.1552	0.00975	0.05900	192.3(0.5)	198.8(0.6)
374.34	10.038	0.1552	0.00975	0.05905	192.0(0.5)	198.4(0.6)
374.33	10.035	0.1740	0.01093	0.06593	192.2(0.8)	198.7(0.9)
374.32	10.040	0.1740	0.01093	0.06590	192.4(0.8)	198.9(0.9)
374.32	10.040	0.2022	0.01271	0.07614	193(1)	199(1)
374.32	10.038	0.2022	0.01271	0.07590	194(1)	200(1)
			$T = 373.15$ K, $p = 15.00$ MPa			
374.54	15.015	0.0184	0.00116	0.00717	192.6(0.3)	199.2(0.5)
374.54	15.022	0.0184	0.00116	0.00717	193.0(0.3)	199.6(0.5)
374.55	15.020	0.0372	0.00234	0.01447	192.8(0.6)	199.3(0.8)
374.54	15.020	0.0372	0.00234	0.01448	192.5(0.6)	199.0(0.8)
374.53	15.022	0.0560	0.00352	0.02164	193.3(0.2)	199.9(0.5)
374.55	15.024	0.0560	0.00352	0.02169	192.3(0.1)	198.9(0.5)
374.54	15.020	0.0759	0.00477	0.02925	193.0(0.3)	199.6(0.5)
374.54	15.018	0.0759	0.00477	0.02926	192.9(0.3)	199.4(0.5)
374.53	15.018	0.0949	0.00596	0.03648	193(1)	199(1)
374.54	15.020	0.0949	0.00596	0.03640	194(1)	200(1)
374.55	15.024	0.1150	0.00723	0.04394	193.8(0.8)	200.4(0.9)
374.54	15.020	0.1150	0.00723	0.04403	193.0(0.8)	199.5(0.9)
374.54	15.020	0.1364	0.00857	0.05189	193.7(0.7)	200.3(0.8)
374.53	15.022	0.1364	0.00857	0.05197	193.1(0.7)	199.6(0.8)
374.55	15.018	0.1580	0.00993	0.05985	193.8(0.6)	200.4(0.7)
374.53	15.022	0.1580	0.00993	0.05989	193.5(0.6)	200.1(0.7)
374.54	15.020	0.1762	0.01107	0.06654	193.9(0.6)	200.5(0.8)
374.53	15.022	0.1762	0.01107	0.06659	193.6(0.6)	200.1(0.8)
374.53	15.024	0.2022	0.01271	0.07589	194(1)	201(1)
374.54	15.025	0.2022	0.01271	0.07608	193(1)	200(1)

Table 5.6 The relative densities and apparent molar volumes of aqueous solutions of $Yb(CF_3SO_3)_3$ of known concentration at $T = (323.15, 348.15, \text{and } 373.15)$ K and $p = (5.00, 10.00, \text{and } 15.00)$ MPa

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
$T = 323.15$ K, $p = 5.00$ MPa
324.26	5.036	0.0170	0.00536	0.00766	165(2)	192(2)
324.27	5.032	0.0170	0.00536	0.00769	164(2)	189(2)
324.27	5.032	0.0322	0.01015	0.01450	164.5(0.9)	191(1)
324.27	5.030	0.0322	0.01015	0.01448	165.3(0.9)	192(1)
324.27	5.030	0.0486	0.01532	0.02183	164.7(0.2)	190.8(0.3)
324.26	5.031	0.0486	0.01532	0.02180	165.2(0.1)	191.4(0.2)
324.26	5.031	0.0655	0.02064	0.02934	164.5(0.9)	190.4(0.9)
324.26	5.031	0.0655	0.02064	0.02929	165.3(0.9)	191.5(0.9)
324.26	5.030	0.0826	0.02602	0.03685	165.0(0.8)	191.1(0.8)
324.26	5.031	0.0826	0.02602	0.03680	165.6(0.8)	191.9(0.8)
324.26	5.031	0.1008	0.03178	0.04494	164.3(0.3)	190.1(0.3)
324.26	5.029	0.1008	0.03178	0.04494	164.3(0.3)	190.1(0.3)
324.25	5.032	0.1191	0.03752	0.05272	165.8(0.7)	192.1(0.7)
324.25	5.030	0.1191	0.03752	0.05281	165.1(0.7)	191.1(0.7)
324.26	5.032	0.1373	0.04327	0.06064	165.6(0.6)	191.8(0.6)
324.27	5.031	0.1373	0.04327	0.06072	165.0(0.6)	191.1(0.6)
324.26	5.031	0.1564	0.04928	0.06889	165.4(0.7)	191.5(0.7)
324.26	5.027	0.1564	0.04928	0.06878	166.1(0.7)	192.5(0.7)
324.27	5.027	0.1755	0.05532	0.07712	165.3(0.6)	191.3(0.6)
324.27	5.027	0.1755	0.05532	0.07702	165.8(0.6)	192.0(0.6)

Table 5.6 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 323.15$ K, $p = 10.00$ MPa			
324.20	10.038	0.0156	0.00493	0.00706	165.2(0.2)	191.6(0.3)
324.21	10.035	0.0156	0.00493	0.00706	165.0(0.2)	191.3(0.3)
324.21	10.038	0.0325	0.01024	0.01463	165(3)	191(3)
324.21	10.038	0.0325	0.01024	0.01472	162(3)	188(3)
324.21	10.040	0.0480	0.01511	0.02154	165.2(0.2)	191.5(0.2)
324.23	10.037	0.0480	0.01511	0.02154	165.2(0.1)	191.5(0.2)
324.26	10.038	0.0655	0.02066	0.02937	165.0(0.3)	191.2(0.3)
324.26	10.038	0.0655	0.02066	0.02935	165.2(0.3)	191.5(0.3)
324.27	10.037	0.0825	0.02601	0.03687	165.1(0.3)	191.3(0.3)
324.27	10.038	0.0825	0.02601	0.03686	165.3(0.3)	191.5(0.3)
324.27	10.040	0.1011	0.03188	0.04504	165.1(0.4)	191.3(0.4)
324.27	10.038	0.1011	0.03188	0.04505	165.0(0.4)	191.2(0.4)
324.26	10.038	0.1189	0.03748	0.05282	165.0(0.2)	191.1(0.2)
324.27	10.038	0.1189	0.03748	0.05281	165.2(0.2)	191.3(0.2)
324.27	10.035	0.1367	0.04309	0.06052	165.4(0.4)	191.5(0.4)
324.27	10.040	0.1367	0.04309	0.06057	165.0(0.4)	191.1(0.4)
324.27	10.037	0.1561	0.04920	0.06896	164.9(0.7)	190.9(0.7)
324.26	10.032	0.1561	0.04920	0.06885	165.6(0.7)	191.8(0.7)
324.21	10.035	0.1755	0.05532	0.07713	165.8(0.4)	192.0(0.4)
324.21	10.038	0.1755	0.05532	0.07718	165.5(0.4)	191.6(0.4)
			$T = 323.15$ K, $p = 15.00$ MPa			
324.29	15.029	0.0167	0.00526	0.00755	165.0(0.7)	191.3(0.7)
324.28	15.021	0.0167	0.00526	0.00756	164.4(0.7)	190.6(0.7)
324.29	15.020	0.0327	0.01031	0.01477	165(1)	191(1)
324.28	15.024	0.0327	0.01031	0.01479	164(1)	190(1)
324.28	15.016	0.0488	0.01539	0.02201	164.3(0.2)	190.3(0.4)
324.28	15.015	0.0488	0.01539	0.02201	164.2(0.1)	190.2(0.3)
324.28	15.027	0.0658	0.02075	0.02959	164.3(0.7)	190.2(0.8)
324.28	15.034	0.0658	0.02075	0.02961	163.9(0.7)	189.8(0.8)
324.28	15.017	0.0830	0.02616	0.03719	164.4(0.8)	190.4(0.9)
324.28	15.018	0.0830	0.02616	0.03725	163.6(0.8)	189.3(0.9)
324.28	15.025	0.1005	0.03167	0.04496	163.7(0.4)	189.4(0.5)
324.27	15.032	0.1005	0.03167	0.04492	164.1(0.4)	190.0(0.5)
324.27	15.032	0.1182	0.03724	0.05271	163.8(0.7)	189.6(0.8)
324.28	15.023	0.1182	0.03724	0.05272	163.8(0.7)	189.5(0.8)
324.28	15.013	0.1368	0.04312	0.06087	163.7(0.4)	189.4(0.5)
324.27	15.030	0.1368	0.04312	0.06082	164.0(0.4)	189.8(0.5)
324.28	15.040	0.1558	0.04911	0.06903	164.2(0.9)	190.1(0.9)
324.27	15.035	0.1558	0.04911	0.06916	163.4(0.9)	189.0(0.9)
324.27	15.018	0.1755	0.05532	0.07747	164.5(0.6)	190.3(0.7)
324.27	15.004	0.1755	0.05532	0.07751	164.2(0.6)	190.0(0.7)

Table 5.6 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 5.00$ MPa			
349.57	5.033	0.0171	0.00538	0.00756	170(2)	197(2)
349.57	5.031	0.0171	0.00538	0.00757	169(2)	195(2)
349.57	5.031	0.0332	0.01046	0.01466	169.4(0.9)	196(1)
349.56	5.031	0.0332	0.01046	0.01468	169.1(0.9)	195(1)
349.56	5.030	0.0495	0.01560	0.02187	168.0(0.2)	193.9(0.3)
349.56	5.031	0.0495	0.01560	0.02193	166.6(0.1)	192.0(0.3)
349.57	5.030	0.0656	0.02068	0.02887	169(1)	195(1)
349.56	5.031	0.0656	0.02068	0.02888	169(1)	195(1)
349.56	5.030	0.0830	0.02616	0.03642	169(4)	195(4)
349.57	5.030	0.0830	0.02616	0.03675	165(4)	189(4)
349.56	5.031	0.1008	0.03176	0.04422	167(2)	193(2)
349.57	5.029	0.1008	0.03176	0.04407	169(2)	195(2)
349.56	5.030	0.1174	0.03700	0.05120	169(2)	195(2)
349.56	5.028	0.1174	0.03700	0.05141	167(2)	193(2)
349.57	5.025	0.1374	0.04329	0.05981	168(1)	194(1)
349.57	5.027	0.1374	0.04329	0.05986	168(1)	193(1)
349.57	5.026	0.1553	0.04893	0.06746	167.8(0.5)	193.5(0.5)
349.56	5.027	0.1553	0.04893	0.06750	167.6(0.5)	193.1(0.5)
349.57	5.028	0.1755	0.05532	0.07606	168(2)	193(2)
349.57	5.029	0.1755	0.05532	0.07569	170(2)	196(2)
			$T = 348.15$ K, $p = 10.00$ MPa			
349.48	10.040	0.0166	0.00522	0.00735	169(2)	196(2)
349.50	10.040	0.0166	0.00522	0.00734	170(2)	197(2)
349.50	10.042	0.0317	0.01000	0.01407	168.3(0.6)	194.4(0.5)
349.50	10.040	0.0317	0.01000	0.01407	168.2(0.6)	194.4(0.5)
349.50	10.037	0.0486	0.01533	0.02156	167.4(0.2)	193.1(0.5)
349.50	10.040	0.0486	0.01533	0.02154	167.8(0.1)	193.7(0.5)
349.50	10.040	0.0653	0.02057	0.02890	166.8(0.6)	192.2(0.6)
349.50	10.038	0.0653	0.02057	0.02886	167.3(0.6)	193.0(0.6)
349.50	10.038	0.0816	0.02571	0.03598	167.3(0.9)	192.8(0.9)
349.50	10.040	0.0816	0.02571	0.03605	166.5(0.9)	191.7(0.9)
349.50	10.040	0.1000	0.03152	0.04400	167.2(0.3)	192.6(0.4)
349.50	10.040	0.1000	0.03152	0.04397	167.4(0.3)	192.9(0.4)
349.50	10.043	0.1198	0.03775	0.05251	167.3(0.6)	192.7(0.6)
349.50	10.040	0.1198	0.03775	0.05252	167.2(0.6)	192.5(0.6)
349.50	10.040	0.1355	0.04270	0.05927	167(1)	192(1)
349.50	10.040	0.1355	0.04270	0.05914	168(1)	194(1)
349.50	10.043	0.1549	0.04880	0.06753	167(1)	192(1)
349.49	10.040	0.1549	0.04880	0.06734	168(1)	194(1)
349.49	10.040	0.1755	0.05532	0.07605	168.2(0.2)	193.2(0.3)
349.49	10.040	0.1755	0.05532	0.07602	168.4(0.2)	193.1(0.3)

Table 5.6 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			$T = 348.15$ K, $p = 15.00$ MPa			
349.48	15.025	0.0166	0.00524	0.00741	168(2)	194(2)
349.48	15.022	0.0166	0.00524	0.00742	167(2)	193(2)
349.47	15.022	0.0328	0.01035	0.01458	168(2)	194(2)
349.48	15.022	0.0328	0.01035	0.01464	166(2)	192(2)
349.49	15.016	0.0491	0.01547	0.02180	166.8(0.2)	192.6(0.3)
349.49	15.015	0.0491	0.01547	0.02182	166.5(0.1)	192.1(0.3)
349.49	15.020	0.0661	0.02083	0.02932	166.2(0.3)	191.7(0.4)
349.49	15.020	0.0661	0.02083	0.02931	166.5(0.3)	192.0(0.4)
349.48	15.018	0.0836	0.02636	0.03697	167(1)	192(1)
349.48	15.025	0.0836	0.02636	0.03700	166(1)	192(1)
349.48	15.024	0.1007	0.03175	0.04441	166.6(0.7)	192.1(0.8)
349.47	15.024	0.1007	0.03175	0.04448	165.9(0.7)	191.2(0.8)
349.47	15.030	0.1188	0.03743	0.05220	167(1)	192(1)
349.47	15.023	0.1188	0.03743	0.05232	166(1)	191(1)
349.48	15.025	0.1371	0.04322	0.06019	166(1)	191(1)
349.47	15.022	0.1371	0.04322	0.06005	167(1)	192(1)
349.47	15.027	0.1561	0.04920	0.06814	167.0(0.8)	192.5(0.8)
349.47	15.023	0.1561	0.04920	0.06827	166.2(0.8)	191.5(0.8)
349.47	15.024	0.1755	0.05532	0.07615	168.3(0.4)	194.2(0.5)
349.47	15.025	0.1755	0.05532	0.07622	167.9(0.4)	193.7(0.5)
			$T = 373.15$ K, $p = 5.00$ MPa			
374.59	5.018	0.0161	0.00506	0.00696	175(6)	198(6)
374.59	5.022	0.0161	0.00506	0.00704	169(6)	191(6)
374.57	5.023	0.0324	0.01020	0.01422	167.1(0.6)	188.5(0.7)
374.56	5.021	0.0324	0.01020	0.01422	167.1(0.6)	188.6(0.7)
374.57	5.025	0.0490	0.01543	0.02137	168.7(0.2)	190.4(0.4)
374.58	5.021	0.0490	0.01543	0.02128	170.5(0.1)	192.8(0.4)
374.57	5.021	0.0664	0.02091	0.02884	169.3(0.3)	191.0(0.5)
374.59	5.023	0.0664	0.02091	0.02884	169.3(0.3)	191.0(0.5)
374.57	5.021	0.0827	0.02607	0.03595	168.0(0.5)	189.3(0.6)
374.57	5.021	0.0827	0.02607	0.03592	168.5(0.5)	189.8(0.6)
374.56	5.024	0.1007	0.03173	0.04377	167(2)	187(2)
374.58	5.023	0.1007	0.03173	0.04356	169(2)	190(2)
374.57	5.024	0.1188	0.03743	0.05147	167(2)	187(2)
374.57	5.025	0.1188	0.03743	0.05129	168(2)	189(2)
374.58	5.026	0.1368	0.04312	0.05892	168.4(0.8)	189.4(0.9)
374.57	5.024	0.1368	0.04312	0.05901	167.6(0.8)	188.4(0.9)
374.57	5.023	0.1562	0.04923	0.06700	168.8(0.8)	189.9(0.9)
374.57	5.025	0.1562	0.04923	0.06711	168.1(0.8)	188.8(0.9)
374.58	5.023	0.1755	0.05532	0.07513	168.4(0.4)	189.2(0.5)
374.59	5.021	0.1755	0.05532	0.07507	168.7(0.4)	189.6(0.5)

Table 5.6 (continued)

T /(K)	p /(MPa)	m_2 /(mol·kg^{-1})	m_3 /(mol·kg^{-1})	$\rho_{expt} - \rho_l$ /(g·cm^{-3})	$V_{\phi,expt}$ /(cm^3·mol^{-1})	$V_{2\phi}$ /(cm^3·mol^{-1})
			T = 373.15 K, p = 10.00 MPa			
374.37	10.040	0.0161	0.00507	0.00710	167(6)	192(6)
374.38	10.040	0.0161	0.00507	0.00702	172(6)	199(6)
374.38	10.035	0.0323	0.01017	0.01410	170(4)	196(4)
374.38	10.037	0.0323	0.01017	0.01420	167(4)	192(4)
374.39	10.040	0.0487	0.01536	0.02127	169.5(0.2)	195.0(0.5)
374.39	10.040	0.0487	0.01536	0.02132	168.5(0.1)	193.7(0.4)
374.39	10.038	0.0654	0.02060	0.02851	168.4(0.3)	193.4(0.5)
374.39	10.038	0.0654	0.02060	0.02850	168.5(0.3)	193.6(0.5)
374.39	10.040	0.0821	0.02589	0.03577	168(2)	193(2)
374.39	10.040	0.0821	0.02589	0.03593	166(2)	190(2)
374.39	10.037	0.0990	0.03121	0.04302	168.0(0.6)	192.8(0.7)
374.38	10.038	0.0990	0.03121	0.04306	167.5(0.6)	192.2(0.7)
374.38	10.040	0.1172	0.03693	0.05075	167.9(0.8)	192.6(0.9)
374.38	10.038	0.1172	0.03693	0.05080	167.5(0.8)	192.1(0.9)
374.38	10.038	0.1376	0.04336	0.05934	168(1)	193(1)
374.39	10.038	0.1376	0.04336	0.05945	168(1)	192(1)
374.39	10.037	0.1553	0.04896	0.06687	168.0(0.8)	192.6(0.9)
374.39	10.040	0.1553	0.04896	0.06676	168.7(0.8)	193.6(0.9)
374.38	10.040	0.1755	0.05532	0.07482	171(3)	196(3)
374.39	10.038	0.1755	0.05532	0.07534	168(3)	192(3)
			T = 373.15 K, p = 15.00 MPa			
374.56	15.037	0.0162	0.00512	0.00710	172(2)	198(2)
374.56	15.045	0.0162	0.00512	0.00712	170(2)	196(2)
374.56	15.047	0.0321	0.01011	0.01405	169.9(0.9)	196(1)
374.57	15.047	0.0321	0.01011	0.01403	170.4(0.9)	196(1)
374.56	15.047	0.0492	0.01550	0.02149	169.6(0.2)	195.1(0.5)
374.57	15.042	0.0492	0.01550	0.02153	168.8(0.1)	194.2(0.4)
374.57	15.045	0.0654	0.02060	0.02854	168.7(0.7)	194.0(0.8)
374.54	15.045	0.0654	0.02060	0.02855	168.6(0.7)	193.8(0.8)
374.56	15.044	0.0822	0.02591	0.03585	168.1(0.9)	193(1)
374.56	15.045	0.0822	0.02591	0.03581	168.6(0.9)	194(1)
374.57	15.024	0.1005	0.03168	0.04368	168.3(0.5)	193.3(0.6)
374.56	15.035	0.1005	0.03168	0.04370	168.0(0.5)	193.0(0.6)
374.55	15.030	0.1188	0.03742	0.05148	168(1)	193(1)
374.57	15.037	0.1188	0.03742	0.05150	168(1)	193(1)
374.56	15.027	0.1370	0.04319	0.05930	167.5(0.4)	192.2(0.6)
374.56	15.034	0.1370	0.04319	0.05924	168.0(0.4)	192.8(0.6)
374.56	15.035	0.1359	0.04283	0.05870	168(1)	193(1)
374.57	15.034	0.1359	0.04283	0.05883	167(1)	192(1)
374.56	15.034	0.1755	0.05532	0.07542	167.95(0.05)	192.7(0.4)
374.56	15.037	0.1755	0.05532	0.07542	168.00(0.05)	192.7(0.4)

Table 5.7 Estimation and comparison of parameters to the Pitzer-ion interaction model equation, shown as equation (2.37), for aqueous solutions of Gd(CF$_3$SO$_3$)$_3$ at T = (323.15, 348.15, 373.15, and 423.15) K and p = (5.00, 10.00, and 15.00) MPa

T /(K)	p /(MPa)	V_2^0 /(cm^3·mol^{-1})	$10^4(\beta^{(0)V})$ /(kg·mol^{-1}·MPa^{-1})	$10^3(\beta^{(1)V})$ /(kg·mol^{-1}·MPa^{-1})
324.29	5.01	194.06(0.07)	-5.4(0.7)	-2.0(0.3)
324.23	10.02	193.1(0.1)	-13(1)	-1.4(0.5)
324.28	15.00	193.28(0.03)	-4.5(0.3)	-1.4(0.1)
349.52	5.01	196.03(0.08)	-1.2(0.7)	-8.4(0.3)
349.44	10.01	195.9(0.1)	4(1)	-10.4(0.5)
349.52	15.03	195.69(0.09)	-3.1(0.8)	-8.0(0.4)
374.48	5.03	196.9(0.1)	16(6)	9(2)
374.64	10.01	196.85(0.08)	5.3(0.7)	-13.0(0.3)
374.54	15.02	194.9(0.3)	-15(2)	-3(1)
423.87	10.03	189.91(0.09)	1.2(0.7)	-17.1(0.3)

Table 5.8 Estimation and comparison of parameters to the Pitzer-ion interaction model equation, shown as equation (2.37), for aqueous solutions of Nd(CF$_3$SO$_3$)$_3$ at T = (323.15, 348.15, and 373.15) K and p = (5.00, 10.00, and 15.00) MPa

T /(K)	p /(MPa)	V_2^0 /(cm^3·mol^{-1})	$10^4(\beta^{(0)V})$ /(kg·mol^{-1}·MPa^{-1})	$10^3(\beta^{(1)V})$ /(kg·mol^{-1}·MPa^{-1})
324.26	5.03	189.7(0.2)	-3(1)	-3.7(0.7)
324.28	10.01	190.50(0.06)	-4.5(0.5)	-2.2(0.3)
324.28	15.03	189.26(0.05)	-5.9(0.5)	-1.0(0.2)
349.56	5.03	194.1(0.1)	9(1)	-13.3(0.5)
349.54	10.01	194.3(0.1)	5(1)	-11.3(0.5)
349.54	15.03	193.4(0.2)	19(2)	-15.1(0.7)
374.58	5.02	198.0(0.3)	5(2)	-17(1)
374.32	10.04	197.8(0.6)	25(4)	-25(2)
374.54	15.02	195.5(0.3)	8(2)	-14(1)

Table 5.9 Estimation and comparison of parameters to the Pitzer-ion interaction model equation, shown as equation (2.37), for aqueous solutions of $Yb(CF_3SO_3)_3$ at $T = (323.15, 348.15,$ and $373.15)$ K and $p = (5.00, 10.00,$ and $15.00)$ MPa

T /(K)	p /(MPa)	V_2^0 /(cm^3·mol^{-1})	$10^4(\beta^{(0)V})$ /(kg·mol^{-1}·MPa^{-1})	$10^3(\beta^{(1)V})$ /(kg·mol^{-1}·MPa^{-1})
324.26	5.03	189.8(0.2)	11(2)	-13.1(0.8)
324.24	10.04	189.7(0.4)	6(5)	-12(2)
324.28	15.02	190.0(0.2)	19(2)	-18.2(0.8)
349.56	5.03	195.7(0.4)	12(5)	-22(2)
349.50	10.04	194.8(0.3)	28(4)	-27(2)
349.48	15.02	193.7(0.3)	38(4)	-28(2)
374.57	5.02	198.7(0.7)	54(6)	-48(3)
374.38	10.04	198.8(0.4)	47(4)	-41(2)
374.56	15.04	197.0(0.4)	32(4)	-33(2)

Table 5.10 A comparison of literature and calculated $V_2^0(R^{3+}$; aq) values for $R^{3+}_{(aq)} = (Gd^{3+}, Nd^{3+},$ and $Yb^{3+})$ at $T \approx (323.15, 348.15,$ and $373.15)$ K and $p \approx (5.00, 10.00,$ and $15.00)$ MPa

T /(K)	p /(MPa)	$Gd^{3+}_{(aq)}$	$Nd^{3+}_{(aq)}$	$Yb^{3+}_{(aq)}$
		$V_2^0(R^{3+}$; aq) /(cm^3·mol^{-1})		
323.15	5.00	-40.0(0.3)	-44.4(0.3)	-44.3(0.3)
323.15	10.00	-40.9(0.2)	-43.5(0.2)	-44.3(0.4)
				-44.4(0.9)[α]
323.15	15.00	-40.5(0.5)	-44.4(0.5)	-43.7(0.5)
348.15	5.00	-45.6(0.5)	-47.5(0.5)	-45.9(0.6)
348.15	10.00	-44.4(0.3)	-46.0(0.3)	-45.5(0.8)
				-45.8(0.9)[α]
348.15	15.00	-44.6(0.5)	-46.9(0.5)	-46.6(0.6)
373.15	5.00	-49.7(0.7)	-48.6(0.8)	-47.9(0.9)
373.15	10.00	-49.1(0.7)	-48(1)	-47.1(0.8)
				-48.8(0.9)[α]
373.15	15.00	-49.4(0.8)	-48.8(0.8)	-47.3(0.9)
423.15	10.00	-55.0(0.8)		

[α]Hakin *et al.* (2004a)

6) THE MODELING OF APPARENT MOLAR PROPERTIES OF AQUEOUS SOLUTIONS OF THE REE TRIFLATES OVER THE TEMPERATURE RANGE T = (288.15, 298.15, 313.15, 323.15, 328.15, 348.15, 373.15, AND 423.15) K AND PRESSURE RANGE p = (0.1, 5.00, 10.00, and 15.00) MPa

6.1 Introduction

The apparent molar volumes and heat capacities of aqueous solutions of the REE triflates show a strong temperature and pressure dependence. However, there is less of a dependence on pressure than on temperature, at least over the range investigated in this study. This phenomenon has been observed in the past for other REE salts (Hakin *et al.*, 2004a; Xiao *et al.*, 1999) and also for several acids (Hovey, 1988) and in general holds for many aqueous electrolytes. Such dependences have also been discussed in Chapters 4 and 5 (and shown in Figures 4.4, 4.7, 4.8, 5.1, and 5.3). Although calculations of $V_{2\phi}$, $C_{p,2\phi}$, V_2^0, and C_{p2}^0 at various temperatures and pressures presented so far in this thesis provide information pertaining to the thermodynamic behavior of $R^{3+}_{(aq)}$ ions in aqueous solution, they are limited to set temperature and pressure conditions. The density model, described in Chapter 2, has been found to be suitable for probing the temperature and pressure dependences of V_2^0 and C_{p2}^0 values for REE triflates over the larger temperature and pressure surfaces investigated in this thesis.

6.2 Modeling of Apparent Molar Volumes and Apparent Molar Heat Capacities of Aqueous Solutions of the REE Triflates Over the Temperature Range 288.15 ≤ T /(K) ≤ 328.15 K and p = 0.1 MPa

For each of the REE triflates investigated at close to ambient temperature and ambient pressure conditions (presented in Chapter 4), the temperature dependences of the

values for the V_2^0, C_{p2}^0, $\beta^{(0)V}$, $\beta^{(1)V}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ parameters to equations (2.37) and

(2.38) have been modeled over the temperature range $T = (288.15, 298.15, 313.15,$ and

328.15) K and $p = 0.1$ MPa. The model selected for use is the density model that has

been previously used by Xiao and Tremaine (1997b). The equations utilized within the

density model take the form:

$$V_2^0 = v_1 + \frac{v_2}{(T-\theta)} + v_3 \cdot T + v_4 \cdot \beta \cdot T, \tag{6.1}$$

$$\beta^{(0)V} = \frac{v_5}{T} + v_6 \cdot \beta + v_7 \cdot \beta \cdot T, \tag{6.2}$$

$$\beta^{(1)V} = \frac{v_8}{T} + v_9 + v_{10} \cdot T + v_{11} \cdot \beta + v_{12} \cdot \beta \cdot T^2, \tag{6.3}$$

$$C_{p2}^0 = e_1 + \frac{e_2}{(T-\theta)^2} + e_3 \cdot T + e_4 \cdot \beta + e_5 \cdot \beta \cdot T, \tag{6.4}$$

$$\beta^{(0)J} = \frac{e_6}{T} + e_7 + e_8 \cdot \beta + e_9 \cdot \beta \cdot T, \tag{6.5}$$

$$\beta^{(1)J} = \frac{e_{10}}{T} + e_{11} + e_{12} \cdot T + e_{13} \cdot \beta \cdot e_{14} \cdot \beta \cdot T^2, \tag{6.6}$$

where θ is equal to 228 K. Estimates of the parameters, v_1 to v_{12} and e_1 to e_{14}, have been

obtained using multiple regression analyses and are reported for $Gd(CF_3SO_3)_{3(aq)}$,

$Dy(CF_3SO_3)_{3(aq)}$, $Nd(CF_3SO_3)_{3(aq)}$, $Er(CF_3SO_3)_{3(aq)}$, $Yb(CF_3SO_3)_{3(aq)}$, and $Y(CF_3SO_3)_{3(aq)}$

in Tables 6.1 and 6.2, along with their associated standard errors (in parentheses). Figure

6.1 shows a comparison of the $V_{2\phi}$ values calculated using equation (4.17) along with

Young's rule (equation (2.40)), $V_{2\phi}(calc)$, and those $V_{2\phi}$ values calculated using equation

(2.37) and the calculated fitting parameters for equations (6.1) to (6.3), $V_{2\phi}(global)$, for

aqueous solutions of $Gd(CF_3SO_3)_3$. A similar comparison is made between the
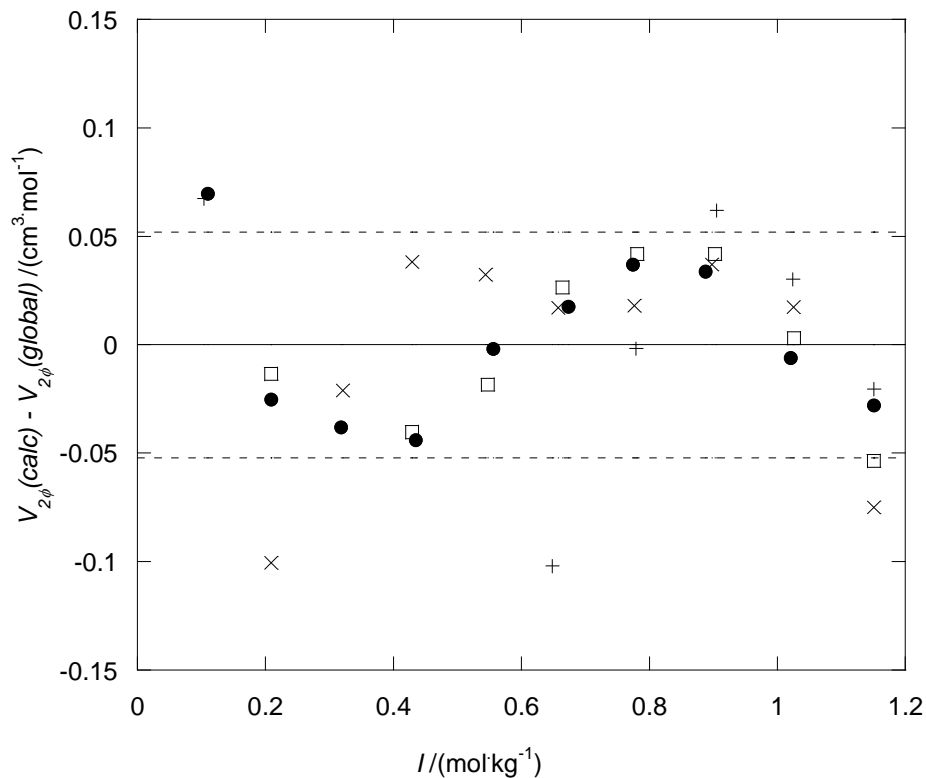
Figure 6.1 Comparison of $V_{2\phi}$ values (as a function of molality) calculated using equation (4.17) ($V_{2\phi}$(calc)) with those calculated using equations (2.37) and (6.1) to (6.3) ($V_{2\phi}$(global)) for $Gd(CF_3SO_3)_{3(aq)}$ at: •, $T = 288.15$ K; ×, $T = 298.15$ K; +, $T = 313.15$ K; and □, $T = 328.15$ K; and $p = 0.1$ MPa (the dashed lines represent the standard error).

$C_{p,2\phi}$(calc) values (calculated using equation (4.18) in conjunction with Young's rule) and

$C_{p,2\phi}$(global) values (calculated using equation (2.38) and the fitting parameters for

equations (6.4) to (6.6)) for $Gd(CF_3SO_3)_{3(aq)}$ in Figure 6.2. As can be seen, equations

(6.1) to (6.6) provide an adequate estimation of the $V_{2\phi}$ and $C_{p,2\phi}$ values for

$Gd(CF_3SO_3)_{3(aq)}$ over the temperature range $T = 288.15$ K to $T = 328.15$ K at the pressure

$p = 0.1$ MPa. Further verification of this consistency is seen in Figures 6.3 and 6.4. In
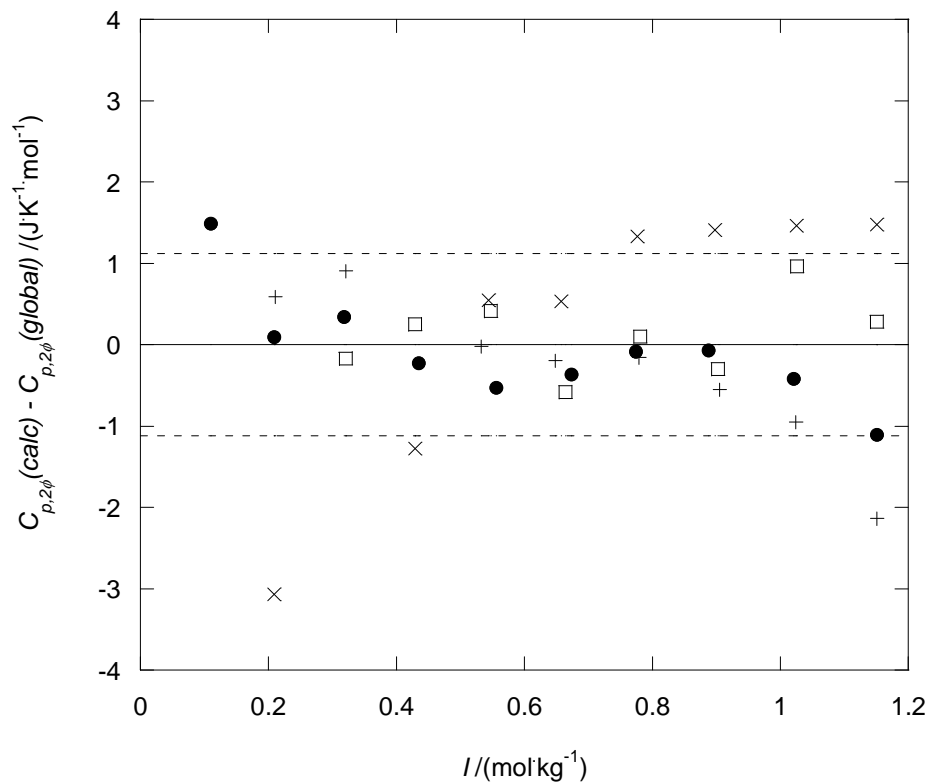
Figure 6.2 Comparison of $C_{p,2\phi}$ values (as a function of molality) calculated using equation (4.18) ($C_{p,2\phi}$(calc)) with those calculated using equations (2.38) and (6.4) to (6.6) ($C_{p,2\phi}$(global)) for Gd(CF$_3$SO$_3$)$_{3(aq)}$ at: ●, T = 288.15 K; ×, T = 298.15 K; +, T = 313.15 K; and □, T = 328.15 K; and p = 0.1 MPa (the dashed lines represent the standard error).

Figure 6.3, the V_2^0(calc) values (reported in Table 4.14) are compared to the V_2^0(global)

values (calculated using equation (6.1)) for Gd(CF$_3$SO$_3$)$_{3(aq)}$. Figure 6.4 shows a

comparison between the C_{p2}^0(calc) values (reported in Table 4.14) and the C_{p2}^0(global)

values (calculated using equation (6.4)) for Gd(CF$_3$SO$_3$)$_{3(aq)}$. Similar agreements are
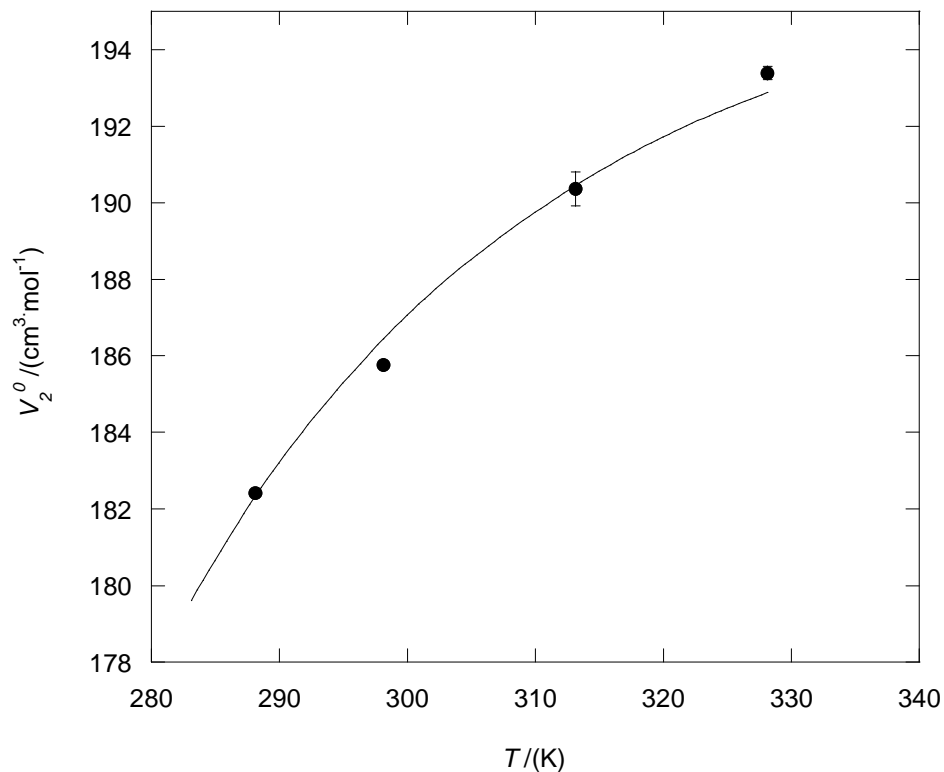
Figure 6.3 The apparent molar volumes at infinite dilution, V_2^0, against temperature for aqueous solutions of $Gd(CF_3SO_3)_3$: •, reported in Table 4.14; ————, calculated using equation (6.1) and the parameters reported in Table 6.1.

also observed for $Dy(CF_3SO_3)_{3(aq)}$, $Nd(CF_3SO_3)_{3(aq)}$, $Er(CF_3SO_3)_{3(aq)}$, $Yb(CF_3SO_3)_{3(aq)}$, and $Y(CF_3SO_3)_{3(aq)}$, but are not shown in this thesis.
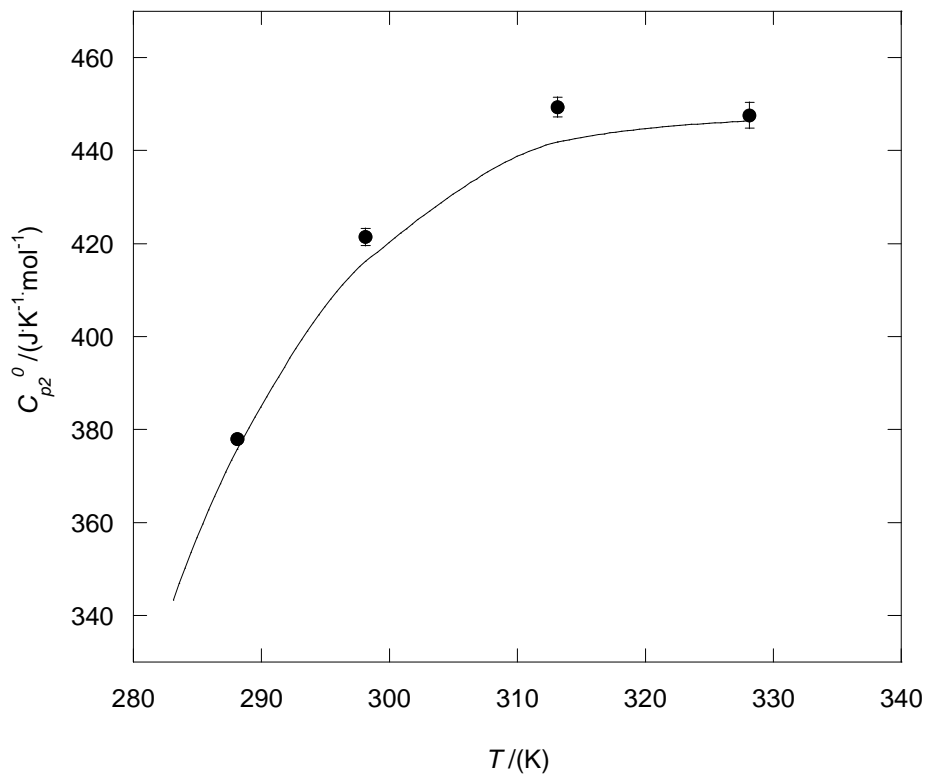
Figure 6.4 The apparent molar heat capacities at infinite dilution, $C_{p2}{}^{0}$, against temperature for aqueous solutions of $Gd(CF_3SO_3)_3$: •, reported in Table 4.14; ———— , calculated using equation (6.4) and the parameters reported in Table 6.1.

Table 6.1 Estimated values of the parameters to equations (6.1) through (6.6), that model the temperature dependences of $V_{2\phi}$ and $C_{p,2\phi}$ values for aqueous solutions of $Gd(CF_3SO_3)_3$, $Dy(CF_3SO_3)_3$, and $Nd(CF_3SO_3)_3$ at $p = 0.1$ MPa

Parameter	Value: $Gd(CF_3SO_3)_3$	$Dy(CF_3SO_3)_3$	$Nd(CF_3SO_3)_3$
$V_{2\phi}$			
$v_1/(cm^3 \cdot mol^{-1})$	240(11)	293(9)	138(1)
$v_2/(cm^3 \cdot K \cdot mol^{-1})$	-2.1×10^3(168)	-2×10^3(1×10^3)	--------
$v_3/(cm^3 \cdot K^{-1} \cdot mol^{-1})$	-0.08(0.03)	--------	0.300(8×10^{-3})
$v_4/(cm^3 \cdot MPa \cdot K^{-1} \cdot mol^{-1})$	--------	-530(56)	-333(20)
$v_5/(cm^3 \cdot kg \cdot K \cdot mol^{-1} \cdot J^{-1})$	-7×10^4(2×10^4)	--------	9×10^{-3}(2×10^{-3})
$v_6/(cm^3 \cdot MPa \cdot kg \cdot mol^{-1} \cdot J^{-1})$	431(148)	17(6)	--------
$v_7/(cm^3 \cdot kg \cdot MPa \cdot mol^{-1} \cdot J^{-1} \cdot K^{-1})$	-0.7(0.2)	-2.4×10^{-5}(8×10^{-6})	-0.07(0.01)
$v_8/(cm^3 \cdot K \cdot kg \cdot mol^{-1} \cdot J^{-1})$	1.5(0.7)	--------	--------
$v_9/(cm^3 \cdot kg \cdot mol^{-1} \cdot J^{-1})$	-0.01(5×10^{-3})	1.8(0.2)	-1.8×10^{-2}(5×10^{-3})
$v_{10}/(cm^3 \cdot kg \cdot mol^{-1} \cdot J^{-1} \cdot K^{-1})$	1.7×10^{-5}(9×10^{-6})	-5.6×10^{-3}(6×10^{-4})	5×10^{-5}(1×10^{-5})
$v_{11}/(cm^3 \cdot kg \cdot MPa \cdot mol^{-1} \cdot J^{-1})$	--------	-1.98×10^4(220)	--------
$v_{12}/(cm^3 \cdot kg \cdot MPa \cdot mol^{-1} \cdot K^{-2})$	-5×10^{-3}(4×10^{-3})	0.020(2×10^{-3})	--------
Standard error $/(cm^3 \cdot mol^{-1})$	0.05	0.20	0.10
$C_{p,2\phi}$			
$e_1/(J \cdot K^{-1} \cdot mol^{-1})$	1.08×10^3(71)	750(64)	137(45)
$e_2/(J \cdot K \cdot mol^{-1})$	-7.8×10^5(4×10^4)	--------	--------
$e_3/(J \cdot K^{-2} \cdot mol^{-1})$	-1.7(0.2)	4.4(0.2)	3.2(0.2)
$e_4/(J \cdot MPa \cdot K^{-1} \cdot mol^{-1})$	--------	--------	--------
$e_5/(J \cdot MPa \cdot K^{-2} \cdot mol^{-1})$	--------	-1.2×10^4(828)	-5.3×10^3(604)
$e_6/(kg \cdot mol^{-1} \cdot K^{-1})$	--------	-5.0(0.7)	0.4(0.2)
$e_7/(kg \cdot mol^{-1} \cdot K^{-2})$	-6×10^{-4}(2×10^{-4})	0.015(2×10^{-3})	-2×10^{-3}(1×10^{-3})
$e_8/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-2})$	1.4(0.4)	36(5)	--------
$e_9/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-3})$	--------	-0.11(0.01)	8×10^{-3}(4×10^{-3})
$e_{10}/(kg \cdot mol^{-1} \cdot K^{-1})$	--------	--------	-40(33)
$e_{11}/(kg \cdot mol^{-1} \cdot K^{-2})$	--------	--------	5(3)
$e_{12}/(kg \cdot mol^{-1} \cdot K^{-3})$	7×10^{-6}(2×10^{-6})	--------	1.7×10^{-6}(8×10^{-7})
$e_{13}/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-2})$	-3.2(0.9)	1.6(0.6)	-1.3×10^4(6×10^3)
$e_{14}/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-4})$	-1.1×10^{-5}(8×10^{-6})	-1.1×10^{-5}(7×10^{-6})	--------
Standard error $/(J \cdot K^{-1} \cdot mol^{-1})$	1.12	2.23	1.46

Table 6.2 Estimated values of the parameters to equations (6.1) through (6.6), that model the temperature dependences of $V_{2\phi}$ and $C_{p,2\phi}$ values for aqueous solutions of $Er(CF_3SO_3)_3$, $Yb(CF_3SO_3)_3$, and $Y(CF_3SO_3)_3$ at $p = 0.1$ MPa

Parameter	Value: $Er(CF_3SO_3)_3$	$Yb(CF_3SO_3)_3$	$Y(CF_3SO_3)_3$
$V_{2\phi}$			
$v_1/(cm^3 \cdot mol^{-1})$	214(4)	153(3)	184(13)
$v_2/(cm^3 \cdot K \cdot mol^{-1})$	-1.43×10^3(38)	--------	-1.0×10^3(190)
$v_3/(cm^3 \cdot K^{-1} \cdot mol^{-1})$	--------	$0.44(8 \times 10^{-3})$	0.05(0.03)
$v_4/(cm^3 \cdot MPa \cdot K^{-1} \cdot mol^{-1})$	-80(25)	-753(38)	--------
$v_5/(cm^3 \cdot kg \cdot K \cdot mol^{-1} \cdot J^{-1})$	-0.6(0.2)	-0.14(0.02)	$9 \times 10^{-3}(\times 10^{-3})$
$v_6/(cm^3 \cdot MPa \cdot kg \cdot mol^{-1} \cdot J^{-1})$	--------	--------	--------
$v_7/(cm^3 \cdot kg \cdot MPa \cdot mol^{-1} \cdot J^{-1} \cdot K^{-1})$	--------	--------	-0.07(0.02)
$v_8/(cm^3 \cdot K \cdot kg \cdot mol^{-1} \cdot J^{-1})$	18(13)	--------	85(28)
$v_9/(cm^3 \cdot kg \cdot mol^{-1} \cdot J^{-1})$	-0.11(0.08)	570(16)	-0.6(0.2)
$v_{10}/(cm^3 \cdot kg \cdot mol^{-1} \cdot J^{-1} \cdot K^{-1})$	$1.4 \times 10^{-4}(1.3 \times 10^{-4})$	-1.85(0.05)	$9 \times 10^{-4}(3 \times 10^{-4})$
$v_{11}/(cm^3 \cdot kg \cdot MPa \cdot mol^{-1} \cdot J^{-1})$	--------	$-6.2 \times 10^5(2 \times 10^4)$	--------
$v_{12}/(cm^3 \cdot kg \cdot MPa \cdot mol^{-1} \cdot K^{-2})$	--------	6.5(0.2)	--------
Standard error /$(cm^3 \cdot mol^{-1})$	0.09	0.06	0.13
$C_{p,2\phi}$			
$e_1/(J \cdot K^{-1} \cdot mol^{-1})$	1.17×10^3(56)	538(89)	230(26)
$e_2/(J \cdot K \cdot mol^{-1})$	$-7.4 \times 10^5(3 \times 10^4)$	--------	--------
$e_3/(J \cdot K^{-2} \cdot mol^{-1})$	-2.0(0.2)	3.0(0.4)	3.11(0.08)
$e_4/(J \cdot MPa \cdot K^{-1} \cdot mol^{-1})$	--------	--------	--------
$e_5/(J \cdot MPa \cdot K^{-2} \cdot mol^{-1})$	--------	$-7 \times 10^3(1 \times 10^3)$	-5.5×10^3(283)
$e_6/(kg \cdot mol^{-1} \cdot K^{-1})$	1.8(0.5)	2(1)	-1.8(0.3)
$e_7/(kg \cdot mol^{-1} \cdot K^{-2})$	$3 \times 10^{-4}(1 \times 10^{-4})$	$-7 \times 10^{-3}(5 \times 10^{-3})$	$5.7 \times 10^{-3}(8 \times 10^{-4})$
$e_8/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-2})$	-26(7)	-23(13)	13(2)
$e_9/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-3})$	88(23)	0.06(0.04)	$-0.042(6 \times 10^{-3})$
$e_{10}/(kg \cdot mol^{-1} \cdot K^{-1})$	-42(10)	--------	-34(9)
$e_{11}/(kg \cdot mol^{-1} \cdot K^{-2})$	--------	-0.10(0.02)	--------
$e_{12}/(kg \cdot mol^{-1} \cdot K^{-3})$	$1.9 \times 10^{-6}(3 \times 10^{-7})$	$2.9 \times 10^{-4}(6 \times 10^{-5})$	--------
$e_{13}/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-2})$	--------	112(23)	--------
$e_{14}/(kg \cdot MPa \cdot mol^{-1} \cdot K^{-4})$	--------	$-1.0 \times 10^{-3}(2 \times 10^{-4})$	$4.4 \times 10^{-3}(7 \times 10^{-4})$
Standard error /$(J \cdot K^{-1} \cdot mol^{-1})$	1.24	1.18	1.01

6.3 Modeling of the Apparent Molar Volumes of Aqueous Solutions of the REE Triflates over the Temperature Range 288.15 ≤ T /(K) ≤ 423.15 K and the Pressure Range 0.1 ≤ p /(MPa) ≤ 15.00

The apparent molar volumes of aqueous solutions of the REE triflates are dependent upon both temperature and pressure. In Section 6.2, an isobaric model was described ($p = 0.1$ MPa). However, for the systems investigated in Chapter 5, the model may be extended to higher pressures. To achieve this goal, equations (6.1) to (6.6) must be modified to account for both pressure and temperature changes.

For each of the aqueous REE triflate salt solutions investigated over the extended temperature and pressure surface (presented in detail in Chapter 5), the forms of the equations follow those presented by Simonson *et al.* (1994):

$$V_2^0 = g_1 + g_2 \cdot \beta + g_3 \cdot \beta \cdot (T - T_m) + g_4 \cdot \beta \cdot (T - T_m)^2, \tag{6.7}$$

$$\beta^{(0)V} = g_5 + g_6 \cdot (T - T_m) + g_7 \cdot (T - T_m)^2 + g_8 \cdot (p - p_m) \cdot (T - T_m)$$

$$+ g_9 \cdot (p - p_m) \cdot (T - T_m)^2, \tag{6.8}$$

$$\beta^{(1)V} = g_{10} + g_{11} \cdot (T - T_m) + g_{12} \cdot (T - T_m)^2 + g_{13} \cdot (p - p_m) \cdot (T - T_m)$$

$$+ g_{14} \cdot (p - p_m) \cdot (T - T_m)^2. \tag{6.9}$$

T_m is the mid-point temperature of study (where $T_m = 353.15$ K for $Gd(CF_3SO_3)_{3(aq)}$ and $T_m = 330.15$ K for both $Nd(CF_3SO_3)_{3(aq)}$ and $Yb(CF_3SO_3)_{3(aq)}$). $p_m = 7.5$ MPa for all the aqueous REE triflates studied. Estimates of the parameters g_1 to g_{14} were obtained using least squares multiple regression analyses and are reported together with their standard errors in Table 6.3 for the systems $Gd(CF_3SO_3)_{3(aq)}$, $Nd(CF_3SO_3)_{3(aq)}$, and $Yb(CF_3SO_3)_{3(aq)}$. Figure 6.5 shows a comparison between $V_{2\phi}$(calc) values (calculated using equation (4.17) in conjunction with Young's rule) and $V_{2\phi}$(global) values
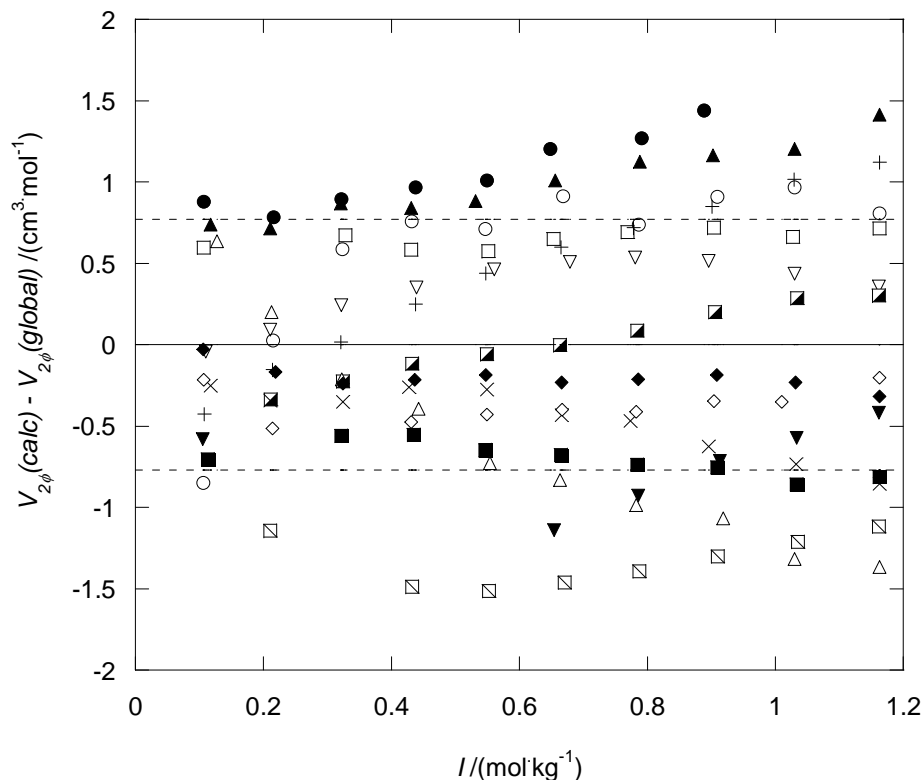
Figure 6.5 Comparison of $V_{2\phi}$ values (as a function of molality) calculated using equation (4.17) ($V_{2\phi}$(calc)) with those calculated using equations (2.37) and (6.7) to (6.9) ($V_{2\phi}$(global)) for $Gd(CF_3SO_3)_{3(aq)}$ at: ▽, T = 288.15 K, p = 0.1 MPa; ◩, T = 298.15 K, p = 0.1 MPa; ▼, T = 313.15 K, p = 0.1 MPa; ◨, T = 328.15 K, p = 0.1 MPa; ●, T = 323.15 K, p = 5.00 MPa; ×, T = 323.15 K, p = 10.00 MPa; +, T = 323.15 K, p = 15.00 MPa; ▫, T = 348.15 K, p = 5.00 MPa; ◇, T = 348.15 K, p = 10.00 MPa; ■, T = 348.15 K, p = 15.00 MPa; △, T = 373.15 K, p = 5.00 MPa; ▲, T = 373.15 K, p = 10.00 MPa; ○, T = 373.15 K, p = 15.00 MPa; and ◆, T = 423.15 K, p = 10.00 MPa (The dashed lines represent the standard error).

(calculated using equation (2.37) and the fitting parameters for equations (6.7) to (6.9)) for $Gd(CF_3SO_3)_{3(aq)}$. Figure 6.5 shows that there is good agreement between $V_{2\phi}$(calc) and $V_{2\phi}$(global) values. This agreement is confirmed in Figure 6.6, where the V_2^0 values calculated using equation (2.37) (which are reported in Table 5.7) are compared with
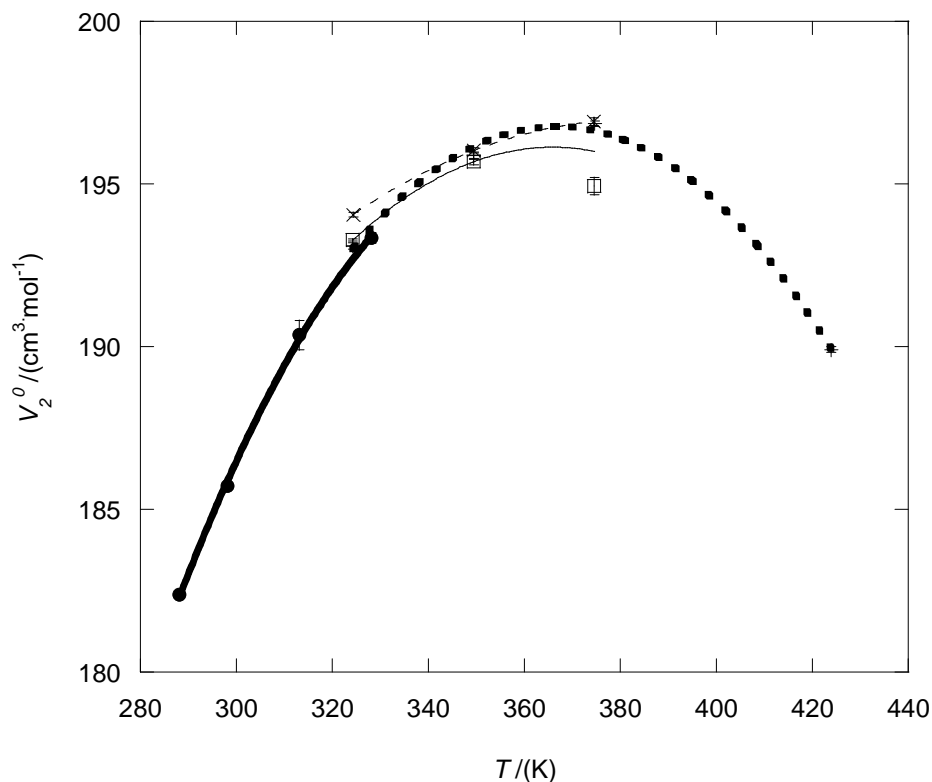
Figure 6.6 Values of V_2^0 for aqueous solutions of $Gd(CF_3SO_3)_3$ calculated from equation (2.37) as a function of temperature and the pressures of interest: •, $p = 0.1$ MPa; ×, $p = 5.00$ MPa; +, $p = 10.00$ MPa; and □, $p = 15.00$ MPa and equation (6.7): ——————, $p = 0.1$ MPa; -----------, $p = 5.00$ MPa; ••••••••••••, $p = 10.00$ MPa; and ————— , $p = 15.00$ MPa.

those calculated using equation (6.7) over the temperature and pressure ranges

investigated in this thesis. Similar trends are seen for $Nd(CF_3SO_3)_{3(aq)}$ and

$Yb(CF_3SO_3)_{3(aq)}$.

A similar global fit for $Gd(CF_3SO_3)_{3(aq)}$ has been reported by Xiao *et al.* (1999)

over an extended temperature and pressure surface. Xiao *et al.* (1999) report

$V_{2\phi}(calc) - V_{2\phi}(global)$ differences from 1.5 cm³·mol⁻¹ to 3.0 cm³·mol⁻¹ for

Table 6.3 Estimated values for the parameters to equations (6.7) through (6.9), that model the temperature and pressure dependence of $V_{2\phi}$ values for aqueous solutions of $Gd(CF_3SO_3)_3$, $Nd(CF_3SO_3)_3$, and $Yb(CF_3SO_3)_3$ over the temperature range $288.15 \leq T$ /(K) ≤ 423.15 and the pressure range $0.1 \leq p$ /(MPa) ≤ 15.00

Parameter	Value: $Gd(CF_3SO_3)_3$	$Nd(CF_3SO_3)_3$	$Yb(CF_3SO_3)_3$
$V_{2\phi}$			
g_1 /(cm^3·mol^{-1})	232(8)	237(5)	112(6)
g_2 /(cm^3·MPa·mol^{-1})	$-8 \times 10^4 (2 \times 10^4)$	$-1.1 \times 10^5 (1 \times 10^4)$	$1.8 \times 10^5 (1.4 \times 10^4)$
g_3 /(cm^3·MPa·mol^{-1}·K^{-1})	257(36)	454(22)	445(25)
g_4 /(cm^3·MPa·mol^{-1}·K^{-2})	-1.9(0.5)	2.0(0.8)	-11.9(0.9)
g_5 /(cm^3·kg·mol^{-1}·J^{-1})	--------	--------	$1.8 \times 10^{-3} (3 \times 10^{-4})$
g_6 /(cm^3·kg·mol^{-1}·J^{-1}·K^{-1})	$3 \times 10^{-5} (1 \times 10^{-5})$	$3 \times 10^{-5} (1 \times 10^{-5})$	$6 \times 10^{-5} (1 \times 10^{-5})$
g_7 /(cm^3·kg·mol^{-1}·J^{-1}·K^{-2})	--------	$-7 \times 10^{-7} (3 \times 10^{-7})$	--------
g_8 /(cm^3·kg·mol^{-1}·J^{-1}·K^{-1}·MPa^{-1})	$1.2 \times 10^{-2} (6 \times 10^{-3})$	$7 \times 10^{-6} (1 \times 10^{-6})$	$-3 \times 10^{-6} (2 \times 10^{-6})$
g_9 /(cm^3·kg·mol^{-1}·J^{-1}·K^{-2}·MPa^{-1})	$-4 \times 10^{-5} (2 \times 10^{-5})$	--------	--------
g_{10} /(cm^3·kg·mol^{-1}·J^{-1})	$-9.6 \times 10^{-3} (4 \times 10^{-4})$	$-5.3 \times 10^{-3} (3 \times 10^{-4})$	$-1.8 \times 10^{-2} (1 \times 10^{-3})$
g_{11} /(cm^3·kg·mol^{-1}·J^{-1}·K^{-1})	$-7 \times 10^{-2} (2 \times 10^{-2})$	$-3.0 \times 10^{-4} (4 \times 10^{-5})$	$-5.3 \times 10^{-4} (5 \times 10^{-5})$
g_{12} /(cm^3·kg·mol^{-1}·J^{-1}·K^{-2})	$-6 \times 10^{-7} (3 \times 10^{-7})$	$2 \times 10^{-6} (1 \times 10^{-6})$	$-7 \times 10^{-7} (5 \times 10^{-7})$
g_{13} /(cm^3·kg·mol^{-1}·J^{-1}·K^{-1}·MPa^{-1})	$1.7 \times 10^{-5} (7 \times 10^{-6})$	$-3.5 \times 10^{-5} (4 \times 10^{-6})$	$1.6 \times 10^{-5} (5 \times 10^{-6})$
g_{14} /(cm^3·kg·mol^{-1}·J^{-1}·K^{-2}·MPa^{-1})	$1.8 \times 10^{-4} (6 \times 10^{-5})$	$2.0 \times 10^{-7} (4 \times 10^{-8})$	$3.1 \times 10^{-7} (4 \times 10^{-8})$
Standard error /(cm^3·mol^{-1})	0.77	0.55	0.62

$Gd(CF_3SO_3)_{3(aq)}$. In Figure 6.5, the maximum $V_{2\phi}$(calc) $- V_{2\phi}$(global) difference for this study is no greater than 1.5 cm^3·mol^{-1}, and many are within the 0.77 cm^3·mol^{-1} 95% standard error limit. Similar trends are also seen for $Nd(CF_3SO_3)_{3(aq)}$ and $Yb(CF_3SO_3)_{3(aq)}$ over the surface of temperatures and pressures studied. As of this time, this study has presented the most thorough set $V_{2\phi}$(calc) $- V_{2\phi}$(global) calculations for any aqueous solutions of the REE triflates.

7) CONCLUSIONS AND POSSIBLE FUTURE DIRECTIONS

The REEs are very important from a socioeconomic perspective. A complete

thermodynamic investigation of the REEs in aqueous solution is essential in order to

understand how these trivalent ions behave in a solvent such as water. This thesis has

provided such a study on the REE triflates in aqueous solution over an extended surface

of temperature and pressure. Such studies were conducted in order to provide detailed

volumetric and calorimetric information regarding these salts.

The triflate anion was used because of its apparent minimal speciation and

oxidation concerns in aqueous solution (which commonly affect the nitrate, chloride,

sulfate, and perchlorate ions). These concerns regarding the lack of speciation were

discussed in Chapter 4 (and presented in Figures 4.9 and 4.10). As a result, the

thermodynamic studies reported in this thesis have provided precise volumetric and

calorimetric data for $CF_3SO_3H_{(aq)}$, $NaCF_3SO_{3(aq)}$, $Gd(CF_3SO_3)_{3(aq)}$, $Dy(CF_3SO_3)_{3(aq)}$,

$Nd(CF_3SO_3)_{3(aq)}$, $Er(CF_3SO_3)_{3(aq)}$, $Yb(CF_3SO_3)_{3(aq)}$, and $Y(CF_3SO_3)_{3(aq)}$ at $T = (288.15,$

298.15, 313.15, and 328.15) K and $p = 0.1$ MPa by measuring relative densities and

massic heat capacities on the Picker system described in Chapter 3. The internal

consistency of calculated single ion volumes and heat capacities, $V_2^0(R^{3+};$ aq) and

$C_{p2}^0(R^{3+};$ aq), has been checked by comparing values obtained in this study with those

values previously reported in the literature (presented in Table 4.15 and Figures 4.11 and

4.12).

In addition to the volumetric and calorimetric studies at ambient pressure and near

ambient temperature reported in Chapter 4, volumetric studies have been performed at

higher temperatures and pressures (reported in Chapter 5). These measurements were made on a home and purpose-built high temperature and pressure vibrating tube densimeter (described in Chapter 3). The precision of the instrument was verified by a comparison with precise $NaBr_{(aq)}$ volumetric data reported by Archer (1991). Chapter 5 reported density data for aqueous solutions of $CF_3SO_3H_{(aq)}$, $Gd(CF_3SO_3)_{3(aq)}$, $Nd(CF_3SO_3)_{3(aq)}$, and $Yb(CF_3SO_3)_{3(aq)}$ over the temperature range $T = (323.15, 348.15, 373.15,$ and $423.15)$ K and the pressure range $p = (5.00, 10.00,$ and $15.00)$ MPa. These measurements provided single ion volume data, $V_2^0(R^{3+}; aq)$, for $Gd^{3+}_{(aq)}$, $Nd^{3+}_{(aq)}$, and $Yb^{3+}_{(aq)}$ at all the temperatures and pressures investigated for each aqueous REE salt. The $V_2^0(Yb^{3+}; aq)$ values have been compared with values previously reported in the literature. Such comparisons indicated a high degree of internal consistency across the temperature and pressure surface of interest between the current study and previous work conducted by Hakin *et al.* (2004a).

Equations of state have been determined for aqueous solutions of each of the REE triflate salts. These equations permit the calculation of apparent molar volumes and heat capacities over the entire temperature and pressure surface investigated for each system. Comparisons with data in the literature indicate that the equations of state presented in this thesis are the most precise at the current time for calculating estimates of the volumetric and calorimetric properties of aqueous REE triflate salt solutions.

Although the thermodynamic studies presented in this thesis are thorough, they have not been extensive enough to fully probe the nature of solute-solvent and solute-solute interactions for aqueous REE solutions at near ambient conditions. Additional work is required for a complete understanding of the behavior of the

thermodynamic properties of REE systems in aqueous solutions. Further studies (using the Picker system) can be conducted on other REE systems that have not been explored in detail; such as Cerium (Ce), Samarium (Sm), Europium (Eu), Terbium (Tb), Thulium (Tm), and Lutetium (Lu). Volumetric and calorimetric measurements on these systems can complete the analysis of the REE ions in aqueous solution, thus providing potential information relating to their hydration properties at near ambient conditions.

To investigate solute-solvent and solute-solute interactions at conditions removed from ambient, additional information is needed on the volumetric and calorimetric properties of the REEs over extended surfaces of temperature and pressure. Precise density measurements obtained using the high temperature and pressure vibrating tube densimeter can also be used to probe the temperature and pressure dependences of volume data (expansibilities and compressibilities) for aqueous solutions of the REE triflates. Precise heat capacity measurements are also required at elevated temperatures and pressures for the aqueous REE triflates. Such measurements will be possible using a high temperature and pressure transitiometer recently obtained by the Hakin laboratory group. After a set-up and extensive calibration of this new piece of equipment, the required heat capacity measurements will be completed.

Finally, the temperature and pressure dependences of volumetric and calorimetric data of the REEs in aqueous solution can be further subjected to global modeling. These models will provide further expressions to represent solute-solvent and solute-solute interactions within aqueous solution.

These continued studies and models over a large surface of temperatures and pressures will provide opportunities to expand the comprehensive database of

thermodynamic data for aqueous REE salt solutions which is still being constructed by

the Hakin research group.

REFERENCES

Anderson, G. M., & Crerar, D. A. (1993) *Thermodynamics in geochemistry: The equilibrium model*, Oxford university press, New York.

Archer, D. G. (1991) Thermodynamics properties of the NaBr+H_2O system. *J. Phys. Chem. Ref. Data*, **20**, 793-829

Archer, D. G. (1992) Thermodynamics properties of the NaCl+H_2O system II: Thermodynamic properties of $NaCl_{(aq)}$, $NaCl \cdot 2H_2O_{(cr)}$, and phase eqilibria. *J. Phys. Chem. Ref. Data*, **21**, 793-829

Archer, D. G., & Wang, P. (1990) The dielectric constant of water and Debye-Hückel limiting law slope. *J. Phys. Chem. Ref. Data*, **19**, 371-411

Bent, H. A. (1972) A note on the notation and terminology of thermodynamics. *J. Chem. Education*, **49**, 44-46

Cotton, F. A., & Wilkinson, G. (1988) *Advanced Inorganic Chemistry*, 5th Ed. Wiley-Interscience Publication, New York

Debye, P., & Hückel, E. (1923) The theory of electrolytes 1. Lowering the freezing point and related phenomena. *Phys. Z*, **24**, 185-206

Debye, P., & Hückel, E. (1924) Remarks on a theorm on the cataphorical migration velocity of suspended particles. *Phys. Z*, **25**, 49-52

Desnoyers, J. E., Visser, C., Perron, G., & Picker P. (1976) Reexamination of the heat capacities obtained by flow microcalorimetry. Recommendation for the use of a chemical standard. *J. Soln. Chem*, **5**, 605-616

Dessauges, G., Mljevic, N., & Van Hook, A. (1980) Isotope effects in aqueous systems 9. Partial molar volumes of NaCl/H$_2$O and NaCl/D$_2$O solutions at 15, 30, and 45°C. *J. Phys. Chem*, **84**, 2587-2595

Erickson, K. M., Hakin, A. W., Jones, S. N., Liu, J. L., & Zahir, S. N. (2007) Thermodynamics of selected aqueous rare earth element containing triflate salts at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa. *J. Soln. Chem.*, currently in press

Gates, J. A., Wood, R. H., & Quint, J. R. (1982) Experimental evidence for the remarkable behavior of the partial molar heat capacity at infinite dilution of aqueous electrolytes at the critical point. *J. Phys. Chem*, **86**, 4948-4951

Hakin, A. W., Daisley, D. C., Delgado, L., Liu, J. L., Marriott, R. H., Marty, J. L. et al. (1998) Volumetric properties of glycine in water at elevated temperatures and pressures measured with a new optically driven vibrating-tube densimeter. *J. Chem. Thermodynamics*, **30**, 583-606

Hakin, A. W., Lukacs, M. J., Liu, J. L., Erickson, K., & Madhavji, A. (2003a) The volumetric and thermochemical properties of Y(ClO$_4$)$_{3(aq)}$, Yb(ClO$_4$)$_{3(aq)}$, Dy(ClO$_4$)$_{3(aq)}$, and Sm(ClO$_4$)$_{3(aq)}$ at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa. *J Chem. Thermodynamics*, **35**, 775-802

Hakin, A. W., Lukacs, M. J., Liu, J. L., & Erickson, K. (2003b) The volumetric and thermochemical properties of YCl$_{3(aq)}$, YbCl$_{3(aq)}$, DyCl$_{3(aq)}$, SmCl$_{3(aq)}$, and GdCl$_{3(aq)}$ at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa. *J. Chem. Thermodynamics*, **35**, 1861-1895

Hakin, A. W., Lukacs, M. J., & Liu J. L. (2004a) Densities and apparent molar volumes of $HClO_{4(aq)}$ and $Yb(ClO_4)_{3(aq)}$ at elevated temperatures and pressures. *J. Chem. Thermodynamics*, **36**, 759-772

Hakin, A. W., Liu, J. L., Erickson, K., & Munoz, J-V. (2004b) Apparent molar heat capacities and apparent molar volumes of $Pr(ClO_4)_{3(aq)}$, $Gd(ClO_4)_{3(aq)}$, $Ho(ClO_4)_{3(aq)}$, and $Tm(ClO_4)_{3(aq)}$ at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa. *J. Chem. Thermodynamics*, **36**, 773-786

Hakin, A. W., Liu, J. L., Erickson, K., Munoz, J-V., & Rard J. A. (2005) Apparent molar volumes and apparent molar heat capacities of $Pr(NO_3)_{3(aq)}$, $Gd(NO_3)_{3(aq)}$, $Ho(NO_3)_{3(aq)}$, and $Y(NO_3)_{3(aq)}$ at $T = (288.15, 298.15, 313.15,$ and $328.15)$ K and $p = 0.1$ MPa. *J. Chem. Thermodynamics*, **37**, 153-167

Harris, D. C. (2002) *Quantitative chemical analysis*, 6th Ed., W. H. Freeman and Company, New York, 150

Hill, P. G. (1990) A unified fundamental equation for the thermodynamic properties of H_2O. *J. Phys. Chem. Ref. Data*, **19**, 1233-1274

Hovey, J. K. (1988) *Thermodynamics of aqueous solutions*, Ph.D. thesis, University of Alberta

Hovey, J. K., Hepler, L. G., & Tremaine, P. R. (1988) Thermodynamics of aqueous Aluminate ion: Standard partial molar heat capacities and volumes of $Al(OH)_4^-{}_{(aq)}$ from 10 to 55[o]C. *J. Phys. Chem*, **92**, 1323-1332

Kell, G. S. (1967) Precise representation of volume properties of water at one atmosphere. *J. Chem. Eng. Data*, **12**, 66-69

Klotz, I. M., & Rosenberg, R. M. (1972) *Chemical thermodynamics: Basic theory and methods*, W. A. Benjamin Inc, Menlo Park, California

Lukacs, M. J. (2003) *Thermodynamics of 3+ metal cation containing systems*, M.Sc. thesis, University of Lethbridge

Lide, D. R. (1999-2000) *Handbook of Chemistry and Physics.* 80th Ed., Chemical Rubber Publishing Co., Clevland, OH, 14-14

Marriott, R. M. (1999) *Thermodynamic investigations of some aqueous solutions through calorimetry and densimetry*, M.Sc. thesis, University of Lethbridge

Marriott, R. M., Hakin, A. W., & Rard, J. A. (2001) Apparent molar heat capacities and apparent molar volumes of $Y_2(SO_4)_{3(aq)}$, $La_2(SO_4)_{3(aq)}$, $Pr_2(SO_4)_{3(aq)}$, $Nd_2(SO_4)_{3(aq)}$, $Eu_2(SO_4)_{3(aq)}$, $Dy_2(SO_4)_{3(aq)}$, $Ho_2(SO_4)_{3(aq)}$, and $Lu_2(SO_4)_{3(aq)}$ at $T = 298.15$ K and $p = 0.1$ MPa. *J. Chem. Thermodynamics*, **33**, 643-687

Marshall, W. L. (1970) Complete equilibrium constants, electrolyte, equilibria, and reaction rates. *J. Phys. Chem*, **74**, 346-355

Mesmer, R. E., Marshall, W. L., Palmer, D. A., Simonson, J. M., & Holmes, H. F. (1988) Thermodynamics of aqueous association and ionization reactions at high temperatures and pressures. *J. Soln. Chem*, **17**, 699-718

Millero, F. J. (1970) The apparent and partial molal volume of aqueous sodium chloride solutions at various temperatures. *J. Phys. Chem*, **74**, 356-360

Perron, G., Fortier, J.-L., & Desnoyers, J. E. (1975) the apparent molar heat capacities and volumes of aqueous NaCl from 0.01 to 3 $mol \cdot kg^{-1}$ in the temperature range 274.15 to 318.15 K. *J. Chem. Thermodynamics*, **7**, 1177-1184

Picker, P., Leduc, P-A., Philip, P. R., & Desnoyers, J. E. (1971) Heat capacity of solutions by flow microcalorimetry. *J. Chem. Thermodynamics*, **3**, 631-642

Picker, P., Tremblay, E., & Jolicoeur, C. (1974) A high-precision digital readout flow densimeter for liquids. *J. Soln. Chem*, **3**, 377-384

Pitzer, K. S. (1991) *Activity coefficients in electrolyte solutions.* 2nd Ed., CRC press, Boca Ranton

Pytkowicz, R. M. (1979) *Activity coefficients in electrolyte solutions.* 1st Ed., CRC press, Boca Ranton

Rard, J.A., Shiers, L. E., Heiser, D. J., & Spedding, F. H. (1977) Isopiestic determination of the activity coefficients of some aqueous rare earth electrolyte solutions at 25°C. 3. The rare earth nitrates. *J. Chem. Eng. Data*, **22**, 337-347

Rard, J. A., Miller, D. G., & Spedding, F. H. (1979) Isopiestic determination of the activity coefficients of some aqueous rare earth electrolyte solutions at 25°C. 4. La(NO$_3$)$_3$, Pr(NO$_3$)$_3$, and Nd(NO$_3$)$_3$. *J. Chem. Eng. Data,* **24**, 348-354

Rard, J. A., & Spedding, F. H. (1981) Isopiestic determination of the activity coefficients of some aqueous rare earth electrolyte solutions at 25°C. 5. Dy(NO$_3$)$_3$, Ho(NO$_3$)$_3$, and Lu(NO$_3$)$_3$. *J. Chem. Eng. Data*, **26**, 391-395

Rard, J. A., & Spedding, F. H. (1982) Isopiestic determination of the activity coefficients of some aqueous rare-earth electrolyte solutions at 25°C. 6. Eu(NO$_3$)$_3$, Y(NO$_3$)$_3$, and YCl$_3$. *J. Chem. Eng. Data,* **27**, 454-461

Robinson, R. A., & Stokes, R. H. (1965) *Electrolyte solutions.* 2nd Ed. revised, Butterworths, London

Sabot, J-L., & Maestro, P. (1995) in: Howe-Grant M. (Ed.) *Kirk-Othermer Encyclopedia of Chemical Technology.* **14**, 4th Ed. Wiley-Interscience, New York, 1091-1115

Simonson, J. M., Oakes, C. S., & Bondar, R. J. (1994) Densities of $NaCl_{(aq)}$ to the temperature 523 K and pressures to 40 MPa measured with a new vibrating tube densimeter. *J. Chem. Thermodynamics*, **26**, 345-359

Skoog, D. A., & West. (1982) *Fundamentals of analytical chemistry.* 4th Ed., Saunders College Publishing, Harcourt Inc.

Spedding, F. H., & Jones, K. C. (1966a) Heat capacities of aqueous rare earth chloride solutions at 25[o]. *J. Phys. Chem*, **70**, 2450-2455

Spedding, F. H., Rikal, M. J., & Ayers, B. O. (1966b) Apparent molal volumes of some aqueous rare earth chloride and nitrate solutions at 25[o]. *J. Phys. Chem*, **70**, 2440-2449

Spedding, F. H., Baker, J. L., & Walters, J. P. (1975a) Apparent and partial molal heat capacities of aqueous rare earth perchlorate solutions at 25[o]C. *J. Chem. Eng. Data*, **20**, 189-195

Spedding, F. H., Walters, J. P., & Baker, J. L. (1975b) Apparent and partial molar heat capacities of some aqueous rare earth chloride solutions at 25[o]C. *J. Chem. Eng. Data*, **20**, 438-443

Spedding, F. H., Baker, J. L., & Walters, J. P. (1979) Apparent and partial molal heat capacities of aqueous rare earth nitrate solutions at 25[o]C. *J. Am. Chem. Soc*, **24**, 298-305

Stimson, H. F. (1955) Heat units and temperature scales for calorimetry. *J. Am. Phys*. **23**, 614-622

Xiao, C., & Tremaine, P. R. (1996a) Apparent molar volumes of La(CF$_3$SO$_3$)$_3$ $_{(aq)}$ and

Gd(CF$_3$SO$_3$)$_3$ $_{(aq)}$ at 278 K, 298 K, and 318 K at pressures to 30.0 MPa. *J. Chem. Eng. Data*, **41**, 1075-10787

Xiao, C., & Tremaine, P. R. (1996b) Apparent molar heat capacities and volumes of

LaCl$_{3(aq)}$, La(ClO$_4$)$_{3(aq)}$, and Gd(ClO$_4$)$_{3(aq)}$ between temperatures 283 K and 338 K. *J. Chem. Thermodynamics*, **28**, 43-66

Xiao, C., & Tremaine, P. R. (1997a) The thermodynamics of aqueous trivalent rare earth

elements. Apparent molar heat capacities and volumes of Nd(ClO$_4$)$_{3(aq)}$, Eu(ClO$_4$)$_{3(aq)}$, Er(ClO$_4$)$_{3(aq)}$, and Yb(ClO$_4$)$_{3(aq)}$ from the temperatures 283 K to 328 K. *J. Chem. Thermodynamics*, **29**, 827-852

Xiao, C., & Tremaine, P. R. (1997b) Apparent molar volumes of sodium

trifluoromethane sulfonate and trifluoromethanesulfonic acid from 283 K to 600 K and pressures up to 20 MPa. *J. Soln. Chem*, **26**, 277-294

Xiao, C., Simonson, J. M., & Tremaine, P. R. (1999) Densities and apparent molar

volumes of Gd(CF$_3$SO$_3$)$_3$ at T = (373, 423, and 472) K and p = (7 and 26) MPa. *J. Chem. Thermodynamics*, **31**, 1055-1065

Xiao, C., Pham, T., Xie, W., & Tremaine, P. R. (2001) Apparent molar volumes and heat

capacities of aqueous trifluoromethanesulfonic acid and its sodium salt from 283 to 328 K. *J. Soln. Chem*, **30**, 201-211

Young, T. F., & Smith, M. B. (1954) Thermodynamic properties of mixtures of

electrolytes in aqueous solutions. *J. Phys. Chem*, **58**, 716-724