APPARENT AND PARTIAL MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS CHELATING AGENTS: EDTA AND NTA

ZHONGNING WANG

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APPARENT AND PARTIAL MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS CHELATING AGENTS: EDTA AND NTA

by

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ABSTRACT

Ethylenedinitrilotetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are aminopolycarboxylic acids which are among the most common sequestrants used in industrial and medical applications. Copper is a common heavy metal contaminant and a 'model' divalent transition metal cation. Although a large database of stability-constant and enthalpy data has been developed for 25°C, there are few data at other temperatures and pressures. Standard partial molar heat capacities $C_p°$ and volumes $V°$ are important in this context because they define the temperature- and pressure-dependence of the stability constants, respectively, and because they are sensitive indicators of hydration effects for fundamental studies. To date, EDTA is the only chelant system studied by flow calorimetry, and only the apparent and partial molar properties at 25°C have been reported. Values of $C_p°$ and $V°$ are known for the aqueous sodium salts of $H_2EDTA^{2-}(aq)$, $HEDTA^{3-}(aq)$, $EDTA^{4-}(aq)$ and $NaEDTA^{3-}(aq)$, and ten metal complexes including $Na_2CuEDTA$ (aq) at 25°C. No apparent and partial molar properties for NTA species or NTA complexes have been reported in the literature.

The objectives of this project were: (i) to determine the apparent molar

properties $C_{p,\phi}$ and V_ϕ for the EDTA species and the EDTA-copper(II) complex from 10 to 55°C, so that the temperature dependence of $C_p°$ and V° could be derived, (ii) to determine the apparent and partial molar properties for two NTA species and the NTA complex with copper from 10 to 55°C, (iii) to extrapolate the standard partial molar properties for use in industrial applications at temperatures above 200°C by the Helgeson-Kirkham-Flowers (HKF) model.

A Sodev CP-C Picker flow microcalorimeter and a Sodev 03D vibrating tube densitometer equipped with platinum cells were employed in this work. Apparent molar properties V_ϕ and $C_{p,\phi}$ were determined as a function of ionic strength, then extrapolated to infinite dilution by means of the Guggenheim form of the extended Debye-Hückel equation to obtain the standard partial molar properties V° and $C_p°$.

EDTA and NTA are complex molecules, with three or more ionizable carboxylic acid groups and one or more ionizable amino groups, all of which can act as ligands. Since $C_{p,\phi}$ and V_ϕ include contributions from all the species present, it was necessary to adjust the pH by adding an excess of acid or base to control the speciation. Apparent molar heat capacities and volumes were measured for aqueous solutions of $Cu(ClO_4)_2$, Na_2H_2EDTA, $Na_2CuEDTA$,

Na_2HNTA, Na_3NTA and NaCuNTA, with a carefully calculated excess of $HClO_4$ or NaOH where required, from 10 to 55 °C and molalities up to 1.0 mol kg^{-1}. Theoretical methods based on Young's rule were used to derive values of $C_{p,\phi}$ and V_ϕ for the aqueous salts of each species, and to subtract the "chemical relaxation" effects that arise from temperature dependent shifts in equilibrium speciation.

The resulting corrected values of $C_{p,\phi}$ and V_ϕ were treated with the Holmes-Mesmer equation to derive a model for the temperature- and ionic-strength dependance of $C_{p,\phi}$ and V_ϕ over this range, and standard partial molar heat capacities and volumes for the species Cu^{2+}, H_2EDTA^{2-}, $CuEDTA^{2-}$, $HNTA^{2-}$, NTA^{3-}, and $CuNTA^-$. Our results for the apparent molar properties of $Cu(ClO_4)_2(aq)$ are consistent with the data published by Spitzer et al. (1978). Our values of V_ϕ and $C_{p,\phi}$ for $Na_2H_2EDTA(aq)$ are in reasonable agreement with those reported by Hovey and Tremaine (1985) and Hovey et al. (1988) at 25°C. The values of apparent and standard partial molar properties for $Na_2CuEDTA(aq)$ differ significantly from those determined by Hovey and Tremaine (1985) at 25°C. The ionic strength dependence of apparent molar properties for $NaH_2NTA(aq)$ and $Na_2CuNTA(aq)$ is linear, but for Na_3NTA, this relationship is more complicated.

The experimental results have been extrapolated to elevated temperatures

with the revised Helgeson-Kirkham-Flowers (HKF) model. For $Na_2H_2EDTA(aq)$ and $Na_2CuEDTA(aq)$, the temperature dependence of standard partial molar properties is similar, which indicates that the solvation behavior of the ions: H_2EDTA^{2-} and $CuEDTA^{2-}$ is similar in aqueous solution. This may reflect the structure of EDTA complex, in which the Cu^{2+} cation is inside the EDTA chelate structure. This result is consistent with the assumption of HKF equation that the solvent polarization is adequately represented by a Born term which considers the ion to be a charged sphere, and that only the charge on the ion is responsible for long range ion-solvent interactions. The temperature dependence of standard partial molar properties for NTA species is more complicated than that for EDTA species. The structure of NTA complex allows the cation inside the NTA molecule to have direct interactions with solvent, so that for the NTA species $HNTA^{2-}(aq)$, $CuNTA^{2-}(aq)$ and $NTA^{3-}(aq)$, the HKF treatment for the standard partial molar properties is expected to be less successful.

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Finally, financial support from Memorial University of Newfoundland is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

a	parameter in the Holmes and Mesmer equations for curve fit of standard partial molar properties in Chapter 2, Equation (2.51).
b	parameter in the Holmes and Mesmer equations for curve fit of standard partial molar properties in Chapter 2, Equation (2.51).
c	parameter in the Holmes and Mesmer equations for curve fit of standard partial molar properties in Chapter 2, Equation (2.51).
c_i	(I = 1-4) parameters in HKF equation, Equation (2.52) and (2.53).
d	density of solute or solvent, $g\ cm^{-3}$.
f	volumetric flow rate. $cm^3 \cdot sec^{-1}$.
ff	heat leak correction factor
m	molality, $mol\ kg^{-1}$.
n	number of moles.
p	pressure, MPa.
q	heat in the process.
r	effective electrostatic radius.
t	time, sec.
x	mole fraction.
y	molar activity coefficient in Section 2.2.3.

A	Helmholtz free energy, J .
A_Y	limiting slope of Debye-Hückel limiting law.
C_p	constant pressure heat capacity, $J \cdot K^{-1} \cdot mol^{-1}$
G	Gibbs free energy, J.
H	enthalpy, $J \cdot mol^{-1}$.
K	equilibrium constant.
M	molar mass, $g \cdot mol^{-1}$.
Q	heat, J.
R	gas constant, $J \cdot K^{-1} \cdot mol^{-1}$; $cm^3 \cdot bar \cdot mol^{-1}$
S	entropy, $J \cdot K^{-1} \cdot mol^{-1}$.
T	temperature, K.
U	internal energy of a system, J.
V	molar volume, $cm^3 \cdot mol^{-1}$.
W	the power of the heater defined by Equation (2.36), watts.
X	extensive molar value.
Y	generic symbol for apparent molar properties, C_p and V, etc.
Z	zener diode.

Greek Letters

α	degree of dissociation, first equilibrium.
β	degree of dissociation, second equilibrium.
γ	activity coefficient.
δ	deferral.
Δ	difference.
ϵ	static dielectric constant.
θ	solvent dependent "structural" temperature.
μ	chemical potential, J mol^{-1}.
ν	stoichiometry number.
σ	volumetric heat capacity, J K^{-1} cm^{-3}.
τ	period of vibration of a vibrating tube at the resonance condition, sec.
ω	valence factor.
ω_B	Born coefficient.
Γ	activity coefficient quotient.

Subscripts

a	cell a in Picker calorimeter.
b	cell b in Picker calorimeter.
c	symbol of temperature gradient.
I	*component* I.
j	component j.
m	symbol of specific temperature in calorimeter.
sol	solution.
sp	species.
A	component A in solution.
B	component B in solution.
C	component C in solution.
J	component J in an ideal solution.
L	saturation liquid.
p	constant pressure.
T	constant temperature.
V	constant volume.
W	pure water.

Y	relative to the apparent molar properties.
ϕ	apparent molar properties.

Superscripts

rel	chemical relaxation contribution.
$^{\circ}$	symbol for standard partial molar properties.

Chapter 1

INTRODUCTION

Ethylenedinitrilotetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are aminopolycarboxylic acids which are among the most common sequestrants used in industrial applications. These applications include cleaning various kinds of boilers, softening boiler and process water, treating oil wells to remove and control scales and certain minerals, and decontaminating nuclear reactor systems. There are also medicinal uses of EDTA and NTA that include treating Alzheimer's disease by the complexation of aluminum (Yaeger, 1983), treating ulcers, periarthritis and similar ailments (Guazzotti, 1986), and injection as agents for increased contrast in NMR body imaging (Runge et al., 1984). Na_2H_2EDTA salts are used to remove cadmium, mercury, and lead from the body (Boscolo et al., 1983). EDTA treatment of metal poisoning may introduce risks (Wedeen et al.,1983), but its wide versatility in the complexation of many heavy metal ions makes it a valuable chemical treatment (Jones and Pratt, 1976; Cooper, 1955).

In all of these applications of EDTA and NTA, the principal focus is on the complexation of divalent or trivalent ions. The complexation equilibria of most metal ions of interest have already been investigated at or near 25°C, but many of the applications involve temperatures considerably higher than 25°C for which there are no equilibrium data. Values in the range 0-37°C are very useful for environmental and medical applications. Data in the range 80 to 300°C are required to model the use of EDTA and NTA as chelating agents for cleaning metal oxides and scale from boilers or nuclear reactor components. The desired equilibrium constants for high temperature solutions can be calculated by combining known stability constants and enthalpies of complexation at 25°C with the experimental heat capacities that form the main part of this work. Measurements of the densities of aqueous EDTA and NTA solutions yield parameters required for the heat capacity calculations, and partial molar volumes that provide useful information on hydration effects. The results of such equilibrium calculations are presented later in this thesis.

There is now a reasonably complete thermodynamic data base for aqueous complexes of EDTA and NTA with many cations near 25°C (Martell and

Motekaitis, 1988; Martell and Smith, 1982; Christensen and Izatt, 1983; Anderegg, 1975). The data base for log K and ΔH° is summarized in Section 2.3.4 of Chapter 2.

On the other hand, potentially valuable thermodynamic data for complexes of EDTA and NTA with some other important cations are lacking. Accurate values of ΔC_p° would allow both ΔH° and ln K to be extrapolated to temperatures beyond the range of the original measurements, thereby permitting calculations of ΔC_p° values by way of $(\partial \ln K / \partial T)_p = \Delta H^\circ / (RT^2)$ and $(\partial \Delta H^\circ / \partial T)_p = \Delta C_p^\circ$. Unfortunately, the magnification of errors and uncertainties associated with differentiation, and also the complications mentioned above, cause many ΔC_p° values to have very large uncertainties. Calorimetric measurements of heat capacities have therefore been carried out as described in the following chapters. Densities have also been measured, leading to new apparent and partial molar volumes. Analysis of the resultant experimental data to obtain the desired standard partial molar properties of specified ions is complicated by the fact that some of the solutions investigated contained multiple species in equilibrium with one another. Thermodynamic measurements carried out at constant ionic strength in solutions of alkali metal salts are also complicated by the formation of alkali metal complexes EDTA (Martell and Smith, 1982; Anderegg, 1977). To date, the only chelant system studied by flow calorimetry is EDTA and its complexes, and only the apparent and partial molar properties at 25°C have been reported. Hovey and Tremaine (1985) measured C_p° and V° for Na_2H_2EDTA (aq) and ten metal complexes including $Na_2CuEDTA$ (aq) at 25°C. In 1988, C_p° and V° for Na_2H_2EDTA (aq) at 25°C were measured again by Hovey et al. (1988) as part of a study leading to values for H_2EDTA^{2-}(aq), $HEDTA^{3-}$(aq), $EDTA^{4-}$(aq) and $NaEDTA^{3-}$(aq). No apparent and partial molar properties for NTA species or NTA complexes have been reported in the literature.

The purposes of this study are

I. To determine the apparent molar and partial molar heat capacities and volumes for the anionic EDTA species and one of the EDTA metal complexes from 10 to 55°C, so that the temperature dependence of the standard partial molar properties may be derived. Copper has been chosen as a model system.

II. To determine the apparent molar and partial molar properties for two NTA species and the NTA complex with copper from 10 to 55°C, so that the temperature dependence of the standard partial molar properties may be determined.

III. To extrapolate the standard partial molar properties to high temperatures (above 200°C) by the HKF model for use in industrial applications. Smaller, more accurate extrapolations in the range 0-37°C relevant to environmental and medical applications have been made by means of the Holmes and Mesmer (1983) equation.

Because copper is a transition metal with many applications in industry, it was chosen as a model system for the EDTA and NTA complexes to be examined in this study. The apparent molar and partial molar properties of copper(II) perchlorate from 10 and 55°C were also measured to determine temperature-dependant standard partial molar properties for Cu^{2+} (aq) over the range of interest.

All of these measurements have been used in various classical thermodynamic calculations involving the standard partial molar volumes and heat capacities of individual species. These calculations include models for the temperature dependence of standard partial molar properties, and chemical relaxation calculations on solutions containing mixed electrolytes and systems comprised of two equilibria.

This thesis deals mostly with thermodynamic studies of aqueous solutions, both experimental and theoretical. A large fraction of the thesis describes the use of flow microcalormeters and densimeters for the determination of the standard partial molar volumes and heat capacities of aqueous solutions.

The thesis is comprised of six chapters, three of which deal with the thermodynamics of aqueous solutions of $Cu(ClO_4)_2$ (aq), Na_2H_2EDTA(aq), $Na_2CuEDTA$(aq), Na_2HNTA(aq), NaCuNTA(aq) and Na_3NTA(aq). The experimental and theoretical techniques that have been used to provide thermodynamic data for these systems are presented in Chapter 2.

Chapter 2

EXPERIMENTAL EQUIPMENT AND TECHNIQUES FOR THE DETERMINATION OF APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS ELECTROLYTES

2.1. Introduction

The importance of partial molar volumes and heat capacities can be seen upon consideration of the thermodynamic equations that describe many equilibrium processes. From an analysis of the first and second laws of thermodynamics, the Gibbs free energy change of a process defines whether or not it is spontaneous. This result when combined with the definition of the Gibbs free energy $dG = d(H-TS)$, leads to the conclusion that the Gibbs free energy is a measure of the spontaneity of a process at constant temperature and pressure. Here G is the Gibbs free energy, H the enthalpy, and S the entropy. A state of equilibrium is defined when the change in the Gibbs free energy of a process is equal to zero at constant temperature and pressure (Pitzer and Brewer, 1961; Klotz and Rosenberg, 1986; Prigogine and Defay, 1954). Combining $dG = 0$ with $dG = d(H - TS)$, and the equations resulting from the first ($dU = \delta q + \delta \omega$) and second ($dS = \delta q_{rev} / T$) laws leads to the expression

$$dG = -S\,dT + V\,dp \tag{2.1}$$

where V is the volume associated with the system, and dp is the corresponding change in pressure associated with a change in the Gibbs free energy of dG.

The following equation is easily derived to show that the pressure dependence of the Gibbs free energy for a system is equal to the volume of that system.

$$(\partial G \,/\, \partial p)_T = V \tag{2.2}$$

The classical definition of the heat capacity (at constant pressure): $C_p = q_p / \Delta T$ which is valid only for small values of ΔT, may be combined with the first and second laws to yield

$$C_p = (\partial H \,/\, \partial T)_p \tag{2.3}$$

and

$$C_p = T\,(\partial S \,/\, \partial T)_p \tag{2.4}$$

These expressions clearly show the importance of the heat capacity function in determining the temperature dependence of the entropy and enthalpy that in turn may be used to determine the temperature dependence of the Gibbs free energy.

In this chapter, the thermodynamics of aqueous solutions, the experimental methods for determining of the apparent molar heat capacities and volumes of aqueous solutions, and related calculations are discussed.

2.2. Thermodynamics of Aqueous Systems

2.2.1. Thermodynamic Functions of State for Water

In general, if the nature and amounts of substances are specified, the volume, temperature, and pressure are related by an equation of the form: $V = f(T,p)$ known as the equation of state. Only two of V, T, and p can be varied independently.

Since a principal aim of the present research work is to obtain thermodynamic properties of aqueous solutions, accurate functions of state for pure water are very important. These will be used to calculate heat capacities, volumes and other thermodynamic properties of the pure solvent required to calculate the partial molar properties of aqueous species from the experimental data. Accurate thermodynamic properties of water are also required for use in modeling the properties of aqueous species at elevated temperature and pressure.

Our heat capacity measurements require accurate values for the specific heat of water at atmospheric pressure. According to Kell (1972), the most accurate values for the temperature dependence of $c_{p,w}$ at atmospheric pressure are those from the work of Osborne et al. (1939) of the U. S. Bureau of Standards. The values of $c_{p,w}$ at 1 atm are given by

$$c_{p,w} / (\mathrm{J\ g^{-1}}) = 4.1855\ \{\ 0.996185 + 0.0002874\ [(t + 100) / 100]^{5.26} + 0.011160 \times 10^{-0.036t}\} \qquad (2.5)$$

Kell (1967,1972) has reported critically compiled values for density of H_2O and D_2O from 0 to 150°C, that can be represented by a rational function with seven parameters,

$$d_w = (a_0 + a_1\, t + a_2\, t^2 + a_3\, t^3 + a_4\, t^4 + a_5\, t^5\ ) / (1 + b\, t) \qquad (2.6)$$

with smaller numbers of parameters needed for the less extensive data of other isotopic forms of water; the coefficients obtained are given in Table 2.1.

Many equations have been proposed to represent the behavior of liquid water at elevated pressures, but only a few can be mentioned here. The experimental observations at low pressure can be represented rather closely by any of a number of equations with three parameters, one of which is usually the volume. One such equation,

$$(V_0 - V) / V_0 p = A / (B + p) \tag{2.7}$$

where V_o is the volume at zero pressure (sometimes approximated by the volume at atmospheric pressure) and A and B are adjustable constants, was published by Tait (1889). This equation is identical with

$$(p + B) (V - V_\infty) = C \tag{2.8}$$

(Kell, 1972) where $C = ABV_o$, $V_\infty = V_o(1-A)$, and V_∞ is defined as the volume of the fluid if the equation is valid at infinite pressure. Equation 2.7 is often called the Tumlirz equation (Kell, 1972), though the form used by Tumlirz had DT in place of C. Equation 2.7 was used for water by Eckart (1958). The equation that bears Tait's name,

$$(-1 / V_0)(\partial V / \partial p) = A / (B + p) \qquad (2.9a)$$

or

$$V = V_0 (1 - A \ln[(B + p) / b]) \qquad (2.9b)$$

where A and B differ from the values in Equation 2.6 for the ordinary range of data, was proposed by Tammann (Kell, 1972). Equations 2.8 and 2.9 have been widely used for a number of liquids, including water (Li, 1967), but Hayward (1967a; 1967b) finds that Equation 2.6 is to be preferred.

Kell (1972) has reported that volumetric data in the region from 0 to 150°C and 1 bar to 1 kbar, could be represented by the equation

$$V_w = V_{w,A} (1 + a_1 x + a_2 x^2) / (1 + b x) \qquad (2.10)$$

where $V_{w.A}$ is the volume of water at atmospheric pressure (1.013 bars), $x = p - 1.013$. where p is the pressure in bars, and a_1, a_2 and b are functions of the temperature. This equation provides an adequate fit to the accurate experimental

PVT data over this rather limited range of temperatures without the complications necessary in full equation of state.

Detailed and accurate equations of state for water over a very wide range of temperature and pressure have been developed by Haar et al. (1984), Hill (1990) and Wagner (1995). Levelt Sengers (1994) has provided a summary of the new international formulations for the functions of state for pure water.

2.2.2. Partial molar properties

Partial molar properties can be derived by considering the total differential of the Gibbs free energy. For systems of variable composition, the Gibbs free energy must be a function of temperature T, pressure p and the amount of each component (moles)

$$G = G(T,\ p,\ n_1,\ n_2, \cdots,\ n_i, \cdots) \qquad (2.11)$$

Here n_i represents the number of moles of component i. The total differential for the Gibbs free energy for these types of systems is

$$dG = (\partial G/\partial T)_{p,n_i}\, dT + (\partial G/\partial p)_{T,N_i}\, dp + \sum (\partial G/\partial n_i)_{T,\,p,\,N_j \bullet n_i}\, dn_i \qquad (2.12)$$

The third term in equation above is related to the chemical potential for species i, μ_i (Pitzer and Brewer, 1961). By definition:

$$\mu_i = (\partial G / \partial n_i)_{T,\, p,\, n_j \neq n_i} \tag{2.13}$$

Partial molar properties are defined generally by

$$\overline{Y} = (\partial Y / \partial n_i)_{T,\, p,\, n_j \neq n_i} \tag{2.14}$$

so that the chemical potential μ_i is equal to the partial molar Gibbs free energy.

All of the thermodynamic equations that describe the relationship between the Gibbs free energy and derivatives of the Gibbs free energy with respect to temperature and pressure are valid for the corresponding relations with partial molar properties. For example, the following equations show these relationships for partial molar volumes:

$$(\partial G / \partial p)_T = V \quad \textbf{then} \quad (\partial \overline{G_i} / \partial p)_T = (\partial \mu_i / \partial p)_T = \overline{V_i} \tag{2.15}$$

For aqueous solutions, the chemical potential of a substance is therefore defined as the Gibbs free energy change per mole of substance added to the solution when the amount added becomes vanishingly small; or the Gibbs free energy change when 1 mol of the substance is added to an infinite amount of the aqueous phase, the temperature and pressure being held constant in either case.

Partial molar properties are very important for the description of the properties of dilute aqueous solutions. The temperature dependence of the partial molar heat capacities and volumes of aqueous solutions at constant pressure must be known to obtain the partial molar Gibbs free energy. These will be discussed below.

2.2.3. Apparent Molar Properties and Ionic Strength Effects

As discussed in the above section, partial molar properties are additive. That means for the extensive thermodynamic properties Y,

$$Y = \sum_i n_i \overline{Y}_i \qquad (2.16)$$

where n_i is the number of moles for component i and $\overline{Y}_i$ is the partial molar property for component i.

The apparent molar property $Y_{\Phi,J}$ is used as a convenient parameter for determining partial molar quantities from experimental data (Pitzer and Brewer, 1961). By definition:

$$Y_{\phi,2} = (Y - n_w\ Y_w^\circ)\ /\ n_2 \tag{2.17}$$

where n_w and n_2 are the numbers of moles of pure water and substance dissolved respectively, Y is the value of the extensive property for the total quantity of solution ($n_w + n_2$ mol), and Y_w° is the molar extensive property for pure water at the same temperature and pressure. For example, if 1 mole of NaCl is added to 1000 g of water, the change in volume of the solution represents the apparent molar volume of the solute. The bulk properties of the solution may be calculated from tabulated properties for $Y_{\phi,2}$ by rearranging Equation 2.17,

$$Y = n_w\ Y_w^o + n_2\ Y_{\phi,2} \tag{2.18}$$

Partial molar properties are usually determined by measuring the apparent molar property of interest. From the definition of apparent molar properties, Equation 2.18 can be differentiated with respect to n (holding n_w as constant) to obtain

$$\overline{Y_2} = Y_{\phi,2} + n_2\ (\partial Y_{\phi,2}\ /\ \partial n_2)_{n_w,T,p} \tag{2.19}$$

and since the molality m is defined for constant n_w, this becomes

$$\overline{Y_2} = Y_{\phi,2} + m\ (dY_{\phi,2}\ /\ dm) \tag{2.20}$$

For example, the apparent molar property $V_{\phi,2}$ can be directly calculated from the composition and densities of the solution and the pure solvent by Equation 2.17; the differentiation is then carried out graphically or analytically using Equation 2.19. Equations 2.19 and 2.20 can be used along with Y_ϕ values obtained over a range of concentrations to calculate the corresponding partial molar properties.

At infinite dilution, n = 0 and the important relationship $Y^\circ = Y_\phi^\infty$ is obtained from Equation (2.19). Here the superscript ° indicates the hypothetical one $\text{mol}\cdot\text{kg}^{-1}$ thermodynamic standard state, and Y° is, by definition, the standard partial molar property.

The concentration dependence of an apparent molar property, $Y_{\phi,2}$, can be extrapolated to infinite dilution with the aid of the Debye-Hückel limiting law.

$$Y_{\phi,2} = Y_2^o + A_Y\ \omega\ I^{1/2} + B_Y\ I + C_Y\ I^{3/2} \tag{2.21}$$

where A_Y is the Debye-Hückel limiting slope for apparent molar properties and can be calculated from theory reviewed by Bradley and Pitzer (1979). The ionic strength I and the " valence factor" ω are defined and related by

$$I = \omega m = (1/2) \sum m_i z_i^2 \tag{2.22}$$

B_Y and C_Y are adjustable constants.

Several extended Debye-Hückel equations have been developed in recent years to describe the molality dependence of apparent molar properties over a wide range of temperatures (Pitzer et al., 1984; Helgeson et al., 1981; Holmes and Mesmer, 1983; Millero, 1979). For very dilute solutions, from Equation 2.20 and the extended form of the Debye-Hückel equation (Hovey,1988; Millero, 1979), the relationship between partial molar properties and ionic strength is as follows:

$$\overline{Y} = Y^{\circ} + 1.5\, A_Y\, \omega\, I^{1/2} / (1 + I^{1/2}) \tag{2.23}$$

The relationship was first proposed by Guggenheim (1949). From this expression and Equation 2.20, an empirical expression for the ionic strength dependence of apparent molar properties may be derived from the Debye-Hückel limiting law:

$$\begin{aligned} Y_{\phi} = Y^{\circ} + 1.5\, \omega\, A_Y\, [I - 2\, I^{1/2} + 2\, \ln(1 + I^{1/2}]\, /\, I \\ + B_Y\, I + C_Y\, I^{3/2} \end{aligned} \tag{2.24}$$

Apparent molar properties of aqueous electrolytes are represented satisfactorily to moderate ionic strengths by the Guggenheim form of the extended Debye-Hückel equation presented above (Equation 2.24). The apparent molar property data in this thesis are represented well by this expression.

2.2.4 Young's Rule

Sometimes, aqueous solutions contain additional solute species. For example, in H_2EDTA^{2-} (aq) solutions, there must be an equilibrium concentration of the species $HEDTA^{3-}$ (aq) and H_3EDTA^{-} (aq). The presence of the additional species in these solutions must be accounted for in analyzing the heat capacities and volumes that come directly from the calorimetric and densimetric measurements. This is done by using Young's rule (Young and Smith, 1954). Young's rule results from the definition of "mean" apparent molar properties of a solution that contains k-1 solute species by the expression

$$Y_{\phi,j} = (Y - n_1\ Y_1{}^{\circ}) \ / \ (\textstyle\sum_{j=2}^{k} n_j) \tag{2.25}$$

where Y is the extensive property of a specified quantity of solution, $Y_1{}^{\circ}$ is the property of one mole of water, and n_1 and n_j are the stoichiometric number of moles of water and solute j in the specified quantity of solution.

Young's rule can be expressed for the systems of present interest by

$$Y_{\phi} = F_2 \, Y_{\phi,2} + F_3 \, Y_{\phi,3} + \ldots + F_k \, Y_{\phi,k} + \delta \qquad (2.26)$$

where $F_j = m_j / \sum m_j$, and the apparent molar properties $Y_{\phi,j}$ all pertain to the total ionic strength of the solution. The term δ is an interaction parameter. If the solutes share a common anion or cation, it may be justified to take $\delta = 0$ (Young and Smith, 1954).

Equation 2.26 is valid for all experimental values of L_{ϕ} and V_{ϕ}. Heat capacity measurements on solutions with species in equilibrium are complicated by chemical relaxation effects, discussed below.

2.2.5 Chemical Relaxation

Early heat capacity measurements on aqueous solutions containing partially dissociated solutes (Randall and Taylor, 1941), showed peculiar trends in the observed specific heat as a function of ionic strength. The apparent molar heat capacities of sulphuric acid at ionic strength from about 0.2 to 0.05 molal were observed to increase, contrary to the behavior expected for totally dissociated solutes. The explanation was given by Randall and Taylor (1941):

> "If a reaction, for example, the dissociation of bisulfate ion into hydrogen and sulfate ions, is more complete at a higher temperature than at a lower, then the heat corresponding to the additional fraction of bisulfate ion dissociated at the higher temperature will be measured as though it were a part of the heat capacity of the solution."

This is one of the earliest direct statements regarding the contributions that are presently labeled "chemical relaxation". However, it turns out that this effect is not limited to reactions that are more complete at higher temperatures (endothermic) but also those that are less complete (exothermic) as will be shown below.

The most comprehensive descriptions of the contributions from "chemical relaxation" were derived by Hepler and his colleagues (Woolley and Hepler, 1977; Mains et al., 1984) to interpret precise calorimetric measurements from flow calorimeters.

The effect of chemical relaxation on heat capacities can be visualized by expressing the total enthalpy of a system (containing solvent, solute, and products obtained from dissociation or polymerization of the solute) as:

$$H = \sum_j n_j H_j \tag{2.27}$$

where n_j and H_j are the number of moles and partial molar enthalpies of each component in the system. Equation 2.27 can be differentiated with respect to temperature at constant pressure to yield

$$C_p = (\partial H/\partial T)_p = \sum_j n_j (\partial H_j/\partial T)_p + \sum_j H_j (\partial n_j/\partial T)_p \tag{2.28}$$

For systems that do not undergo any change in the relative concentration of components, the only contributions to the heat capacities are those arising from the first term in Equation 2.28. However, for many other systems, including those consisting of a liquid in equilibrium with its vapor, and the solute equilibria present in aqueous solution, the total heat capacity is due to all species present (1st term) and also to the change in the number of moles of each species present (2nd term).

It is convenient to discuss chemical relaxation in terms of the fractional extent of a reaction and its relation to apparent molar properties. Following Woolley and Hepler (1977), the terms in Equation 2.28 can be expressed by

$$C_{p,\,sol} = (\partial H \,/\, \partial T)_p^{sp} + (\partial H \,/\, \partial T)_p^{rel} \qquad (2.29)$$

where "sp" represents species and "rel" represents the contribution from chemical relaxation. From the definition of Y_ϕ in Equation 2.17, the experimental apparent molar heat capacity $C_{p,\phi}^{exp}$ is described by the equation

$$C_{p,\,\phi}^{exp} = [(\partial H \,/\, \partial T)_p^{sp} + (\partial H \,/\, \partial T)_p^{rel} - 55.51\ C_{p,w}^{o}\ ] \,/\, m \qquad (2.30)$$

The heat capacity of solutions of non-dissociating solutes contains no contributions from chemical relaxation. The desired apparent molar heat capacity of the species $C_{p,\,\phi}^{sp}$ from solutions containing partially dissociated solutes can be calculated using

$$C_{p,\phi}^{sp} = C_{p,\phi}^{exp} - m^{-1}\ (\partial H/\partial T)_p^{rel} \qquad (2.31)$$

This last term in Equation 2.31 is the relaxation term that must be carefully evaluated in order to subtract the effects of chemical relaxation.

As presented by Woolley and Hepler (1977), the relaxation term can be written

$$(\partial H/\partial T)_p^{rel} = (\partial H^{rel}/\partial \alpha m)_p \cdot (\partial \alpha m/\partial T)_p \tag{2.32}$$

where α represents the fractional extent of reaction. The quantity $(\partial H/\partial \alpha m)_p$ is directly related to the enthalpy of reaction

$$(\partial H^{rel}/\partial \alpha m)_p = \Delta H_{rxn} \tag{2.33}$$

where ΔH_{rxn} corresponds to the enthalpy of the reaction at the ionic strength of interest. Combination of the above equations leads to an expression for the contribution of chemical relaxation to apparent molar heat capacities

$$C_{p,\Phi}^{sp} = C_{p,\Phi}^{exp} - \Delta H_{rxn}\ (\partial \alpha/\partial T)_p \tag{2.34}$$

It is worth considering the sign of chemical relaxation corrections in a general sense. If the quantity $(\partial \alpha/\partial T)_p$ is positive, this implies that the enthalpy of the reaction is endothermic (increasing dissociation with increasing temperature). Similarly, if $(\partial \alpha/\partial T)_p$ is negative then the enthalpy of reaction must be exothermic. Since the relaxation contribution is evaluated by the product of the enthalpy change and $(\partial \alpha/\partial T)_p$, the contribution is always positive.

A discussion in detail about the form of $(\partial \alpha/\partial T)_p$ and the appropriate calculations will be given in next chapters.

2.2.6. Temperature and Pressure Dependant Equilibrium Constants and Activity Coefficients

The differential relations between thermodynamic functions and the Gibbs-Helmholtz equation yield the relevant thermodynamic relationships for the temperature and pressure dependence of equilibrium constants as follows:

$$(\partial \ln K / \partial T)_p = \Delta H^\circ / RT^2 \qquad (2.35)$$

$$(\partial\, \Delta\overline{H^\circ} / \partial T)_p = \Delta C^\circ{}_p \qquad (2.37)$$

$$(\partial \ln K / \partial p)_T = -\, \Delta V^\circ / RT \qquad (2.36)$$

Below 200°C, steam saturation pressures are so small that the effect of pressure on ln K is negligible, so that

$$\Delta H^\circ(T) = \Delta H^\circ(T_o) + \int_{T_o}^{T} \Delta C_p^o(T)\, dT \qquad (2.38)$$

and

$$\ln K(T) - \ln K(T_o) = \int_{T_o}^{T} \Delta H^\circ(T) / (RT^2)\, dT. \qquad (2.39)$$

If T_o is chosen to be 25°C or 298.15K, the temperature dependence of the formation constants for the complexes can be obtained by

$$\begin{aligned} \ln K(T) = \ln K_{298} + R^{-1} \Delta H^\circ (298^{-1} - T^{-1}) + (R^{-1}) \\ \int_{298}^{T} (\Delta C^\circ_p / T)\, dT - (RT)^{-1} \int_{298}^{T} \Delta C^\circ_p\, dT \\ - R^{-1} \int_{1}^{P} (\Delta V^\circ / T)\, dp \end{aligned} \qquad (2.40)$$

The relationships between mean ionic activity coefficients and the partial molar volume and heat capacity are provided by Millero (1979). The pressure dependence is described by the equations:

$$(\partial \ln \gamma_\pm / \partial p)_T = (\overline{V} - V^\circ) / (\nu RT) \qquad (2.41)$$

and

$$\partial (\overline{V} - V^\circ) / \partial p = -(\overline{\kappa} - \kappa^\circ) \qquad (2.42)$$

where ν is the number of ions formed by one molecule of electrolyte, R is the gas constant, T is the absolute temperature, $\overline{V}$ is the partial molar volume of the electrolyte at infinite dilution and κ is the partial molar isothermal compressibility of the electrolyte, $\kappa = (\partial \overline{V} / \partial p)_T$.

For the temperature dependence of $\gamma_\pm$, the expressions are:

$$(\partial \ln \gamma_\pm / \partial T)_p = (\overline{H} - H^\circ) / (\nu R T^2) \tag{2.43}$$

and

$$(\partial^2 \ln \gamma_\pm / \partial T^2)_p = (\overline{C_p} - C^\circ_p) / (\nu R T^2) - 2 (\overline{H} - H^\circ) / (\nu R T^3) \tag{2.44}$$

where $\overline{H}$ is the partial molar enthalpy of the electrolyte. From Equations 2.41-2.44, the temperature and pressure effects on the activity coefficients of electrolytes can be calculated as follows:

$$\begin{aligned} \ln \gamma_{\pm, T} = \ln \gamma_{\pm, 298} &- Y \overline{L}_{298} / \nu - Z \overline{J}_{298} / \nu \\ &- (\overline{V} - V^\circ) p / (\nu R T) \\ &- (\overline{\kappa} - \kappa^\circ) p^2 / (2 \nu R T) \end{aligned} \tag{2.45}$$

where

$$Y = (298.15 - T) / (2.3026 \cdot 298.15 \cdot R T) \tag{2.45a}$$

and

$$Z = 298.15\ Y + (1/R)\ \log(T\ /\ 298.15) \qquad (2.45b)$$

Here $\overline{L} = \overline{H} - H^\circ$ is the relative partial molar enthalpy, and $\overline{J} = \overline{C_p} - C_p^\circ$ is the relative partial molar heat capacity. The values of Y and Z at various temperatures are given by Millero (1979).

2.3. Aqueous Electrolytes

2.3.1. The Born Equation and the Hydration of Simple Ions

An approximate model for ion-solvent interactions was suggested by Born in 1920. In the Born model (Born, 1920), an ion is viewed as a rigid conducting sphere of radius r_i bearing a charge $z_i e_0$ (e_0 is the electronic charge), and the solvent is taken to be a structureless dielectric continuum. Thus, the problem of ion-solvent interaction assumes the following form: *What is the work done in transferring a charged sphere from vacuum into a continuum?*

The Born model views the free energy of ion-solvent interactions as equal to the work of transferring a charged sphere from vacuum into a continuum of static dielectric constant ϵ. The Gibbs free energy is the sum of the work of discharging the ion in vacuum and work of charging the ion in the solvent.

$$\Delta G^{o}_{BORN} = -(Z_i e_0)^2 \; (1 - \epsilon^{-1}) \; / \; (2r_i) \qquad (2.46)$$

Equation 2.46 predicts that the smaller the ion and the larger the dielectric constant ϵ, the greater will be the magnitude of the free energy change in the negative direction.

By considering a charged sphere equivalent to an ion, the Born model is assuming that it is only the charge on the ion (or charged sphere) that is responsible for ion-solvent interactions. The interactions between the solvent and the ion are considered to be solely electrostatic in origin. Although the Born model over-simplifies the problem, its approach to ion-solvent interactions, and the fact that it gave answers of the same order of magnitude as experiment, helped to confirm the hypothesis that ions exist in solution. The Born theory provides a simple and important model for the role of long-range solvent polarization in the hydration of simple ions.

2.3.2. Various Models for Ion-Solvent Interactions

Early comparisons between the predictions of the Born theory and the results of experiment revealed that the Born values for the heats of ion-solvent interactions are numerically too high, in some cases nearly 50% higher (Bockris and Reddy, 1970). This suggests that ion-solvent interactions are much weaker than the Born theory predicts them to be. Also, there is no provision in the Born theory for considering to what extent the values of dielectric constants near an ion may be different from the bulk values. Clearly the structure of the solvent near an ion must be considered.

A structural treatment of ion-solvent interactions was initiated by Bernal and Fowler (1933). In this ion-dipole model, the neighborhood of an ion was considered to consist of three regions with differing solvent structure: (1) the primary or structure-forming region, (2) the secondary or structure breaking region, and (3) the bulk solvent. The ion-solvent interactions consist of several contributions. The Gibbs free-energy change arising from ion-solvent interactions, $\Delta G_{I\text{-}S}^{\circ}$, is composed of both enthalpy changes and entropy changes. In this ion-dipole model, as a simplified treatment, only the enthalpy changes will be treated.

The work of transferring a solvated ion from vacuum into a cavity in the solvent is equal to the Born heat of solvation. This contribution to the total heat of ion-solvent interactions shall be called the Born "charging" contribution, W_{BC}. Thus, per mole of ions,

$$W_{BC} = - N_A \, (z_i \, e_o)^2 \, [1 - \epsilon_s^{-1} - \epsilon_s^{-2} T(\partial \epsilon_s / \partial T)_p] \, / \, 2(r_i + 2r_s) \tag{2.47}$$

W_{BC} is the work associated with solvent-dipole polarization beyond the first hydration shell. The total heat of ion-solvent interactions $\Delta H_{I\text{-}S}$ contains contributions from the work of cavity formation (W_{CF}), cluster dissociation (W_D), formation of the primary solvated ion ($W_{I\text{-}D}$), Born charging (W_{BC}), structure breaking (W_{SB}) and condensation (W_C), hence

$$\begin{aligned} \Delta H_{I\text{-}S} &= W_{CF} + W_D + W_{I\text{-}D} + W_{BC} + W_{SB} + W_C \\ &= W + W_{I\text{-}D} + W_{BC} \\ &= W + W_{BC} - N_A n z_i e_o \mu_s \, / \, (r_i + r_s)^2 \end{aligned} \tag{2.48}$$

The last term is the work of formation of primary solvated ion $W_{I\text{-}D}$.

Semi-continuum models for the calculation of standard state changes in Gibbs free energy, enthalpy and entropy treat the water in the primary hydration sphere as discrete molecules, and consider the secondary hydration sphere to be a dielectric continuum. Goldman and Bates (1972) developed a semi-continuum model for ionic solvation. Tremaine and Goldman (1978) have extended this model to high temperature. In this model, the primary hydration sphere is taken to consist of discrete water molecules, each considered as an isotropic polarizable sphere containing an off-centered dipole. The potential energy change for the ions and water molecules in the primary hydration sphere is a sum of potential energy terms which are: the energy of interaction of the charge on the central ion with the n permanent, off-centered dipoles of the surrounding primary water molecules; the energy of interaction of the charge on the central ion with the n induced dipoles in the primary water molecules; the dispersion interaction energy of the central ion with the surrounding primary water molecules; the energy of interaction between the primary water molecules around the central ion; plus a general electron-cloud repulsion term. Goldman and Bates (1972) treated the secondary hydration sphere as part of the dielectric continuum. The model is an adequate approximation for the Gibbs energies of hydration of mono- and di-valent ions, and has been extended to tri-valent cations. It is unable to model the behavior of derivative transfer functions (entropy, heat capacity, etc.). A principal limitation is that there is no specific treatment for the secondary hydration sphere which is very important at low temperature. The model is expected to be more successful at high temperatures, where the secondary hydration sphere can be treated as a dielectric continuum (Tremaine and Goldman, 1978; Tanger and Pitzer,1989).

Another approach is to describe the primary hydration sphere by a bi-layer continuum model (Abraham, 1986). These treatments represent the primary and secondary solvation shells as a continuum layers each with a lower dielectric constant than that in the bulk solvent. A general equation for the Gibbs free energy of solvation for a n-layer model can be obtained. Abraham (1983) summarized equations for one layer and two-layer as follows:

(i)The Born model, $r_i = a$

$$\Delta G_{I-S} = -(Z_i e_0)^2 \; (1 - \epsilon_s^{-1}) \; / \; (2r_i) \tag{2.46}$$

(ii)The one-layer model, (first layer $r = b$ and $\epsilon = \epsilon_1$)

$$\Delta G_{I-S}^{1} = \frac{Z^2}{8\pi\epsilon_o} \; [\frac{1}{\epsilon_1} \; (\frac{1}{a} - \frac{1}{b}) + \frac{1}{\epsilon_s \, b} - \frac{1}{a}] \tag{2.49}$$

(iii)The two-layer model (first layer $r = b$ and $\epsilon = \epsilon_1$, second layer $r = c$ and $\epsilon = \epsilon_2$)

$$\Delta G_{I\text{-}S}^{2} = \frac{Z^{2}}{8\pi\epsilon_{o}} [\frac{1}{\epsilon_{2}} (\frac{1}{b} - \frac{1}{c}) + \frac{1}{\epsilon_{1}} (\frac{1}{a} - \frac{1}{b}) + \frac{1}{\epsilon_{s} b} - \frac{1}{a}] \qquad (2.50)$$

Abraham (1986) assumed the standard thermodynamic functions were composed of electrostatic and non-electrostatic contributions. Values for the non-electrostatic term were obtained from corresponding solvation parameters of non-polar gaseous solutes. Abraham used the one-layer model, with an assumed configuration term and a neutral term in addition to the electrostatic Born term, E,

$$\Delta C_{p,hyd}{}^{\circ} = N + E + C \qquad (2.51)$$

The neutral term N represented cavity formation and dispersion forces and was estimated from $C_p{}^{\circ}$ data for the aqueous noble gases. The configuration term C was obtained by subtracting N and E from the experimental data. Two possible models of summation had been used.

In the first summation, E_1 was calculated by the one-layer model, and N_1 was obtained by fitting the standard heat capacities of noble gases to an equation. The empirical configuration term C_1, which is related to the viscosity B-coefficient and includes hydrophobic effects, was then calculated. Taking C_1 as a measure of structure-making and structure-breaking, the common ions can be classified into two categories by Abraham model: (i) structure-making ions such as H^+, Li^+, Na^+ with $C_1 > -100$ J $K^{-1}mol^{-1}$; and (ii) structure-breaking ions such as K^+, Cl^- with $C_1 < -250$ J $K^{-1}mol^{-1}$. Because C_1 depends on the constants used to calculate E_1, it is difficult to find a general equation to calculate the C_1 term even at 298 K.

In the second summation, the neutral term N_2 was obtained from data for hydrophobic solutes, so that the hydrophobic effects were included in the neutral term. E_2 was calculated by the equation,

$$E_2 = \frac{Z^2}{8\pi\epsilon_o} T \left[-\frac{2}{\epsilon_s^3} \left(\frac{\partial\epsilon_s}{\partial T}\right)^2 + \left(\frac{1}{\epsilon_s^2}\right) \left(\frac{\partial^2\epsilon_s}{\partial T^2}\right)\right] \frac{1}{b} \qquad (2.52a)$$

where $b = r + 2.8$Å. Therefore E_2 refers to the energy for transferring a hydrated ion with radius $r + 2.8$Å from gas phase to solvent. Then C_2 was computed by subtracting N_2 and E_2 from the experimental heat capacity data. It was possible to correlate C_2 with ionic radius. For singly, doubly, and triply charged cations, and singly charged anions, mono- or poly-atomic, C_2 was given by,

$$C_2 / |z| = 15 - 1350(r/nm)\ J\ K^{-1}\ mol^{-1} \qquad (2.52b)$$

A related model is presented below in which the dielectric constant of the primary solvation layer is assumed to be $\epsilon = 1$.

2.3.3. Helgeson-Kirkham-Flowers Model (HKF Equation)

As the Equation 2.46 shows, the change in standard state heat capacity of a chemical reaction is related to the second derivative of the equilibrium constant with respect to temperature. Equilibrium constants or Gibbs free energies of reaction can be calculated at elevated temperatures using heat capacity data providing that room temperature equilibrium and enthalpy data are available (see the discussion in Section 2.2.6).

A classic description of the thermodynamic properties of aqueous ions is provided by the Born equation as discussed in Section 2.3.1. The Born equation can be derived by considering the difference in free energy of charging a hard sphere (of fixed radius) in *vacuo* and in a solvent that can be regarded as a continuous dielectric medium from the surface of the ion to an infinite distance from the ion.

There are numerous difficulties with use of the Born equation for solutions near room temperature. Most of the problems are related to the inadequate assumption that water is a continuous dielectric fluid (especially near an ion where dielectric saturation is known to occur) and to uncertainties in assigning ionic radii to solutes in water. Generally these radii are larger than the crystallographic radii and are denoted "effective" aqueous radii. The dielectric constant of water decreases from a value of approximately 78 at 25°C to less than 20 at 300°C (Uematsu and Franck, 1980). It is expected that because of this decrease in the static dielectric constant (due mainly to breakdown of ordered water structure because of increased thermal motion) the Born equation will become better at representing thermodynamic properties as the temperature is increased. Helgeson et al. (1974, 1976, 1981) have applied the Born equation modeling the standard partial molar volumes and heat capacities of electrolyte solutions.

The Helgeson-Kirkham-Flowers "HKF" model is special case of Marcus-Abraham model. This model adds an empirical term for the secondary solvation layer, and assumes for the primary solvation layer, $\epsilon_1 = 1$ so that Equation 2.49 reduces to the Born equation with $r \geq r_{cryst}$. In all of these equations, the "effective" radii for anionic species are equivalent to crystallographic radii, and for cationic species the effective radii are taken to be equal to the crystallographic radii plus 0.94Z Å, where Z is the charge of the cation.

The Born equation can be represented by (Helgeson et al., 1981)

$$\Delta G = \omega_B \, (\epsilon^{-1} - 1) \tag{2.53}$$

where $\omega_B = 6.94657 \times 10^5 \, (z^2 / r)$ Å J mol^{-1}. The equation for the partial molar properties of ions is based on the choice of conventions for H^+ (aq). These may be expressed through the values of ω_B for the ions (for calculation of the absolute as opposed to the conventional standard partial molar Gibbs free energy of solvation). The relationship of these different ω_B values for ions is shown below:

$$\omega_B^{abs} = \omega_B^{conv} + z \, \omega_{B,H}^{abs}. \tag{2.54}$$

where $\omega_B{}^{abs}$ refers to the "absolute" property of the ion, $\omega_B{}^{conv}$ is the conventional property based on $\omega^{abs}{}_{B,H^+} \equiv 0$, and $\omega^{abs}{}_{B,H^+}$ is equal to the "absolute" ω_B for the aqueous hydrogen ion. No such complications are present when considering solutes as the sum of their ionic components.

The Helgeson-Kirkham-Flowers equations of state for standard state volumes and heat capacities at constant pressure have the form (Shock and

Helgeson, 1988; Tanger and Helgeson, 1988):

$$C_p^o = c_1 + c_2 / (T - \theta)^2 + \Delta C_{p,BORN}^o \tag{2.55}$$

$$V^o = c_3 + c_4 / (T - \theta) + \Delta V_{BORN}^o \tag{2.56}$$

where all c_i ($i = 1\text{-}4$) and θ are fitting coefficients. The $\Delta Y^o{}_{BORN}$ terms come directly from the relationship of the partial molar free energy to partial molar volumes and heat capacities

$$\begin{aligned} \Delta V_{BORN}^o &= (\partial \Delta G_{BORN}^o / \partial p)_T = \omega\ (\partial \epsilon^{-1} / \partial p)_T \\ &= -\ \omega\ \epsilon^{-1}\ (\partial \ln \epsilon / \partial p)_T = -\omega Q \end{aligned} \tag{2.57}$$

and

$$\begin{aligned} \Delta C_{p,BORN}^o &= -\ T\ (\partial^2 \Delta G_{BORN}^o / \partial T^2)_p = -\ \omega\ T\ (\partial^2\ \epsilon^{-1} / \partial T^2)_p \\ &= \omega\ T\ \epsilon^{-1}\ [(\partial^2\ \ln \epsilon / \partial T^2)_p - (\partial \ln \epsilon / \partial T)_p^2] = \omega T X \end{aligned} \tag{2.58}$$

where Q and X are shorthand notations for the terms containing the various pressure and temperature derivatives of the dielectric constant that result from the Born equation. Numerical values for these terms were taken from Helgeson and Kirkham (Helgeson and Kirkham, 1974,1976).

The first two terms in each of Equations 2.55 and 2.56 above are purely empirical and are most important at low temperatures where the Born model is least satisfactory. The third term in each equation results entirely from the Born equation. It dominates at high temperatures where the model is most satisfactory. Because of the balance of empirical and theoretical components, the HKF treatment is particularly well suited for extrapolation of low temperature data for standard state partial molar properties to higher temperatures. A fit of the HKF model to all of the standard partial molar properties data for the systems studied in this thesis is presented in the following chapters.

2.3.4. Chelating Agents: EDTA and NTA

In this thesis, the term complexation is used to describe the bonding of metal ions to a greater number of either organic or inorganic molecules or ions referred to as ligand. The bonding between a metal and its ligand is represented as being covalent for an anionic ligand, and coordinative or dative for a neutral ligand. The holding of a hydrogen or metal atom between two atoms of a single molecule is called *chelation*. The chelates can be soluble or insoluble. Sequestration is defined as the formation of a soluble metal chelate. The term is also used to describe the solubilization of metal ion precipitates. In relation to the industrial problem of scale and other deposits, one finds the terms chelation and sequestration used interchangeably throughout the literature.

Many chemicals can sequester metal ions. These agents can be either organic or inorganic compounds, but most of the known sequestrants are organic. EDTA and NTA are examples of aminopolycarboxylic acids which are among the more common sequestrants used in water treating to control scale and deposit formation. EDTA and NTA have been used for polishing treatments in boiler water and the removal of calcium sulfate and calcium hydroxyapatite deposits, both by themselves and in conjunction with other agents. For example, the use of EDTA and NTA in the one-step removal of anhydrite from heater tubes in distillation-type saline water conversion plants was discussed in detail by Moore et al. (1972). Both of these agents were effective removal agents and apparently functioned in the following manner

$$Na_4\ EDTA\ (aq) + CaSO_4\ (s) = Na_2CaEDTA\ (aq) + Na_2SO_4\ (s) \quad (2.59)$$

or

$$\begin{aligned} &Na_4EDTA(aq) + Ca^{2+}(aq) + CaSO_4(s) \\ &= Na_2CaEDTA(aq) + 2\ Na^{+}(aq) + (Na_2SO_4,aq) \end{aligned} \quad (2.60)$$

Additions of H_2SO_4 to precipitate $CaSO_4$ followed by NaOH additions were shown to be a recovery technique for the chelant.

EDTA and NTA at first contributed to severe boiler corrosion problems, but it was later found that if small residuals of chelant were maintained, little corrosion, if any, occurred. Today's modern boiler water treatment programs use EDTA or NTA along with polymeric sludge conditions. The amount of sequestrant is monitored closely, maintaining only enough sequestrant to complex the residual calcium from pretreatment; large excesses are avoided.

Chelating agents generally react with polyvalent metals on a mol per mol basis. Since the molecular weight of NTA is only two-thirds that of EDTA, 1 part of NTA can usually complex the same amount of polyvalent ion as 1.5 parts EDTA. However, differences in cost and environmental effectiveness will determine which material is selected for use in a given application.

When sequestering agents are added to aqueous solutions containing metal ions a complex is formed. When two or more metals are in solution, which is the case in natural waters, there is a competing reaction for the sequestering agent. One role of chemical equilibrium models is to interpret and predict competition in multicomponent systems.

The formation of complexes with chelating agents are equilibrium reactions. The complexing is influenced by pH, temperature, nature of electrolytes, etc. More cations can be complexed under one set of conditions than under another. The log K value, or stability constant, is commonly used to describe the effectiveness of various sequestrants. The stability constants used in this thesis to describe the ionization of EDTA are expressed as follows:

$$HEDTA^{3-}\,(aq) \rightleftharpoons H^{+}\,(aq) + EDTA^{4-}\,(aq)$$
$$K_1 = \frac{[EDTA^{4-}]\,[H^{+}]}{[HEDTA^{3-}]} \qquad (2.61)$$

$$H_2EDTA^{2-}\ (aq) = H^+\ (aq) + HEDTA^{3-}\ (aq)$$
$$K_2 = \frac{[HEDTA^{3-}]\ [H^+]}{[H_2EDTA^{2-}]} \qquad (2.62)$$

$$H_3EDTA^-\ (aq) = H^+\ (aq) + H_2EDTA^{2-}\ (aq)$$
$$K_3 = \frac{[H_2EDTA^{2-}]\ [H^+]}{[H_3EDTA^-]} \qquad (2.63)$$

$$H_4EDTA\ (aq) = H^+\ (aq) + H_3EDTA^-\ (aq)$$
$$K_4 = \frac{[H_3EDTA^-]\ [H^+]}{[H_4EDTA]} \qquad (2.64)$$

Similarly, the ionization reactions of aqueous NTA are as follows:

$$HNTA^{2-}\ (aq) = H^+\ (aq) + NTA^{3-}\ (aq)$$
$$K_1 = \frac{[NTA^{3-}]\ [H^+]}{[HNTA^{2-}]} \qquad (2.65)$$

$$H_2NTA^- (aq) \rightleftharpoons H^+ (aq) + HNTA^{2-} (aq)$$

$$K_2 = \frac{[HNTA^{2-}]\,[H^+]}{[H_2NTA^-]} \qquad (2.66)$$

$$H_3NTA\ (aq) \rightleftharpoons H^+ (aq) + H_2NTA^- (aq)$$

$$K_3 = \frac{[H_2NTA^-]\,[H^+]}{[H_3NTA]} \qquad (2.67)$$

The values of various thermodynamic properties (K, ΔH°, etc.) associated with the above ionization reactions of EDTA and NTA, and selected for use in our thermodynamic calculations are described in Chapter 4 and 5.

There is now a reasonably complete thermodynamic data base for aqueous complexes of EDTA and NTA with many cations near 25°C (Martell and Motekaitis, 1988; Martell and Smith, 1982; Christensen and Izatt, 1983; Anderegg, 1975). The data for log K and ΔH° are also summarized in Table 2.2.

2.4. Experimental Equipment

2.4.1 Picker Flow Microcalorimeter

Several different experimental techniques have been used to derive the specific heat or heat capacity of aqueous solutions containing dissolved electrolytes. Usually, these measurements have been made with batch calorimeters that accurately measure known amounts of energy input and the corresponding temperature change so that the heat capacity can be calculated by use of Equation 2.3. These calorimeters are quite accurate for concentrated solutions but become much less accurate for solutions at low concentrations of solute. Accurate measurements on dilute solutions are very important for determining the standard partial molar properties. The principal importance of the Picker flow microcalorimeter (Picker et al. 1971) lies in its use for the determination of heat capacities of dilute solutions.

The Picker flow microcalorimeter contains two symmetrical cells that consist of hollow tubes to which are connected heaters (Zener diodes) and sensitive temperature sensors (thermistors). The temperature increase generated by the heater in the solution flowing through each cell is detected downstream by the thermistor. The heat capacity of the solution can be determined by the following equation:

$$\sigma = W / (f \Delta T) \qquad (2.68)$$

Here σ is the volumetric specific heat capacity $\sigma = c_p / d$, W is the electric power input to the heater, f is the volumetric flow rate of the liquid through the cell, and ΔT is the temperature rise produced by the combination of flow rate and electric power. A single-cell flow calorimeter based on this equation could be used to determine the volumetric heat capacity of a liquid but would be inferior to a batch calorimeter because of problems associated with maintaining and measuring very accurate constant flow rates. The symmetrical twin-cell design of the Picker instrument, however, makes it particularly well-suited for the measurement of the ratio between the heat capacities of two liquids as opposed to the absolute measurement described above.

The Picker heat capacity flow microcalorimeter is described schematically in Figure 2.1. The calorimeter is differential and it is operated by measuring directly the difference in the power required to maintain the same value of ΔT in the two cells. If the volumetric flow rate f is identical, the difference in power is related to the volumetric heat capacity (σ) of the liquids flowing through the reference and working cells.

Liquids A and B are thermostatted at a fixed temperature (T_{bath}) before entering in the cells and are heated initially by an equal heating power W_o dissipated by the two zener diodes (Z_1 and Z_2), which act as heater elements. Differences in the temperature rise in each cell (ΔT) result from differences in either the flow rates or the volumetric heat capacity (σ) of the liquids. The flow rates are made equal by connecting the two cells in series as shown in Figure 2.1, so that differences in ΔT arise only because of dissymmetry in the volumetric heat capacities (σ) and heater power. In practice, differences in ΔT are zeroed by a feedback control on the current passing through the heater Z_1 of the working cell. This mode renders the system independent of the actual flow rate of the liquids, provided it is kept the same in both cells. The amount of energy (ΔW) supplied in feedback to restore thermal equilibrium in the relation with heating power W_o is directly related to the relative difference in the volumetric heat capacity (σ) of liquids A and B. To allow a reasonable time for measurement during the steady state condition with liquid A in one cell and liquid B in the other, a long thermostatted length of small diameter tubing (the "delay line") is used to connect the two cells. This provides an suitable delay time for the replacement of liquid A by liquid B when the input valve (V) is rotated.

The relation between volumetric heat capacity (σ) of liquids A and B, W_o and ΔW is given by the following equations. When liquid B is in the working cell and liquid A in the reference cell:

$$\Delta W / W_o = (\sigma_b - \sigma_a) / \sigma_a \quad \textit{then} \quad 1 + (\Delta W / W_o) = \sigma_b / \sigma_a \qquad (2.69)$$

When liquid A is in the working cell and liquid B in the reference cell:

$$\Delta W / W_o = (\sigma_a - \sigma_b) / \sigma_a \quad \textit{then} \quad 1 - (\Delta W / W_o) = \sigma_b / \sigma_a \qquad (2.70)$$

where σ_b is the volumetric heat capacity of the measured liquid B, σ_a is the volumetric heat capacity of the reference liquid A, W_o is the heating power, and ΔW is the difference between heating power in the working cell relative to the reference cell required to maintain an equal temperature increment in the two calorimetric cells.

Because the specific heat capacity varies with the temperature, it is important to determine the temperature gradient (ΔT_c) produced by the heating power W_o in order to evaluate the mean temperature (T_m) at which c_p is effectively measured. This measurement is considered to be the average specific heat capacity over the temperature gradient (ΔT_c), assuming that the variation of c_p with temperature is linear. The evaluation of T_m can be done by the following relation:

$$T_m = T_{bath} + \Delta T_c / 2 \tag{2.71}$$

where T_m is the mean temperature for the c_p measurement, T_{bath} the temperature at which liquid A and B are thermostated. In this study, nanopure water was used as reference liquid.

The nominal precision of the differential signal output of the Picker calorimeter is of the order of the precision and accuracy of batch calorimeter (0.1 to 0.3 %). However, the signal from the Picker flow calorimeter is a direct differential measurement of the ratio of the heat capacity of the solution and reference. So long as the heat capacity of the reference liquid is known accurately, the measured heat capacity of the unknown liquid should be much more precise than the absolute measurement obtained from a batch instrument. The Picker flow calorimeter generally produces heat capacities of aqueous solutions referenced to water with a precision of 0.01%. Since only the difference in specific heat for a solution and water is required, this calorimeter gives us a direct and accurate measurement of apparent molar heat capacity. There have been no calorimeters developed to date that yield more precise apparent molar heat capacities of dilute aqueous solutions.

It has been noted by Desnoyers et al. (1976) and White and Wood (1982) that the Picker flow calorimeter suffers from very small heat losses due to slight asymmetries in the two cells. This heat leak is normally assessed by measuring the specific heat of a relatively concentrated standard solution of NaCl. The heat leak correction factor ff is defined in terms of Equation 2.69 by

$$ff = W \,/\, (f\ \Delta T\ \sigma) \qquad (2.72)$$

Where all symbols were defined previously. The heat leak correction factor should always be greater than unity, denoting a smaller ΔT than expected.

All of the heat capacity experiments for this thesis project were performed using a Picker flow microcalorimeter (Sodev model CP-C) specially fitted with platinum cells. The calorimeter was connected to a Sodev thermal detection unit (model DT-C) that was used for tuning and calibrating the calorimeter and for output of the differential calorimetric signal, and a precise high velocity circulating bath with temperature control unit (Sodev model CT-L). The differential output voltage of the thermal detection unit, calibration voltages and currents were recorded by a Hewlett-Packard 34401A digital multimeter. Temperature was monitored by a thermistor (Omega type 44107) calibrated against a Hewlett-Packard quartz crystal thermometer (HP 2804A) traceable to NIST standards, which itself was calibrated frequently at the ice point of water. The data collected from the calorimeter were stored in a computer for further analysis. HP Instrument© and SigmaPlot© software were used in the data recording and analysis.

2.4.2. Vibrating Tube Densimeter

As mentioned in the previous section, accurate densities of the solutions are required to convert the volumetric heat capacity ratios obtained from the Picker flow microcalorimeter into the specific heat capacities that are required to calculate $C_{p,\phi}$. Also, the densities yield the apparent molar volumes of the aqueous solutions being studied.

One of the most sensitive pieces of apparatus for measurement of the densities of aqueous solutions is the vibrating tube densimeter. The measurement principle of the vibrating tube densimeter is based on the properties of a mechanical oscillator. The natural vibration frequency of a U-tube, firmly anchored at both ends, is related to its mass per unit length and to a restoring force constant. The resonance frequency of this tube oscillator is thus a function of the density of any fluid it contains. Measurement of the resonance period (τ) yields the density (d) of the fluid according to the relationship:

$$d = A + K\,\tau^2 \qquad (2.73)$$

Where A and K are constants of the system, which may be determined by straightforward calibration using two fluids of known density, typically nitrogen gas and water. The calibration constant K of the densimeter is calculated from

$$K = (d_2 - d_1) \,/\, (\tau_2^2 - \tau_1^2) \qquad (2.74)$$

where d_1 and d_2 are the known densities of the two reference substances and τ_1 and τ_2 are the corresponding time periods for these two substances. The substances traditionally used for this purpose were water (d = 0.997047 g cm^{-3} at 25°C, Kell 1967) and pure nitrogen gas.

The density measurements in our study were carried out in a Sodev model PC-B flow densimeter equipped with a platinum vibrating tube. The mechanical characteristics of platinum made the calibration procedure using nitrogen and water unsatisfactory because of a slightly non-linear response (Hovey, 1988). It was found that calibration of the instrument with a 1 molal NaCl solution and water resulted in experimental densities well within expected uncertainties (Hill, 1990; Archer and Wang, 1990).

Once the densimeter has been calibrated, the density of an unknown aqueous solution could be calculated relative to water by the following equation:

$$d_{sol} = d_w - K\,(\tau^2 - \tau_w^2) \qquad (2.75)$$

where d_w and d are the densities of water and solution and τ_w and τ are the corresponding resonant time periods of the vibrating tube.

The temperature of the densimeter was monitored by a thermistor placed in the circulating fluid lines from the temperature bath. This thermistor was calibrated by the same procedure as that for the calorimeter. Thermistor resistances were measured with a Hewlett-Packard 34401A digital multimeter. Time periods were determined by using a Hewlett-Packard universal counter HP 5328A and averaging the counts acquired for 30 seconds (the internal clock speed of the counter is 10 MHz). The universal counter was interfaced to a computer through a Hewlett-Packard Data acquisition/control unit 3421A interface.

Normally 160 of these 30 second average time periods generated by the universal counter were collected by the computer for each experimental run. These recorded time periods were averaged over specified intervals (baseline, peak etc.) by the computer. These averages normally were made on no less than 40 of the recorded average time periods. The Sodev density apparatus allows density measurements with p.p.m. (part per million) precision to be carried out in a few minutes, using as little as 1 cm^3 of liquid.

2.4.3 Calculation of Apparent Molar Properties

The results of measurements with the Picker flow calorimeter are volumetric heat capacity ratios σ/σ_w. By combining these with the densities that have also been measured, the specific heat capacities ($J\ K^{-1}\ g^{-1}$) and hence the desired apparent molar heat capacities $C_{p,\phi}$ of the solutes may be calculated. Similarly, the densities of the solutions lead to apparent molar volumes V_ϕ of the solute. These apparent molar heat capacities and volumes are defined by Equation 2.17.

The experimental quantities that come directly from measurements with the Picker flow calorimeter and densimeter are $[c_p d/(c_{pw}^\circ d_w^\circ) - 1]$ and $(d - d_w^\circ)$ derived from equations 2.69 and 2.76. The equations for the calculation of experimental specific heat capacities and densities are the following:

$$c_p = c^{o}_{pw}\ d_w\ (1 + ff\ \Delta W\ /\ W_o)\ /\ d \qquad (2.76)$$

and

$$(d - d_w{}^{\circ}) = K\ (\tau^2 - \tau^2_w) \qquad (2.77)$$

For the directly useful equations for calculations of apparent molar heat capacities and volumes, there are

$$C_{p,\phi} = c_p\ M + 1000\ (c_p - c^{o}_{pw})\ /\ m \qquad (2.78)$$

$$V_{\phi} = (M\ /\ d) - [1000\ \Delta d\ /\ (m\ d\ d^{o}_{w})] \qquad (2.79)$$

In these equations, m is the molality of the solution; M is the molar mass of the solute; d and $d_w{}^{\circ}$ are the densities of solution and of pure water; and c_p and $c_{pw}{}^{\circ}$ are the specific heat capacities of the solution and of pure water. The values of specific heat capacities and densities of pure water were taken from the compilation by Hill (1990) as cited by Archer (1992).

The equations that define mean apparent molar volumes and heat capacities for solutions containing two solutes are given below.

$$V_{\phi,Mean} = [(1 + m_2 M_2 + m_3 M_3) / d - d_w^{\circ -1}] / (m_2 + m_3) \tag{2.80}$$

$$C_{p,\phi,\ Mean} = [c_p (1 + m_2 M_2 + m_3 M_3) - c_{p,w}^{\circ}] / (m_2 + m_3) \tag{2.81}$$

Here m_3 is the molality and M_3 is the molar mass, of the additional (electrolyte) species respectively. All other symbols have the same meaning as in Section 2.2.4 above.

2.4.4 Curve Fitting Methods and Assignment of Uncertainties

In this thesis, the Sodev Picker flow calorimeter and densimeter were used to measure the relative specific heat capacities and densities for sample solutions. According to the operating principle of the Picker flow calorimeter, (Equation 2.68) the experimental relative specific heat capacity is determined from $c_{p,1} / c_{p,2} \propto$

(W_1 f_1 d_1 ΔT_2) / (W_2 f_2 d_2 ΔT_1), where f_i is the mass flow rate of the solution, W_i is the power input to the each cell in the Picker calorimeter, d_i is the density of the sample and reference solutions, T is the temperature of each cell. Therefore, the contributions to random errors in our experimental data include fluctuations and relative errors in (a) the heater response, (b) the flow rate, (c) the cell temperature, and (d) the delay line temperature. Recent work by Xiao and Tremaine (1997) has shown that these lead to random errors in $C_{p,\phi}$ and V_ϕ that are inversely proportional to the molality of solutions, m.

Long term experience with the Sodev calorimeter and densimeter has shown that systematic and random errors in measurements at low molalities increase progressively as the experimental temperature is removed from 25°C. (See, for example: Hovey and Tremaine, 1986; Hovey, 1988). Possible reasons for the increased errors are imperfect thermostatting of the internal delay line in the Picker calorimeter and imperfect thermostatting of the incoming fluid in the densimeter, associated with the design of both instruments. The formation of bubbles from dissolved air is a consistent problem that affects accuracy at 55°C.

Systematic errors in the measured heat capacities and densities of the sample solutions also have to be considered. The systematic errors arise from (a) errors in the heat leak correction factor ff, (b) errors in preparing standard solutions, and (c) other calibration errors.

Weighted least squares curve fitting techniques have been used to fit the extended Debye-Hückel equation (Equation 2.24) first to the isothermal data at the experimental temperatures then to a "global" model in which temperature dependent parameters were fitted to all the experimental data for excess properties at different ionic strengths and different temperatures. Since these measurements were made before the work of Xiao and Tremaine (1997), the weighting method was based on a more arbitrary consideration that lower molalities of sample solution will give the higher uncertainties because of the limitations of the calorimeter and densimeter response. Typically, values of $C_{p,\phi}$ and V_ϕ were assigned weighting factors of 1.0 for molality $m > 0.1$, and 0.1 for $m \leq 0.1$.

The purpose of the global fit was to provide equations for interpolating values of $C_{p,\phi}$ and V_ϕ within the range of the experimental data. The uncertainty in the extrapolated values of $C_p°$ and $V°$ was assigned as twice the standard deviation of $C_p°$ and $V°$ as determined from the isothermal curve fits (2σ) plus a subjective estimate of systematic errors derived from (a) differences between the values from isothermal and global curve fits and (b) differences between our results and the limited data from other workers, usually at 25°C only.

The errors in interpolated values of $C_{p,\phi}$ and V_ϕ derived from these expressions at finite ionic strengths in the range of our data are expected to be less than the uncertainties in the extrapolated values for C_p° and V°. We have therefore followed the current practice of many authors by fitting the temperature dependent form of Equation 2.24 directly, without attempting to optimize the equation to remove statistical cross-correlations between the fitting parameters. Because the form of the equation was not optimized, and because no physical interpretation is attached to the excess property parameters, error estimates are only reported for C_p° and V°. (See, for example, Pogue and Atkinson 1988; Hakin et al. 1994; Perron et al. 1975; Lemire et al. 1992; Phutela et al.; 1987.)

Table 2.1 Parameters for temperature dependent densities of H_2O and D_2O*

Coefficient,	H_2O	D_2O
a_0	999.8396	1104.690
a_1	18.224944	20.09315
$10^3\ a_2$	-7.922210	-9.24227
$10^6\ a_3$	-55.44846	-55.9509
$10^9\ a_4$	149.7562	79.9512
$10^{12}\ a_5$	-393.2952	
10^3 b	18.159725	17.96190
Range of function, °C	0-150	3.5-100
Standard error, ppm	0.2-10	3
Estimated accuracy, ppm	0.4-20	10
Temperature of maximum density,°C	3.984	11.185
Maximum density, kg m^{-3}	999.972	1106.00

* Equation 2.6, Units kg m^{-3}.

Table 2.2 Literature data for log K and ΔH° at 25° for EDTA and NTA[a]

Equilibria	EDTA			NTA	
Ref.[b]	Ref. 1	Ref. 2	Ref. 3	Ref. 1	Ref. 2
$Cu^{2+}+L \rightleftharpoons CuL$		20.47[d]/ -33.18[d]	18.83[e]	13.1[c]/ -7.95[f]	13.1[e]/ -4.6[e]
HL/H.L	11.014[d]/ -23.39[c]		10.26[e]	9.65[c]/ -19.25[f]	
H_2L/HL.H	6.320[d]/ -17.99[c]		6.18[e]	2.48[c]/ -0.837[f]	
H_3L/H_2L.H	2.68[c]/ 5.44[c]		2.78[e]	1.9[c]/ -0.837[f]	
H_4L/H_3L.H	1.96[c]/ 1.26[c]		2.1[e]	(0.8)[c]	

[a] Data are log K / ΔH°. The unit of ΔH° is $kJ\ mol^{-1}$. An abbreviated equilibrium quotient expression is included for each constant. For example, H_2L/HL.H for EDTA and H^+ is $HEDTA^{3-} + H^+ \rightleftharpoons H_2EDTA$.

[b] Reference 1: Martell and Smith, (1982); Reference 2: Christensen and Izatt, (1983); Reference 3: Anderegg, (1975).

[c] At 25°C, ionic strength = 0.1.

[d] At 25°C, ionic strength = 0.

[e] At 25°C, ionic strength = 0.1 (KNO_3).

[f] At 20°C, ionic strength = 0.1.

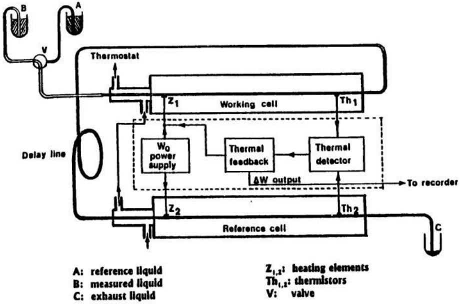

Fig. 2.1 Schematic diagram of the Picker flow microcalorimeter.

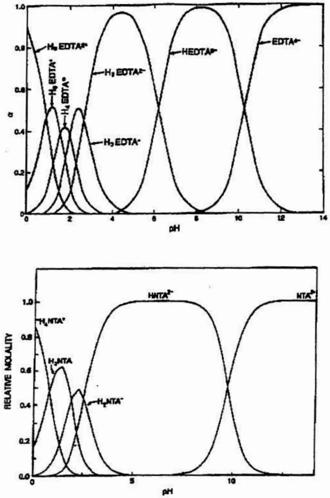

Fig. 2.2 Speciation of aqueous (a) EDTA and (b) NTA at 25°C and 0.1 molar ionic strength.

Chapter 3

APPARENT AND PARTIAL MOLAR HEAT CAPACITIES AND VOLUMES OF $Cu(ClO_4)_2$ FROM 10 TO 55°C

3.1. Introduction

Copper and its aqueous species are fundamentally linked to numerous natural and industrial processes. These include studies of the geochemistry of copper ore-body formation, the corrosion of copper alloys in electric power station steam generators, and hydrometallurgical processes for the recovery of copper ore. All of these require a knowledge of equilibrium properties at high temperature and pressure. A few of the thermodynamic data for Cu^{2+}(aq) were reported previously. The standard partial molar heat capacity and volume for $Cu(ClO_4)_2$ (aq) were measured by Spitzer et al. (1978). Millero (1972) has reviewed earlier measurements of V_ϕ and compiled conventional ionic volumes which permit us to calculate the standard partial molar volume for Cu^{2+}(aq). Larson et al. (1968) determined the standard enthalpy of formation and standard Gibbs energy of formation for Cu^{2+}(aq).

One purpose of this work has been to provide reliable heat capacity and volume values for use in various classical thermodynamic calculations, such as those involving the temperature and pressure dependence of Gibbs energies and related equilibrium properties. As part of our continuing program of measurements leading to thermal and volumetric properties of aqueous solutions, we have made calorimetric and density measurements on solutions of $Cu(ClO_4)_2$ (aq) from 10 to 55°C. Results of these measurements have been used for calculation of apparent molar heat capacities and apparent molar volumes as a function of ionic strength at several concentrations of $Cu(ClO_4)_2$(aq). These results have been analyzed and used to estimate the temperature dependence of the conventional standard-state partial molar heat capacity and volume functions.

3.2. Experimental

Sodev CP-C flow microcalorimeter (Picker et al., 1971) and a Sodev 03D vibrating flow densimeter (Picker et al., 1974) equipped with platinum cells were employed. Procedures are described previously in the work of Hovey and Tremaine (1986) and in Chapter 2. Both the calorimeter and densimeter were calibrated daily with pure water and a standard 1 m NaCl solution. The experimental values for $C_{p,\Phi}$ from the standard NaCl solution were compared with literature values (Archer, 1992) to correct for heat leak effects (Desnoyers et al., 1976). The calibration yielded heat-leak correction factors of 1.033, 1.004, 1.004 and 1.006 at 10, 25, 40 and 55°C, respectively.

Copper(II) perchlorate was synthesized by neutralizing 5 mol kg^{-1} solutions of the metal carbonate to pH 5 with 60% perchloric acid, then recrystallized at least twice from dilute aqueous perchloric acid. The concentration of the stock solution prepared from recrystallized $Cu(ClO_4)_2$ was determined to be 1.0508 ± 0.0042 mol kg^{-1} by titration with standardized EDTA solution using xylenol orange as an indicator. (Vogel, 1989) A small excess of HCl (4.2×10^{-3} mol kg^{-1}), used to suppress hydrolysis, was considered negligible in subsequent calculations. Nanopure water (resistivity > 18 MΩ cm) was used to dilute the stock solution by mass to prepare various lower concentrations. BDH certified ACS grade NaCl was dried at 110°C over-night before using.

3.3. Results

3.3.1. Apparent Molar Properties

The apparent molar properties of a solute are defined by Equation 2.17.

The Picker flow microcalorimeter and vibrating tube densimeter yield experimental data for the functions, $[c_p d/(c_{pw}^\circ d_w^\circ) - 1]$ and $(d - d_w^\circ)$, from which V_ϕ and $C_{p,\phi}$ can easily be calculated. (Desnoyers, 1976; Hovey et al., 1989) Here d, c_p, d_w°, and c_{pw}° are the density and specific heat capacity of the aqueous solutions and water, respectively. The experimental parameters and the corresponding values of V_ϕ and $C_{p,\phi}$, for $Cu(ClO_4)_2$ (aq) are tabulated in Table 3.1. Values for c_{pw}° and d_w° used in the calculations, taken from the compilation by Hill (1990), are listed in Table 3.2.

3.3.2. Standard Partial Molar Properties.

Expressions for the standard partial molar properties were obtained by fitting the Guggenheim form of the extended Debye-Hückel equation (Hovey et al.,1988; Millero, 1979) (Equation 2.24) to the experimental data. Values for A_Y were taken from the compilation by Archer and Wang (1990).

The temperature dependent values of Y°, B_Y and C_Y were represented by the three parameter equations used in previous studies (Tremaine et al., 1986) :

$$Y^\circ = q_{1,1} + q_{1,2}/(T-190) + q_{1,3}T \qquad (3.1)$$

$$B_Y = q_{2,1} + q_{2,2}T \tag{3.2}$$

$$C_Y = q_{3,1} + q_{3,2}T + q_{3,3}T^2 \tag{3.3}$$

where T stands for temperature (K). The parameters q_{ij} are the adjustable fitting constants. The term (T-190) describes the steep rise in Y_ϕ^∞ from very negative values near 0°C and was chosen to be identical to that used for aqueous HCl (Tremaine et al., 1986) for convenience in later calculations. By definition, the limiting value of Y_ϕ at $m = 0$ is equal to the standard state property Y°, $Y_\phi^\infty = Y°$. The fitted values for standard state properties and the adjustable constants were determined by a non-linear least squares analysis of the data in our study, using the Marquardt-Levenberg algorithm in commercial software SigmaPlot©, with temperature and molality as the independent variables. Because the uncertainties for $C_{p,\phi}$ and V_ϕ are larger at lower molalities, a statistical weight of 30% was given to the apparent molar property data for molalities below 0.1 mol kg^{-1}. The standard deviation of the fit to the entire experimental data matrix was 2.35 J K^{-1} mol^{-1} for $C_{p,\phi}$ and 0.16 cm^3 mol^{-1} for V_ϕ respectively.

The standard state and excess parameters are tabulated in Table 3.3. Table 3.4 presents the standard partial molar volumes and heat capacities for aqueous $Cu(ClO_4)_2$ from 10 to 55°C, obtained from both the isothermal and global fits. The results are plotted in Figures 3.3 and 3.4.

3.4. Discussion

3.4.1. Comparison with Previous Studies

In a previous study, the apparent molar heat capacities and volumes of $Cu(ClO_4)_2(aq)$ at 25°C were determined by Spitzer et al (1978). Our results for the apparent molar properties of copper(II) perchlorate at 25°C are consistent with this published data. Figures 3.1 and 3.2 present our experimental data for apparent molar properties from 10 to 55°C together with the data for $Cu(ClO_4)_2(aq)$ solutions at 25°C reported by Spitzer et al. (1978). The values for the standard partial molar properties of $Cu(ClO_4)_2$ (aq) reported by Spitzer et al., are $C_p° = -72.4$ J K^{-1} mol^{-1} and $V° = 63.1$ cm^3 mol^{-1} respectively compared with the values $C_p° = -78.01$ J K^{-1} mol^{-1} and $V° = 63.35$ cm^3 mol^{-1} determined in our study. Fitting Equation 2.24 to the data from Spitzer's measurements, yields the values $C_p° = -74.95$ J K^{-1} mol^{-1} and $V° = 63.07$ cm^3 mol^{-1} with standard deviations of

3.42 J K^{-1} mol^{-1} and 1.78 $cm^3 mol^{-1}$ respectively. The difference between the data in our study and Spitzer's lies within the combined statistical uncertainty from the two sets of experimental data.

Uncertainty limits were estimated as described below: The statistical errors from the isothermal fits(Table 3.4) are $2\sigma = 10.06, 3.38, 5.76$, and 8.66 J K^{-1} mol^{-1} for $C_p°$ at 10, 25, 40, and 55°C respectively; and $2\sigma = 0.74, 0.36, 0.54$, and 0.34 cm^3 mol^{-1} for V° at 10, 25, 40, and 55°C respectively. The agreement between our global and isothermal fits is within ±3 J K^{-1} mol^{-1} for $C_p°$ at 25, 40, and 55°C and ±0.75 cm^3 mol^{-1} for V°, well within these limits. The difference between our values for the standard partial molar properties of $Cu(ClO_4)_2(aq)$, and Spitzer's results(Spitzer et al., 1978) at 25°C are 3.06 J K^{-1} mol^{-1} for $C_p°$, and 0.28 cm^3 mol^{-1} for V°. We therefore estimate our overall uncertainty as $(2\sigma + 3.0)$ J K^{-1} mol^{-1} for $C_p°$ and $(2\sigma + 0.30)$ cm^3 mol^{-1} for V°. These uncertainties were tabulated in Table 3.4.

The fitted values for standard state properties and the adjustable constants at 25°C were re-determined by a non-linear least squares analysis of the data in our study together with the data reported by Spitzer et al., to yield the expressions

$$C_{p,\phi} = -75.36 + 4.5\times(32.059)\ [I - 2I^{1/2} + 2\ln(1 + I^{1/2})]/I + 7.188\times I + 4.041\times I^{3/2} \tag{3.4}$$

$$V_{\phi} = 62.73 + 4.5\times(1.8272)[I - 2I^{1/2} + 2\ln(1 + I^{1/2})]/I - 0.171\times I + 0.3696\times I^{3/2} \tag{3.5}$$

Here I stands for the ionic strength. The final fit yielded the values $C_p^\circ = -75.36$ J K^{-1} mol^{-1}, and $V^\circ = 62.73$ cm^3 mol^{-1}, with overall standard deviations in $C_{p,\phi}$ and V_ϕ of 1.39 J K^{-1} mol^{-1} and 0.39 cm^3 mol^{-1} respectively. Figures 3.5 and 3.6 present the curve fitting results from the two sets of experimental data for apparent molar properties at 25°C. The agreement between the values for $C_p^\circ[Cu(ClO_4)_2$, aq] and $V^\circ[Cu(ClO_4)_2$, aq] from Equations 3.4 and 3.5 with those in Table 3.4 lies within the combined experimental error. This "best" fit to the data at 25°C, lies well within the estimated uncertainties of ± 6 J K^{-1} mol^{-1} and ± 0.6 cm^3 mol^{-1} for the global fit in Table 3.4.

By definition, conventional ionic standard partial molar properties for Cu^{2+}(aq) can be calculated according to the additivity principle,

$$Y^\circ(Cu^{2+}aq) = Y^\circ[Cu(ClO_4)_2,aq] - 2\ Y^\circ(ClO_4^-,aq) \tag{3.6}$$

Several determinations of C_p° and V° for aqueous perchlorate have been reported over the temperature range of interest (Hovey and Hepler, 1989). Recent work in our laboratory (Tremaine and Xiao, 1995; Xiao and Tremaine, 1996) suggests that Hovey and Hepler's data (1989) are most consistent with results from the chloride salts. In this study, the values of C_p° and V° for $ClO_4^-(aq)$ at all temperatures were obtained from Hovey and Hepler. The conventional single-ion values in the work of Hovey et al. (1988) are based on the recent volumetric data for HCl (aq) from Herrington et al. (1985) and Allred and Woolley (1981), in preference to the data from Akerlof and Teare (1938) which cover a broader temperature range but are inconsistent with the more recent results. Chloride heat capacity values are from the expression reported by Tremaine et al. (1986) for $C_p^\circ(HCl,aq)$. The expressions for the volume and heat capacity of NaCl(aq) were obtained from fits to the very precise data of Millero (1970), Perron et al. (1975), and Desnoyers et al. (1976). The results are summarized as follows:

$$V^\circ(NaCl,aq) = 62.333 - 0.09108\ T - 2012.8/\ (T-190);\ 0-55^\circ C \qquad (3.7)$$

$$C_p^\circ(NaCl,aq) = 1885.0\ - 4.305\ T\ - 73838\ /\ (T-190);\ 1-45^\circ C \qquad (3.8)$$

$$V^{\circ}(HCl,aq) = 73.549 - 0.12799\ T - 1897.9\ /\ (T-190);\ 10-75^{\circ}C \quad (3.9)$$

$$C_p^{\circ}(HCl,aq) = 582.2 - 1.467\ T - 29356\ /\ (T-190);\ 10-140^{\circ}C \quad (3.10)$$

$$V^{\circ}(HClO_4,aq) = -107.79 + 0.87322\ T - 0.0012203\ T^2 \quad (3.11)$$

$$C_p^{\circ}(HClO_4,aq) = 1408.1 - 3.0767\ T - 55801\ /\ (T-190) \quad (3.12)$$

The calculated values of the standard state properties C_p° (Cu^{2+},aq) and V° (Cu^{2+},aq) are listed in Table 3.5.

The standard state properties for Cu^{2+}(aq) in Table 3.5 can be compared with the values reported by others, such as the results cited by Millero (1972). In this study, the values for the conventional standard partial molar heat capacity and volume for Cu^{2+}(aq) are -32.8 J K^{-1} mol^{-1} and -24.53 cm^3 mol^{-1}at 25°C, respectively. Millero's ionic volumes lead to V° = 44.1 cm^3 mol^{-1} for ClO_4^- (aq), therefore using Millero's ionic volumes for ClO_4^- (aq) and our V° values for

$Cu(ClO_4)_2$ (aq), the value V° (Cu^{2+}, aq) = -25.25 cm^3 mol^{-1} can be obtained. This is consistent with the value V° = -25.1 cm^3 mol^{-1} for Cu^{2+} (aq) obtained by subtracting Millero's V° = 44.1 cm^3 mol^{-1} for ClO_4^- (aq) from Spitzer's V° values for $Cu(ClO_4)_2$ (aq).

3.4.2. Temperature Dependence of Standard State Properties

As discussed in Section 2.3.3, a semi-empirical equation of state to describe the standard partial molar properties of aqueous electrolytes has been developed by Helgeson and co-workers. (Helgeson et al., 1981; Shock and Helgeson, 1988; Shock et al., 1992; Tanger and Helgeson, 1988) The "Helgeson-Kirkham-Flowers" HKF equation of state has been used with success to extrapolate the standard partial molar properties of aqueous electrolytes to temperatures as high as 300°C (Hovey and Tremaine, 1986; Hovey et al., 1989; Tremaine et al., 1986).

When pressure effects are ignored, the revised HKF equations (Shock et al., 1992) for standard partial molar heat capacity and volume can be written as Equations 2.55-2.56.

Our values of C_p° and V° for aqueous $Cu(ClO_4)_2$ in Table 3.4 from the global fits were extrapolated up to 300°C by fitting the parameters in the HKF equations. Relative statistical weights of 100% were assigned to the values for standard partial molar properties, obtained from individual least squares fits of the equations to the isothermal data. With $\omega = 1.4282 \times 10^6$ J mol^{-1} (= 1.4282×10^7 cm^3 bar mol^{-1}) and values for X and Q taken from the compilation by Helgeson and Kirkham (1974; 1976), the fit yields the expressions listed below:

$$V^\circ\ [Cu(ClO_4)_2]\ /\ (cm^3 mol^{-1}) = 96.67 - 1.718\times10^3\ /\ (T-228) - \omega Q \qquad (3.13)$$

$$C_p^\circ[Cu(ClO_4)_2]\ /(J\ K^{-1} mol^{-1}) = 209.1 - 7.736\times10^5\ /\ (T-228)^2 - \omega TX \qquad (3.14)$$

The standard deviations for the curve fit are 0.26 cm^3 mol^{-1} for V° and 5.33 J K^{-1} mol^{-1} for C_p°, respectively. These results are plotted in Figures 3.7 and 3.8.

The parameters obtained by fitting the HKF equation to the standard partial molar properties of $Cu(ClO_4)_2(aq)$, are presented in Appendix III.

Table 3.1. Experimental apparent molar volumes (V_ϕ) and heat capacities ($C_{p,\phi}$) of aqueous $Cu(ClO_4)_2$ at different concentrations from 10 to 55°C.

m mol kg^{-1}	$d-d_w^\circ$ g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_p d/(c^\circ_{pw} d^\circ_w)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		10°C		
1.05080	0.1954	63.98	-0.06025	3.27
0.78371	0.1491	62.80	-0.04932	-22.61
0.55951	0.1084	61.91	-0.03834	-47.45
0.33898	0.06697	60.77	-0.02569	-80.21
0.16053	0.03224	59.63	-0.01350	-117.7
0.08705	0.01759	59.31	-0.007499	-126.3
0.06392	0.01292	59.49	-0.005651	-134.8
0.04537	0.009176	59.61	-0.004145	-146.8
		25°C		
1.05080	0.1899	68.44	-0.05636	44.11
0.78371	0.1447	67.72	-0.04522	27.40
0.55951	0.1051	67.14	-0.03453	11.23
0.33898	0.06484	66.48	-0.02250	-7.670
0.16053	0.03118	65.81	-0.01143	-27.56
0.08705	0.01703	65.33	-0.006433	-39.48
0.08705	0.01705	65.08	-0.006444	-41.08
0.06392	0.01251	65.53	-0.004788	-42.45
0.04537	0.008928	64.71	-0.003392	-44.80

Table 3.1. Continued

m mol kg^{-1}	d-d$_w$$^{\circ}$ g cm^{-3}	V_{ϕ} cm^3 mol^{-1}	$c_p d/(c^{\circ}_{pw} d^{\circ}_w)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		40°C		
1.05080	0.1858	71.50	-0.05425	63.67
0.78371	0.1415	70.95	-0.04317	50.30
0.55951	0.1028	70.51	-0.03264	37.99
0.33898	0.06340	70.06	-0.02108	23.46
0.16053	0.03049	69.43	-0.01061	7.429
0.08705	0.01661	69.48	-0.005931	0.4789
0.06392	0.01220	69.78	-0.004373	1.041
0.04537	0.008709	68.93	-0.003127	-4.279
0.04537	0.008698	69.17	-0.003141	-4.587
		55°C		
1.05080	0.1827	73.64	-0.05372	71.98
0.78371	0.1392	73.11	-0.04304	57.11
0.55951	0.1011	72.85	-0.03323	40.26
0.33898	0.06233	72.42	-0.02069	35.37
0.16053	0.02999	71.78	-0.01037	20.90
0.08705	0.01639	71.27	-0.005795	11.87
0.06392	0.01204	71.44	-0.004267	12.21
0.04537	0.008586	70.87	-0.003105	3.167

Table 3.2. Parameters for water

Temperature	d_w^{o*} $g\ cm^{-3}$	$c_{p,w}^{o*}$ $J\ K^{-1}\ g^{-1}$	A_v^{**} $cm^3\ kg^{1/2}\ mol^{-3/2}$	A_C^{**} $J\ K^{-1}\ kg^{1/2}\ mol^{-3/2}$
10°C	0.999705	4.1940	1.6006	24.256
25°C	0.997041	4.1800	1.8272	32.059
40°C	0.992206	4.1773	2.1249	37.098
55°C	0.985686	4.1809	2.4914	41.753

* Taken from the compilation by Hill (1990).

** Compiled by Archer and Wang (1992).

Table 3.3 Standard state and excess property parameters for $Cu(ClO_4)_2(aq)$

	$q_{i,1}$	$q_{i,2}$	$q_{i,3}$
		$C_{p,\phi}/(J\ K^{-1}\ mol^{-1})$	
C_p°	2.869×10^{3}	-1.208×10^{5}	-6.157
B_C	6.453×10^{2}	-2.082	—
C_C	7.593×10^{2}	-5.678	1.045×10^{-2}
		V_ϕ / ($cm^3\ mol^{-1}$)	
V°	1.979×10^{2}	-6.490×10^{3}	-2.494×10^{-1}
B_V	1.001×10^{1}	-3.634×10^{-2}	—
C_V	2.465×10^{1}	-0.1623	2.735×10^{-4}

Table 3.4 Standard partial molar heat capacities and volumes of $Cu(ClO_4)_2$ (aq)

Temp °C	V°(isothermal)[1] $cm^3\ mol^{-1}$	V°(global)[2] $cm^3\ mol^{-1}$	C_p° (isothermal)[1] $J\ K^{-1}\ mol^{-1}$	C_p°(global)[2] $J\ K^{-1}\ mol^{-1}$
10	57.59(0.37)	57.37 ± 1.04	-171.86(5.03)	-167.37 ±13.06
25	63.35(0.18)	62.95 ± 0.66	-78.01(1.69)	-79.28 ± 6.38
40	67.42(0.27)	66.71 ± 0.84	-37.87(2.88)	-36.81 ± 8.76
55	68.92(0.17)	69.24 ± 0.64	-27.83(4.33)	-25.10 ± 11.66

[1]. Values in parentheses listed for the isothermal fits are equal to one standard deviation.

[2]. Error limits in V° and C_p° are 2σ(isothermal fit) + estimated uncertainty from systematic errors. The overall standard deviations in V_ϕ and $C_{p,\phi}$ for the global curve fit results are ± 1.85 $cm^3\ mol^{-1}$ and ±14.71 $J\ K^{-1}\ mol^{-1}$, respectively.

Table 3.5 Conventional ionic standard partial molar heat capacities and volumes for $Cu^{2+}(aq)$***.

Temperature (°C)	Na^+ (aq)**	Cl^- (aq)**	ClO_4^- (aq)*	Cu^{2+} (aq)
		$C_p^\circ/(J\ K^{-1}\ mol^{-1})$		
10°C	21.8	-148.4	-62.2±0.7	-43.0 ± 13.1
25°C	42.2	-126.6	-25.0±0.1	-29.3 ± 6.4
40°C	52.8	-115.5	-9.0±1.0	-18.8 ± 8.9
55°C	49.5	-111.7	-5.2±2.0	-14.7 ± 12.0
		$V^\circ/(cm^3 mol^{-1})$		
10°C	-2.21	17.15	41.63±0.04	-25.89±1.04
25°C	-1.27	17.89	44.04±0.02	-25.13±0.66
40°C	-0.44	17.91	46.24±0.03	-25.77±0.84
55°C	0.12	17.81	47.31±0.05	-25.38±0.64

* Hovey et al. (1989).

** Hovey et al. (1988), see also Tremaine and Xiao (1995).

*** Obtained from global fit of equations 3.1 to 3.3 with uncertainties assigned by two standard deviation(2σ) plus a subjective estimate based on the difference between global and isothermal fits and difference between our data and Spitzer's result at 25°C(Spitzer et al., 1978).

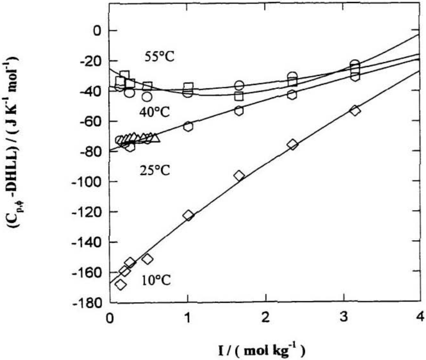

Fig. 3.1. Apparent molar heat capacities of $Cu(ClO_4)_2$ (aq), after subtracting the Debye-Hückel limiting law. The triangular points at 25 °C are data reported by Spitzer et al. (1978).

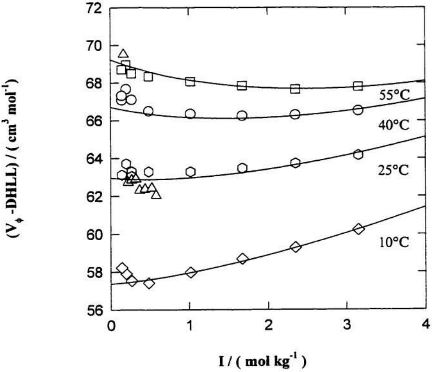

Fig. 3.2. Apparent molar volumes of $Cu(ClO_4)_2$ (aq), after subtracting the Debye-Hückel limiting law. The triangular points at 25 °C are data reported by Spitzer et al. (1978).

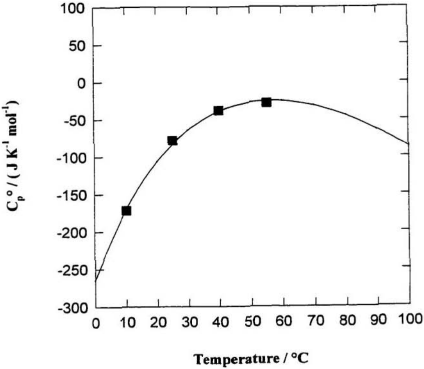

Fig. 3.3. Temperature dependence of standard partial molar heat capacities of $Cu(ClO_4)_2$ (aq). The solid line is the result of a least squares global curve fit to all experimental data.

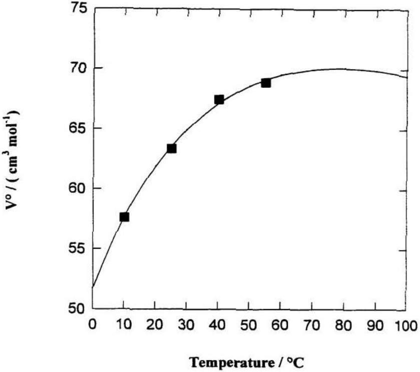

Fig. 3.4. Temperature dependence of standard partial molar volumes of $Cu(ClO_4)_2(aq)$. The solid line is the result of a least squares global curve fit of all experimental data.

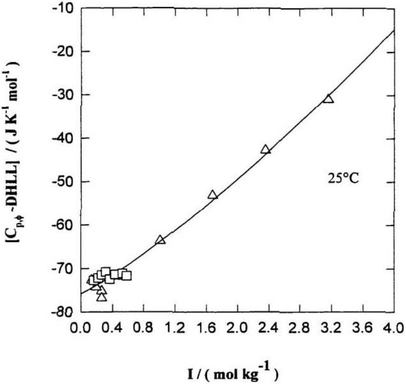

Fig. 3.5. Apparent molar heat capacities of $Cu(ClO_4)_2$ (aq) solutions at 25°C: △ , *this work;* —— , *least squares fit;* □ , data reported by Spitzer et al. (1978).

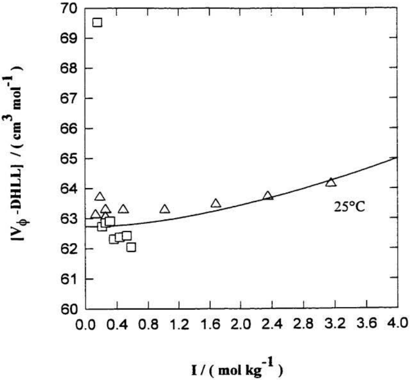

Fig. 3.6. Apparent molar volumes of $Cu(ClO_4)_2$ (aq) solutions at 25°C: △ , this work; —— , least squares fit; □ , data reported by Spitzer et al. (1978).

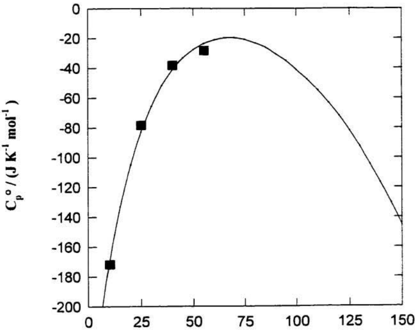

Fig. 3.7. Temperature dependence of standard partial molar heat capacities of $Cu(ClO_4)_2$ (aq). The solid line is the least squares curve fit to the HKF equation.

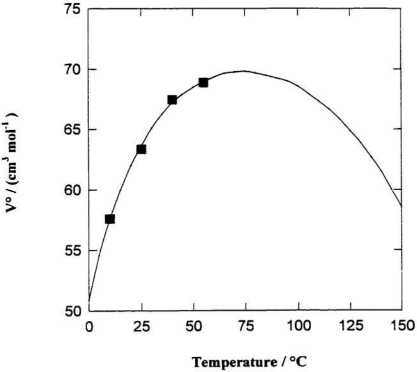

Fig. 3.8. Temperature dependence of standard partial molar volumes of $Cu(ClO_4)_2$ (aq). The solid line is the least squares curve fit to the HKF equation.

Chapter 4

THERMODYNAMICS OF AQUEOUS EDTA SYSTEMS: APPARENT AND PARTIAL MOLAR HEAT CAPACITIES AND VOLUMES OF $Na_2H_2EDTA(aq)$ AND $Na_2CuEDTA(aq)$ FROM 10 TO 55°C AND RELATED CALCULATIONS

4. 1. Introduction

Aqueous solutions of ethylenedinitrilotetraacetic acid (EDTA) are used as sequestering agents in several industrial applications that include cleaning boilers, softening boiler and process water, treating oil wells, decontamination of nuclear reactor systems and remedial treatment of environmental sites. In all of those applications, the main scientific interest is on modeling the complexation of divalent and trivalent ions. The complexation equilibria, stability constants and enthalpies of most metal ions of interest have already been determined at or near 25°C, However, many of the applications involve temperatures considerably higher than 25°C for which there are no equilibrium constants available. The equilibrium constants for high temperature solutions can be calculated from a combination of known stability constants and enthalpies of complexation at 25°C with the apparent molar heat capacities and volumes from this investigation.

The measurements described here have led to heat capacities and densities of aqueous solutions of Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq). Results of these experiments are tabulated in the form of apparent and partial molar heat capacities and volumes, which are directly useful in thermodynamic calculations of pressure and temperature effects.

Previous measurements from our group have led to values of C_p° and V° for H_nEDTA^{4-n} (aq) and over a dozen complexes of the form $MEDTA^{4-n}$ (aq) at 25°C (Hovey and Tremaine, 1985; Hovey et al., 1986; 1988). No values at other temperatures have been reported.

The purpose of this work is to use the complexes of EDTA with copper as a model system to investigate the effects of temperature on C_p° and V° for strongly chelated systems. The results for CuEDTA and H_2EDTA^{2-}(aq), will be combined with the apparent and partial molar properties of Cu^{2+} (aq) described in Chapter 3 of this thesis, to obtain parameters for the thermodynamics of formation of $CuEDTA^{2-}$ (aq) as a function of temperature.

4.2. Experimental

Standard solutions of NaCl were prepared by mass after drying the salt

(BDH, Certified ACS Reagent Grade) at 110°C for about 24 hours, without further purification. All stock solutions were prepared from nanopure water with a final resistivity of 18 MΩ cm or greater. BDH certified analytical reagent grade ethylenediaminetetraacetic acid disodium salt ($Na_2H_2EDTA \cdot nH_2O$) was dehydrated at 80°C for five days until the samples reached constant weight. The number of waters of hydration ($n = 1.99$), and hence the molar mass, were calculated from the weight loss recorded after dehydrating several small samples of the EDTA disodium salt under vacuum, at 135°C. Stock solutions of $Na_2H_2EDTA \cdot 1.99H_2O$ were prepared by weight from the salt without further purification.

The $Na_2CuEDTA$ salt was prepared from Aldrich Certified $Cu(OH)_2$, and BDH Certified Na_2H_2EDTA (AR), both without further purification, and recrystallized by a method derived from Vogel (1989). An excess of $Cu(OH)_2$ was added to a 0.21701 mol L^{-1} solution of Na_2H_2EDTA. The mixture was stirred and heated at 70°C for about 24 hours. The excess solid $Cu(OH)_2$ was filtered out and discarded. Ethanol (95%) was slowly added to the liquid phase at 25°C until some precipitate appeared. After filtering off the precipitate, an equal volume of ethanol was added dropwise to the filtrate after a period of several hours with vigorous stirring. The final crystalline precipitate appeared again when ethanol was added continuously. The crystalline products were washed with ethanol and then recrystallized again by the same procedure. The recrystallized product was dried in bulk in a vacuum oven (5 days at 60°C) until constant weight was reached, then used without further purification. Weight loss after vacuum dehydration at 135°C confirmed the number of waters of hydration ($n = 2.98$), and the molar mass of the salt. The concentration of stock solutions was determined by mass from the hydrated product.

All apparent molar properties measured were corrected for a very slight heat loss by the method described by Desnoyers et al. (1976). The heat loss correction factors were obtained daily by measurement of the heat capacities and volume of the standard NaCl solution to yield values of 1.006, 1.008, 1.005 and 1.034 for Na_2H_2EDTA (aq) at temperatures of 10, 25, 40 and 55°C respectively. For $Na_2CuEDTA$, the heat leak correction factors were 1.006 and 1.028 at 10 and 55°C, respectively, The correction factors at 25 and 40°C, were assumed to be 1.007.

The densities of all solutions were measured relative to water with a Sodev-03D vibrating tube densimeter with platinum cells. The cells were calibrated with water and nitrogen gas. The heat capacities were measured relative to water with a Picker flow microcalorimeter, Sodev Model CP-C, also equipped with platinum cells. Temperature was controlled with a Sodev Model CT-L bath and measured with a thermistor set in a well deep in the coolant circuit. The density and specific heat capacity of water and the NaCl solution from 10 to 55°C were taken from the compilation by Archer and Wang (1990).

Despite several attempts on subsequent days, the experimental results at 55°C were less reproducible than our other measurements at lower temperatures. Those data were included in Table 4.1 and 4.2 but were given a lower statistical weight in the data analysis described below.

4.3. Results

4.3.1. Apparent Molar Properties

Measurements with the Picker flow calorimeter yield volumetric heat capacities relative to the volumetric heat capacity of pure water. (Picker et al., 1971) The specific heat capacities of solutions, and hence the desired apparent molar capacities of the solutions, can be calculated from these quantities together with the densities that have also been measured. Similarly, the densitometer measurements yield relative densities, $d - d_w^\circ$, which lead to apparent molar volumes of the solutions. It is convenient and useful to define the "mean" or "experimental" apparent molar properties by Equation 2.24. The Picker flow microcalorimeter and vibrating tube densitometer yield experimental data for the functions, $[c_p d/(c_{pw}^\circ d_w^\circ) - 1]$ and $(d - d_w^\circ)$, from which V_ϕ and $C_{p,\phi}$ can easily be calculated. Here d, c_p, d_w°, and c_{pw}° are the density and specific heat capacity of the aqueous solutions and water, respectively. Values for c_{pw}° and d_w° used in the calculations, taken from the compilation by Hill (1990) are listed in Table 3.2. The experimental parameters and the corresponding values of V_ϕ and $C_{p,\phi}$ for Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) are tabulated in Tables 4.1 and 4.2.

4.3.2. Relaxation Contributions to Heat Capacities of Mixed Electrolyte Solutions

The values in Tables 4.1 and 4.2 refer to the stoichiometric solutes, that is to the dissolved sodium salts of the complexes, without distinguishing whether significant equilibrium amounts of the free metal ion or hydrolyzed EDTA complex are present at equilibrium. The pHs of the aqueous Na_2H_2EDTA and $Na_2CuEDTA$ stock solutions are 4.70 and 7.31 respectively. Ionization reactions involving H^+ are negligible in these solutions, and less than 0.1% of the EDTA complex in solution dissociates to form free EDTA anions according to Hovey and Tremaine (1985). The contributions of chemical relaxation to $C_{p,\phi}$ in their study are all of the order of 5 J K^{-1} mol^{-1}. Here, we consider the equilibria

$$H_2EDTA^{2-}\ (aq) = HEDTA^{3-}\ (aq) + H^+\ (aq) \qquad 1/K_2 \tag{4.1}$$

and

$$H_2EDTA^{2-}\ (aq) + H^+\ (aq) = H_3EDTA^-\ (aq) \qquad K_3 \tag{4.2}$$

The expressions for the equilibrium constants K_2 and K_3 were presented in Section 2.3.4. The chemical relaxation contributions are given by the expressions

$$C_{p\alpha,\phi}^{rel} = -\Delta H_2\ (\partial\alpha/\partial T)_m \tag{4.3}$$

$$C_{p\beta,\phi}^{rel} = \Delta H_3\ (\partial\beta/\partial T)_m \tag{4.4}$$

Where α and β are the degrees of dissociation of H_2EDTA^{2-} according to equilibria 4.1 and 4.2. For dilute solutions that are only slightly dissociated,

$$(\partial \alpha \; / \; \partial T)_m = \alpha \; (-\Delta H^\circ_2) \; / \; (2RT^2) \tag{4.5}$$

$$(\partial \beta \; / \; \partial T)_m = \beta \; \Delta H^\circ_3 \; / \; (RT^2) \tag{4.6}$$

The critical compilations by Martell and Smith (1982) list the values log $K_2 = 6.11 \pm 0.02$ and log $K_3 = 2.68 \pm 0.02$ for the equilibria given by Equations 4.2 and 4.3 at 25°C and 0.1 m ionic strength respectively. The values $\Delta H_2^\circ = -17.99$ kJ mol^{-1} and $\Delta H_3^\circ = 5.44$ kJ mol^{-1} have been compiled for 25°C and ionic strength equal to 0.1 m. From these data the chemical relaxation contributions can be calculated. Figure 4.1 presents the apparent molar heat capacities of Na_2H_2EDTA (aq) from 10 to 55°C after subtracting the relaxation contribution. The results of chemical relaxation contribution and corrections are tabulated in Table 4.3. The correction lies at the limit of experimental uncertainty. The contribution of the small proportion of the species $HEDTA^{3-}$(aq) and H_3EDTA^-(aq) is much smaller, and was considered to be negligible.

The effect of sodium complexation with H_2EDTA^{2-} is also negligible at these molalities (Anderegg, 1977; Martell and Smith, 1974). No correction for contribution of chemical relaxation to the apparent molar heat capacities of $Na_2CuEDTA$ (aq) has been done, because the equilibrium constant for the dissociation of $CuEDTA^{2-}$ (aq) to form $Cu_2(OH)_2^{2+}$ (aq) and $HEDTA^{3-}$ (aq), logK = -25.45 (Christensen and Izatt, 1983), is too small for these reactions to affect $C_{p,\Phi}$.

4.3.3. Standard Partial Molar Properties

The experimental data and the least squares fits for apparent molar properties of Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) are plotted in Figures 4.1, 4.2, 4.3 and 4.4. Expressions for the standard partial molar properties were obtained by fitting the Guggenheim form of the extended Debye-Hückel equation (Millero, 1979; Hovey et al., 1989), Equation 2.24, to the experimental data. The isothermal standard partial molar properties were obtained from the curve fits.

For Na_2H_2EDTA (aq), the temperature dependence of Y°, B_Y and C_Y were represented by the three parameter expressions, Equations 3.1, 3.2 and 3.3, used in previous studies (see Chapter 3; Hovey et al. 1989). Fitted values for the adjustable constants were determined by a nonlinear least squares analysis of the data in Table 4.1, with both temperature and ionic strength as the independent variables. Because the experimental uncertainties for $C_{p,\phi}$ and V_ϕ are larger at lower molalities, a statistical weight of 30% was given to the apparent molar property data for Na_2H_2EDTA (aq) for molalities below 0.04 mol kg^{-1} at 10 and 25°C, for molalities below 0.13 mol kg^{-1} at 40°C, and for molalities below 0.05 mol kg^{-1} at 55°C.

For $Na_2CuEDTA$ (aq), a linear ionic strength dependence was used in the least squares curve fitting of the Debye-Hückel converted apparent molar properties ($c_Y = 0$ in Equation 2.24 and in Equation 3.3). Again, the temperature dependence of Y_ϕ° and B_Y was represented by the three parameter equations as follows :

$$Y^\circ = q_{1,1} + q_{1,2}/(T-190) + q_{1,3}T \qquad (4.7)$$

$$B_Y = q_{2,1} + q_{2,2}T + q_{2,3}\,T^2 \qquad (4.8)$$

Because experimental problems reduced the precision of the measurements, a statistical weight of 50% was given to all the apparent molar property data for $Na_2CuEDTA$ (aq) at 55°C, a statistical weight of 10% was given to the apparent molar property data for molalities below 0.05 mol kg^{-1} at 10 and 25°C.

The overall standard deviations of the fit to the experimental data matrix for Na_2H_2EDTA (aq) were 6.46 J K^{-1} mol^{-1} for $C_{p,\phi}$ and 0.45 cm^3 mol^{-1} for V_ϕ respectively. For $Na_2CuEDTA$ (aq), the standard deviations were 7.11 J K^{-1} mol^{-1} for $C_{p,\phi}$ and 0.18 cm^3 mol^{-1} for V_ϕ respectively. The standard state and excess parameters are tabulated in Tables 4.6 and 4.7.

For environmental and medical applications, the temperature dependence of standard partial molar properties for EDTA and its complexes must be represented accurately over the temperature range 0 - 37°C. The Holmes and Mesmer (1983) equation used to represent the temperature dependent values of the standard partial molar properties Y° for Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) is adequate within the uncertainties of the experimental data. The temperature dependence of standard partial molar properties is plotted in Figures 4.7, 4.8, 4.9 and 4.10.

Table 4.4 presents the standard partial molar volumes and heat capacities for Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) from 10 to 55°C. The standard deviations were obtained from the least squares curve fit by the calculation with a commercial software SigmaPlot©.

4.4. Discussion

4.4.1. Comparison with Previous Studies

The apparent molar heat capacities and volumes for Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) at 25°C listed in Tables 4.1 and 4.2, can be compared with the values reported by others. The apparent molar properties for Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) at 25°C were reported by Hovey and Tremaine (1985) and more recent values for Na_2H_2EDTA (aq) at 25°C were reported by Hovey et al. (1988). A least squares curve fit of Equation 2.24 to the apparent molar properties at 25°C yields the values $V°$ (Na_2H_2EDTA, aq) = 153.45 cm^3 mol^{-1} and $C_p°$ (Na_2H_2EDTA, aq) = 149.36 J K^{-1} mol^{-1}, which are compared with values in other studies in Table 4.5. The values of $V°$ from the only other two sets of experimental data available are 154.31 cm^3 mol^{-1}(Hovey and Tremaine, 1985) and 153.87 cm^3 mol^{-1} (Hovey et al., 1988), which are in reasonable agreement with our results. The two sets of data reported by Hovey et al. (1985 and 1988) yield values of $C_p°$ (Na_2H_2EDTA, aq) = 168.8 J K^{-1} mol^{-1} and 166.6 J K^{-1} mol^{-1}. These are in reasonable agreement with each other, but the values differ from ours by about 20 J K^{-1} mol^{-1}. The experimental data from this work are plotted together with data from Hovey and Tremaine (1985), and Hovey et al. (1988) in Figures 4.5 and 4.6.

Our results for V_ϕ (Na_2H_2EDTA, aq) differ from the most recent result of Hovey et al. (1988) by up to 1 cm^3 mol^{-1}, just within the combined experimental uncertainty. The most significant differences are in the data at higher ionic strength, $I > 0.5$ mol kg^{-1}. The values for $C_{p,\phi}$(Na_2H_2EDTA,aq) in this work agree with those reported by Hovey et al. (1988) within 4 J K^{-1} mol^{-1} at $I > 0.5$ mol kg^{-1}, but differ by up to 15 J K^{-1} mol^{-1} at the lowest molalities. The slight difference in the slope of the curve yields a difference in $C_p°$ of 20 J K^{-1} mol^{-1} for these two sets of data.

The statistical errors in $C_p°$(Na_2H_2EDTA,aq) from the isothermal fits are estimated as 2σ =22.80, 11.36, 82.98, and 66.96 J K^{-1} mol^{-1} at 10, 25, 40 and 55°C respectively. The agreement between our data for $C_p°$ at 25°C with Hovey's result (Hovey et al., 1988) is about 17 J K^{-1} mol^{-1}, almost equal to $(2\sigma + 6)$ J K^{-1} mol^{-1}, so that the error estimates for $C_p°$ from the global fits were assigned as $(2\sigma + 6)$ J K^{-1}

mol^{-1}. For $V°(Na_2H_2EDTA,aq)$, the statistical errors are $2\sigma = 4.66$, 0.98, 4.16, and 1.36 $cm^3\ mol^{-1}$ at 10, 25, 40 and 55°C, respectively. The difference between our data and Hovey's is 0.43 $cm^3\ mol^{-1}$, so that $(2\sigma + 0.43)\ cm^3\ mol^{-1}$ was used as a reasonable estimate of statistical plus systematic errors for V° from the global fits at different temperatures. Those are tabulated in Table 4.6.

The only literature values for the standard partial molar properties of $Na_2CuEDTA$ (aq) at 25°C, were reported by Hovey and Tremaine (1985) which are $C_p° = 148.5 \pm 0.9\ J\ K^{-1}\ mol^{-1}$ and $V° = 163.20 \pm 0.09\ cm^3\ mol^{-1}$. In our study, the values are $C_p° = 169.13 \pm 20.38\ J\ K^{-1}\ mol^{-1}$ and $V° = 168.48 \pm 5.14\ cm^3\ mol^{-1}$, respectively.

One possible reason for this difference is the hydration number determination for $Na_2CuEDTA$ (aq). The hydration number for those solutes must be determined accurately, otherwise the concentration of the solutions $Na_2CuEDTA$ (aq) can't be correctly determined, so that the calculations for the apparent molar properties will be influenced. To confirm our results, two sets of experiments for the apparent molar properties for $Na_2CuEDTA$ (aq) had been done. The first used the commercial product of $Na_2CuEDTA$ purchased from Sigma® and second used the $Na_2CuEDTA$ (aq) which we prepared at another time.

The results for the apparent molar properties and standard partial molar properties of $Na_2CuEDTA$ (aq) are consistent with our previous results, but still differ from the results reported by Hovey and Tremaine (1985).

For $C_p°(Na_2CuEDTA,aq)$, the statistical errors from the isothermal fits are $2\sigma = 11.28, 6.38, 14.94$, and 56.08 J K^{-1} mol^{-1} at 10, 25, 40 and 55°C respectively. At 25°C the difference between our global fit and Hovey's data is about 21 J K^{-1} mol^{-1}, and we therefore estimate the overall error for $C_p°(Na_2CuEDTA,aq)$ as $(2\sigma + 14)$ J K^{-1} mol^{-1}.

For $V°(Na_2CuEDTA,aq)$, the statistical errors from the isothermal fits are $2\sigma = 0.64, 0.14, 0.60$, and 0.82 cm^3 mol^{-1} respectively, and the agreement at 25°C for our data and Hovey's is within 5.00 cm^3 mol^{-1}, so the estimated error for $V°(Na_2CuEDTA,aq)$ is $(2\sigma + 5.00)$ cm^3 mol^{-1}. The results are tabulated in Table 4.6.

Values for $C_p°$ and V° of the ions H_2EDTA^{2-}(aq) and $CuEDTA^{2-}$(aq) were calculated from the data in Table 4.6 on the conventional scale, $C_p°(H^+) \equiv 0$, $V°(H^+,aq) \equiv 0$. These are listed in Table 4.8.

4.4.2. Extrapolation to Elevated Temperatures

The "Helgeson-Kirkham-Flowers" equation of state (Helgeson et al., 1981; Shock and Helgeson, 1988; Shock et al., 1992) has been used with success to extrapolate the standard partial molar properties of aqueous electrolytes to temperatures as high as 300°C. (Hovey and Tremaine, 1986; Hovey et al., 1989), as mentioned in Chapter 2. When pressure effects are ignored, the revised HKF equations (Shock et al., 1988; Helgeson et al., 1981) for standard partial molar heat capacity and volume can be written as Equations 2.55-2.56.

The crystal structure of Mg-EDTA complex was investigated by Stezowski et al. (1973). From the crystallographic data, the distance from metal ion (Mg^{2+}) to the outermost oxygen atom of the EDTA molecule can be calculated as 4.2110Å. The effective radius for the Cu-EDTA complex was assumed to be equal to this crystallographic radius. The Born coefficient, ω, ,can be calculated according to $\omega_j = \omega_j^{abs} - Z_j\, \omega_{H+}^{abs}$, here Z_j is the charge of ion. $\omega_j^{abs} = 6.94657 \times 10^5 \times Z_j^2 / r_{e,j}$, and $\omega_{H+}^{abs} = 2.2539 \times 10^5$ (J mol^{-1}). It was assumed that the crystallographic radius for the EDTA complex could also be used to calculate the effective radii for H_2EDTA^{2-} (aq). The Born coefficient $\omega = 2.4388 \times 10^5$ (J mol^{-1}) was therefore used for H_2EDTA^{2-} (aq) and $CuEDTA^{2+}$(aq).

Values of *X* and *Q* were taken from the compilations of Helgeson and Kirkham (1974, 1976).

Our values of $C_p°$ and V° for Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq) were extrapolated up to 300°C by fitting the adjustable parameters in the HKF equations to the data from the global fits in Table 4.6. A weight of 1 was assigned to each of the standard partial molar properties used in the HKF fit. The results are plotted in Figures. 4.11-4.14. The parameters for the HKF equations are presented in Appendix III.

4.4.3. Temperature Dependence of Stability

One of the objectives of this work was to use the standard partial molar heat capacities to extrapolate the formation constants for the EDTA complexes to high temperature. The temperature dependence is obtained by

$$\begin{aligned} \ln K_T &= \ln K_{298} + (R^{-1}) \times \Delta H° \times (298^{-1} - T^{-1}) \\ &+ R^{-1} \times \int_{298}^{T} (\Delta C_p° / T)\, dT - (RT)^{-1} \times \int_{298}^{T} \Delta C_p°\, dT \end{aligned} \qquad (4.9)$$

We have chosen to calculate the temperature dependence of the exchange equilibria between the Cu^{2+} and the EDTA complex. $\Delta C_p°$ was calculated from the fitted HKF equation parameters for $Cu^{2+}(aq)$, $H_2EDTA^{2-}(aq)$, $CuEDTA^{2-}(aq)$, and $ClO_4^-(aq)$ according to the following reaction

$$Cu(ClO_4)_2(aq) + Na_2H_2EDTA(aq) \rightleftharpoons Na_2CuEDTA(aq) + 2HClO_4(aq) \quad (4.10)$$

The values ΔH° = 8.20 ± 1.26 kJ mol^{-1}, ΔS° = 87.642 ± 4.492 J K^{-1} mol^{-1}, and ΔG° = -17.90 ± 0.54 kJ mol^{-1} can be calculated from the data in Table 2.2, which are taken from the compilations by Christensen and Izatt (1983) and Martell and Smith (1982). HKF equation parameters for $HClO_4$ (aq) were obtained from Hovey's Ph.D. thesis (Hovey, 1988). The temperature dependence of the equilibrium constants was calculated by using the program SUPCRT92 (Johnson et al., 1992) The results of the calculations are presented in Table 4.9.

The extrapolation of association constants is affected by the precision of the values of log K, ΔH°, and $\Delta C_p°$ chosen and the temperature variation of $\Delta C_p°$. The uncertainties associated with the independent variables X_i in this calculation contribute to the variance of log K according to the expression

$$\sigma_{\log K}^2 = \Sigma\, (\partial \log K / \partial x_i)^2\, \sigma_{xi}^2 \qquad (4.11)$$

assuming cross terms are insignificant. The contribution of ΔV° term is only about +0.03 log units at 573 K and for the purpose of these estimates it can be ignored.

An approximate error analysis of the effects of uncertainties in the non-Born terms can be made by assuming a constant ΔC_p°, where $\Delta V^\circ \approx 0$, so that

$$\begin{aligned}\log K = \quad & \log K_{298K} + \Delta H^\circ_{298K}\,[(1/298) - (1/T)]/(2.303R) \\ & + \Delta C^\circ_{p,298K}\,\{\ln (T/298) + 298\,[(1/T) - (1/298)]\}/(2.303R) \qquad (4.12)\end{aligned}$$

and the propagation of error is as follows:

$$\begin{aligned}\sigma^2_{\log K} = \quad & \sigma^2_{\log K298K} + \sigma^2_{\Delta H^\circ 298K}\,\{[(1/298) - (1/T)]/(2.303R)\}^2 \\ & + \sigma^2_{\Delta C^\circ p,298K}\,\{\ln (T/298) + 298\,[(1/T) - (1/298)]\}^2/(2.303R)^2 \qquad (4.13)\end{aligned}$$

Our estimate of uncertainty is based on the following errors in log K(298K), ΔH°(298K) and ΔC_p°(298K)(Christensen and Izatt, 1983; Martell and Smith, 1982):

$\sigma_{\log K298K} = \pm 0.0943$, $\sigma_{\Delta H^\circ 298K} \leq \pm 1.26$ kJ mol^{-1}, $\sigma_{\Delta Cp^\circ 298K} = [6.38^2 + 17^2 + 20^2 + (2 \times 0.1)^2]^{1/2} = 27.01$ J K^{-1} mol^{-1} [calculated from the overall uncertainty associated with the global fits for C_p° of $Cu(ClO_4)_2(aq)$, $Na_2H_2EDTA(aq)$, $Na_2CuEDTA(aq)$ and $HClO_4(aq)$ at 25°C, in Table 3.4, 4.6 and Hovey's thesis (1988; p64)]. The contributions of errors in ΔH_{298}° and $\Delta C_{p,298}^\circ$ calculated from the above equation are plotted in Figure 4.16.

The effect of uncertainties in the ionic radius used in the HKF model was estimated by varying ω_{BORN} by ± 20%. The uncertainty in log K_T arising from the uncertainty in ω_{BORN} is plotted in Figure 4.17.

The overall uncertainty in the values of log K were estimated by the sum of errors in ω_{BORN}, ΔH_{298}° and $\Delta C_{p,298}^\circ$, that is $\sigma^2_{\log K} = \sigma^2_{\log K}$(Eq. 4.13) + $\sigma^2_{\log K}$(Born term). Uncertainty estimates for log K_T are presented in Table 4.9 along with the values of log K_T. The major contribution to the errors in log K at 300°C arises from uncertainties in the Born term.

Table 4.1. Experimental apparent molar volumes (V_ϕ) and heat capacities ($C_{p.\phi}$) of $Na_2H_2EDTA(aq)$ at different concentrations from 10 to 55°C.

m mol kg^{-1}	d-d$_w^\circ$ g cm^{-3}	V_ϕ cm^3 mol^{-1}	m mol kg^{-1}	$c_pd/(c_{pw}^\circ d_w^\circ)-1$	$C_{p.\phi}$ J K^{-1} mol^{-1}
			10°C		
0.18250	0.03207	155.49	0.23597	-0.02596	180.73
0.13481	0.02402	154.30	0.18651	-0.02156	152.89
0.07980	0.01449	152.37	0.13421	-0.01634	122.40
0.06879	0.01254	152.07	0.08974	-0.01146	93.64
0.04843	0.00888	151.50	0.04381	-0.00588	62.06
0.03050	0.00565	150.08	0.02197	-0.00304	42.50
0.02260	0.00421	149.46			
			25°C		
0.23597	0.03983	160.98	0.23597	-0.0206	289.19
0.18651	0.03185	160.32	0.18651	-0.0169	275.07
0.13421	0.02330	158.88	0.13421	-0.0127	253.21
0.08973	0.01578	157.84	0.08973	-0.00900	229.11
0.04380	0.00782	156.17	0.04380	-0.00461	203.83
0.02197	0.00396	155.48	0.02197	-0.00239	188.12
			40°C		
0.23388	0.03892	163.39	0.23388	-0.01699	360.82
0.20731	0.03471	163.09	0.20731	-0.01498	362.56
0.18285	0.03081	162.67	0.18285	-0.01359	353.11
0.15638	0.02653	162.22	0.15638	-0.01189	345.32
0.13320	0.02288	161.58	0.13320	-0.01024	340.09
0.11147	0.01910	161.31	0.11147	-0.00871	334.74
0.08758	0.01520	159.78	0.08758	-0.00708	318.41

Table 4.1. Continued

m mol kg^{-1}	d-d$_w$° g cm^{-3}	V_ϕ cm^3 mol^{-1}	m mol kg^{-1}	$c_p d/(c_{pw}{}^\circ d_w{}^\circ)-1$	$C_{p,\phi}^{*}$ J K^{-1} mol^{-1}
			55°C		
0.18250	0.02992	167.26	0.23190	-0.01324	427.55
0.13481	0.02235	166.71	0.20576	-0.01204	420.54
0.07980	0.01342	165.78	0.18164	-0.01040	425.87
0.06879	0.01162	165.24	0.15549	-0.00936	411.97
0.04843	0.00822	165.07	0.13256	-0.00887	381.22
0.03050	0.00520	164.83	0.11102	-0.00796	359.55
0.02260	0.00387	164.30	0.11262	-0.00733	389.34
			0.06445	-0.00470	353.29
			0.04381	-0.00329	343.69
			0.04381	-0.00346	326.45

* Apparent molar volumes at 10 and 55°C were measured by Dr. D. Shvedov and Tram Pham, Apparent molar heat capacities at 10 and 55°C are modified by the values of densities according to their measurements.

Table 4.2. Experimental apparent molar volumes (V_ϕ) and heat capacities ($C_{p,\phi}$) of $Na_2CuEDTA(aq)$ at different concentrations from 10 to 55°C.

m mol kg^{-1}	d-d$_w$° g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_pd/(c_{pw}°d_w°)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		10°C		
0.6176	0.12554	172.77	-0.05805	288.11
0.4705	0.09878	170.90	-0.04907	244.00
0.3350	0.07225	169.80	-0.03841	203.69
0.2153	0.04771	168.06	-0.02749	149.61
0.1031	0.02351	165.77	-0.01425	105.29
0.04971	0.01145	165.40	-0.00725	76.69
0.04019	0.00928	165.15	-0.00586	72.85
		25°C		
0.6176	0.12338	176.16	-0.05128	349.47
0.4705	0.09686	174.86	-0.04245	320.71
0.3350	0.07091	173.64	-0.03254	294.19
0.2153	0.04674	172.41	-0.02238	267.83
0.1031	0.02296	170.97	-0.01140	242.12
0.04971	0.01123	169.69	-0.00552	239.31
0.04019	0.00909	169.91	-0.00455	231.29
		40°C		
0.6176	0.12086	180.14	-0.04650	397.38
0.4705	0.09489	178.90	-0.03799	376.05
0.3350	0.06936	178.11	-0.02938	350.27
0.2153	0.04565	177.29	-0.02021	327.74

Table 4.2. Continued

m mol kg^{-1}	$d-d_w^\circ$ g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_pd/(c_{pw}^\circ d_w^\circ)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		40°C		
0.1031	0.02245	175.75	-0.01063	290.03
0.04019	0.00893	173.63	-0.00467	230.79
		55°C		
0.6176	0.12102	181.12	-0.04576	402.51
0.4705	0.09444	179.70	-0.03552	398.61
0.3350	0.06892	179.23	-0.02587	396.73
0.2153	0.04541	178.16	-0.01911	349.07
0.1031	0.02228	177.08	-0.01001	316.34
0.04019	0.000882	175.97	-0.00446	258.19

Table 4.3. Relaxation contributions to heat capacities of Na_2H_2EDTA (aq)

Ionic Strength mol kg^{-1}	$C_{p,\phi}^{rel}$ J K^{-1} mol^{-1}	$C_{p,\phi}^{exp}$ J K^{-1} mol^{-1}	$C_{p,\phi}^{exp}$-$C_{p,\phi}^{rel}$ J K^{-1} mol^{-1}
		10°C	
0.23597	4.20	180.73	176.53
0.18651	4.20	152.89	148.68
0.13421	4.21	122.40	118.19
0.089736	4.22	93.64	89.42
0.043808	4.26	62.06	57.80
0.021974	4.34	42.50	38.16
		25°C	
0.23597	4.82	289.19	284.36
0.18651	4.83	275.07	270.24
0.13421	4.83	253.21	248.38
0.089736	4.85	229.11	224.27
0.043808	4.89	203.83	198.95
0.021974	4.96	188.12	183.15

Table 4.3. Continued

Ionic Strength mol kg^{-1}	$C_{p,\phi}^{rel}$ J K^{-1} mol^{-1}	$C_{p,\phi}^{exp}$ J K^{-1} mol^{-1}	$C_{p,\phi}^{exp}$-$C_{p,\phi}^{rel}$ J K^{-1} mol^{-1}
		40°C	
0.23388	5.43	360.82	355.39
0.20731	5.43	362.55	357.12
0.18285	5.43	353.11	347.68
0.15638	5.44	345.32	339.88
0.13320	5.44	340.09	334.65
0.11147	5.45	334.74	329.29
0.087584	5.45	318.40	312.95
		55°C	
0.23190	6.01	427.55	421.54
0.20576	6.01	420.54	414.53
0.18164	6.01	425.87	419.86
0.15549	6.02	411.97	405.95
0.13255	6.02	381.22	375.20
0.11102	5.45	359.55	354.11
0.11262	6.02	389.34	383.32
0.064451	5.47	353.29	347.82
0.043808	5.49	343.69	338.20
0.043808	5.49	326.45	320.95

Table 4.4 Standard state and excess property parameters for Na_2H_2EDTA (aq)

	$q_{i,1}$	$q_{i,2}$	$q_{i,3}$
		$C_{p,\phi}$ ($J K^{-1} mol^{-1}$)	
C_p°	3.826×10^3	-1.660×10^5	-7.175
B_C	-3.970×10^1	0.9157	—
C_C	1.184×10^4	-7.620×10^1	1.209×10^{-2}
		V_ϕ /($cm^3 mol^{-1}$)	
V°	1.283×10^2	-2.218×10^3	1.546×10^{-1}
B_V	89.56	-2.833×10^{-1}	—
C_V	4.373×10^2	-2.956	4.997×10^{-3}

Table 4.5 Standard state and excess property parameters for $Na_2CuEDTA$ (aq)*

	$q_{i,1}$	$q_{i,2}$	$q_{i,3}$
		$C_{p,\phi}$/(J $K^{-1}mol^{-1}$)	
C_p°	2.385×10^3	-1.136×10^5	-3.909
B_C	5.511×10^2	-1.615	-
		V_ϕ /(cm^3 mol^{-1})	
V°	2.493×10^2	-4.806×10^3	-1.221×10^{-1}
B_V	1.876×10^1	-5.460×10^{-2}	-

* Here C_v and C_c were set to zero, so that linear curve fitting results were achieved.

Table 4.6. Standard partial molar properties of Na_2H_2EDTA (aq) and $Na_2CuEDTA$ (aq)[*]

Temp. / °C	V°(isothermal) / (cm^3 mol^{-1})[1]	V° (global) / (cm^3 mol^{-1})[2]	C_p°(isothermal) / (J K^{-1} mol^{-1})[1]	C_p° (global) / (J $K^{-1}$$mol^{-1}$)[2]
		Na_2H_2EDTA (aq)		
10	152.14(2.33)	148.3 ± 5.1	26.66(11.4)	9 ± 29
25	153.44(0.49)	153.9 ± 1.4	149.36(5.56)	148 ± 17
40	153.45(2.08)	158.7 ± 4.6	225.53(41.49)	227 ± 89
55	161.74(0.68)	163.0 ± 1.8	271.85(33.48)	266 ± 73
		$Na_2CuEDTA$ (aq)		
10	163.19(0.32)	163.2 ± 5.6	45.99(5.64)	59 ± 25
25	168.08(0.07)	168.5 ± 5.1	188.89(3.19)	169 ± 20
40	172.88(0.30)	172.1 ± 5.6	236.42(7.47)	239 ± 29
55	173.70(0.41)	174.5 ± 5.8	267.75(28.04)	280 ± 70

[1] Values in parentheses listed for the isothermal fits are equal to one standard deviation.

[2] *Error limits in* V° *and* C_p° *are* 2σ*(isothermal fit) + estimated uncertainty from* systematic errors. The overall uncertainty for global fits of C_p° and V° of Na_2H_2EDTA(aq) are ±33.13 J K^{-1} mol^{-1} and ±2.08 cm^3 mol^{-1} respectively, the uncertainty for global fits of C_p° and V° of $Na_2CuEDTA$(aq) are ±40.29 J K^{-1} mol^{-1} and ±2.28 cm^3 mol^{-1} respectively.

Table 4.7 Comparison of standard partial molar properties of Na_2H_2EDTA (aq) at 25°C

Experiment	C_p° J K^{-1} mol^{-1}	V° cm^3 mol^{-1}
Hovey and Tremaine (1985)	168.8 ± 1.0	154.31 ± 0.08
Hovey et al. (1988)	166.6 ± 0.7	153.87 ± 0.11
This work*	149.4 ± 5.6	153.44 ± 0.49

* Standard partial molar properties are isothermal curve fitting results.

Table 4.8. Standard partial molar properties of species: H_2EDTA^{2-} (aq) and $CuEDTA^{2-}$ (aq)*

Temp. / °C	Na^+(aq)	Cl^-(aq)	H_2EDTA^{2-} (aq)	$CuEDTA^{2-}$ (aq)
		$C_p°$/ JK^{-1} mol^{-1}		
10	21.8	-148.4	-35 ± 29	15 ± 26
25	42.2	-126.6	64 ± 18	85 ± 21
40	52.8	-115.5	122 ± 89	133 ± 29
55	49.5	-111.7	167 ± 73	181 ± 70
		V° / cm^3 mol^{-1}		
10	-2.21	17.15	152.7 ± 5.1	167.6 ± 5.7
25	-1.27	17.89	156.4 ± 1.5	171.0 ± 5.2
40	-0.44	17.91	159.6 ± 4.6	173.0 ± 5.6
55	0.12	17.81	162.7 ± 1.8	174.2 ± 5.8

*$C_p°$ and V° for H_2EDTA^{2-} (aq) and $CuEDTA^{2-}$ (aq) are from global fits of $C_p°$ and V° of Na_2H_2EDTA(aq) and $Na_2CuEDTA$(aq) after subtracting the $C_p°$ and V° for $2Na^-$(aq). The values for Na^+(aq) and Cl^-(aq) reported here were taken from Equation 3.7 to Equation 3.12, the uncertainties for those values are ± 0.3 cm mol^{-1} for V° and ± 3 J K^{-1} mol^{-1} for $C_p°$.

Table 4.9 Temperature dependence of the stability constant for the EDTA copper complexation reaction (Equation 4.10).

t /°C	log K_T	t /°C	log K_T	t /°C	log K_T
25	3.137 ± 0.094	105	3.695 ± 0.125	185	4.562 ± 0.269
30	3.162 ± 0.094	110	3.740 ± 0.130	190	4.630 ± 0.281
35	3.189 ± 0.095	115	3.785 ± 0.136	195	4.701 ± 0.296
40	3.217 ± 0.095	120	3.832 ± 0.142	200	4.774 ± 0.310
45	3.247 ± 0.095	125	3.879 ± 0.149	205	4.849 ± 0.325
50	3.278 ± 0.096	130	3.928 ± 0.156	210	4.927 ± 0.341
55	3.310 ± 0.097	135	3.978 ± 0.164	215	5.008 ± 0.357
60	3.344 ± 0.098	140	4.030 ± 0.172	220	5.092 ± 0.374
65	3.379 ± 0.100	145	4.083 ± 0.181	225	5.180 ± 0.392
70	3.415 ± 0.101	150	4.137 ± 0.190	230	5.271 ± 0.410
75	3.452 ± 0.103	155	4.193 ± 0.199	250	5.675 ± 0.491
80	3.490 ± 0.106	160	4.250 ± 0.210	260	5.908 ± 0.539
85	3.529 ± 0.109	165	4.309 ± 0.221	270	6.166 ± 0.591
90	3.569 ± 0.112	170	4.369 ± 0.232	280	6.454 ± 0.650
95	3.610 ± 0.116	175	4.432 ± 0.244	290	6.780 ± 0.716
100	3.652 ± 0.120	180	4.496 ± 0.256	300	7.154 ± 0.791

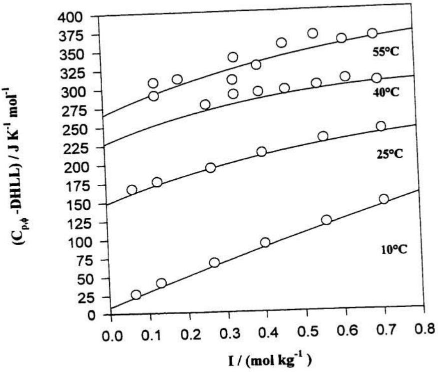

Fig. 4.1 Apparent molar heat capacities of Na_2H_2EDTA (aq), after subtracting the Debye-Hückel limiting law.

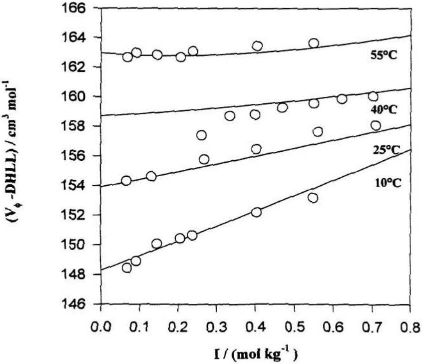

Fig. 4.2 Apparent molar volumes of Na_2H_2EDTA *(aq)*, after subtracting the Debye-Hückel limiting law.

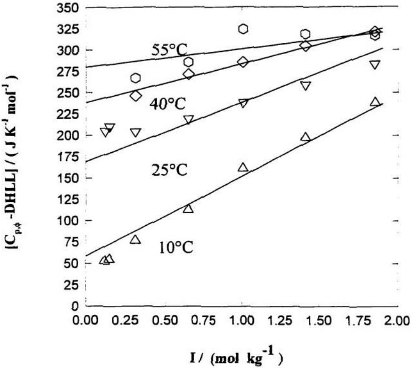

Fig. 4. 3. Apparent molar heat capacities of $Na_2CuEDTA$ (aq), after subtracting the Debye-Huckel limiting law. The solid line is result of global fitting for all the experimental data.

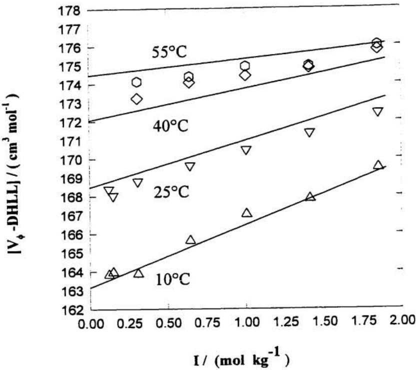

Fig. 4. 4. Apparent molar volumes of $Na_2CuEDTA$ (aq), after subtracting the Debye-Huckel limiting law. The solid line is result of global fitting for all the experimental data.

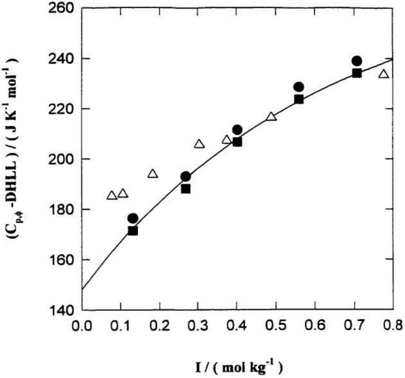

Fig. 4.5 Comparison of apparent molar heat capacities of H_2Na_2EDTA (aq) at 25°C.

● , this work.

■ , this work, after subtracting relaxation contributions.

△ , data reported by Hovey et al. in 1988.

—— , least squares curve fit for our data after subtracting relaxation contributions.

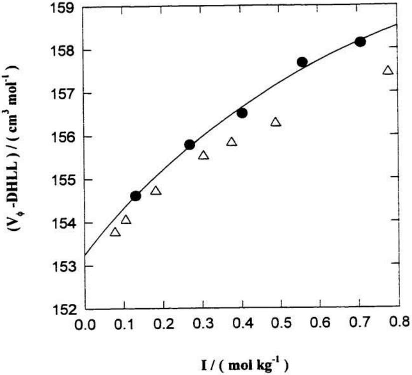

Fig. 4.6 Comparison of apparent molar volume of H_2Na_2EDTA (aq) at 25°C: ● , this work;
△ , data reported by Hovey et al. (1988);
—— , least squares curve fit for our isothermal data at 25°C.

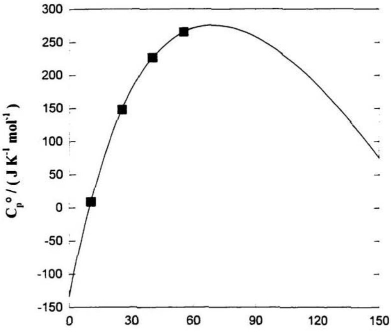

Fig. 4.7 Temperature dependence of standard partial molar heat capacities of Na_2H_2EDTA *(aq)*. *The solid* line is the least squares curve fit of the Holmes-Mesmer equation.

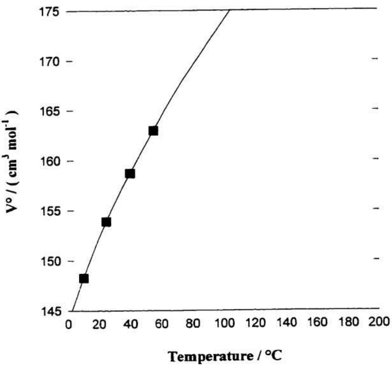

Fig. 4.8 Temperature dependence of standard partial molar volumes of Na_2H_2EDTA (aq). The solid line is the least squares curve fit of the Holmes-Mesmer equation.

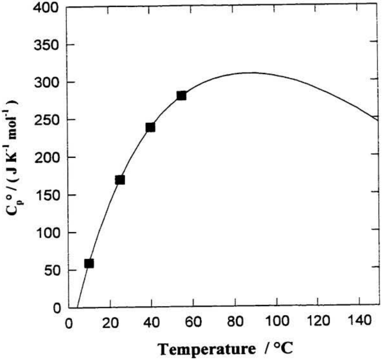

Fig. 4.9. Temperature dependence of standard partial molar heat capacities of $Na_2CuEDTA$ (aq). The solid line is the least squares curve fit of the Holmes-Mesmer equation.

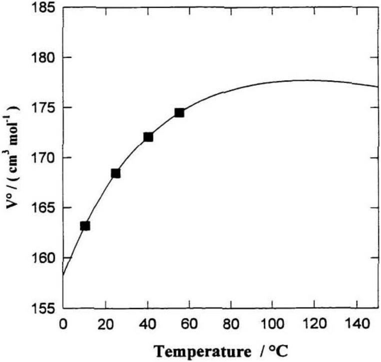

Fig. 4.10. Temperature dependence of standard partial molar volumes of $Na_2CuEDTA$ (aq). The solid line is the least squares curve fit of the Holmes-Mesmer equation.

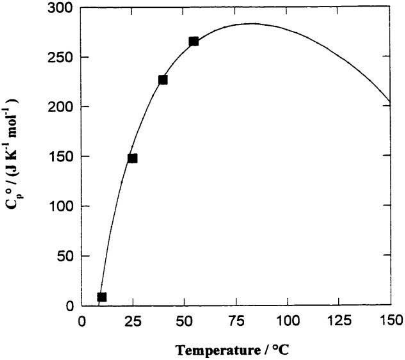

Fig. 4.11. Temperature dependence of standard partial molar heat capacities of Na_2H_2EDTA (aq). The solid line is the least squares curve fit of the HKF equation.

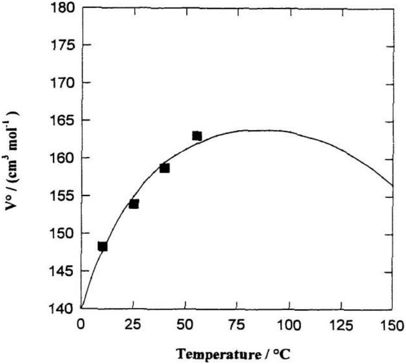

Fig. 4.12. Temperature dependence of standard partial molar volumes of Na_2H_2EDTA (aq). The solid line is the least squares curve fit of the HKF equation.

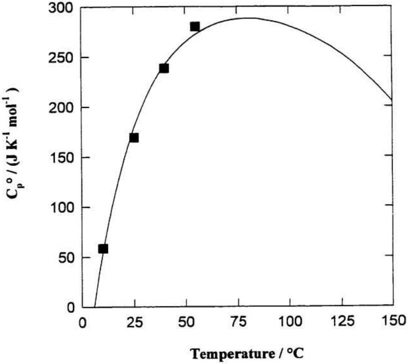

Fig. 4.13. Temperature dependence of standard partial molar heat capacities of $Na_2CuEDTA$ (aq). The solid line is the least squares curve fit of the HKF equation.

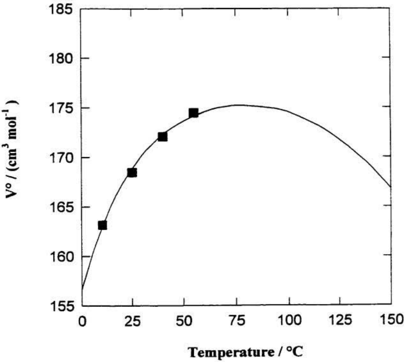

Fig. 4.14. Temperature dependence of standard partial molar volumes of $Na_2CuEDTA$ (aq). The solid line is the least squares curve fit of the HKF equation.

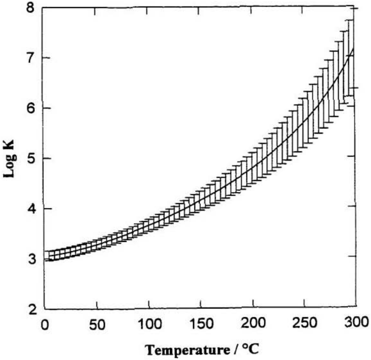

Fig 4.15 Temperature dependence of equilibrium constants for the reaction :

$Cu(ClO_4)_2(aq) + Na_2H_2EDTA(aq) = Na_2CuEDTA(aq) + 2HClO_4(aq)$.

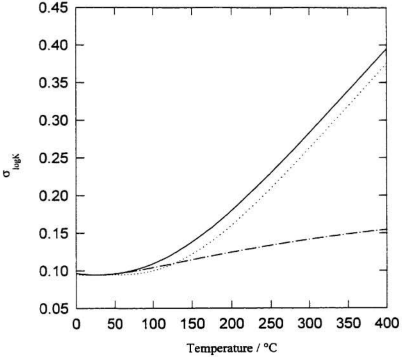

Fig 4.16 Contributions to uncertainty of log K for $\sigma_{\Delta H^\circ}$ and $\sigma_{\Delta Cp^\circ}$

—·— , contribution of $\sigma_{\Delta H^\circ}$ ········ , contribution of $\sigma_{\Delta Cp^\circ}$

—— , $\sigma_{\log K}$ (Equation 4.13).

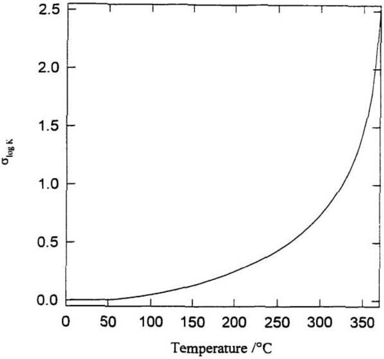

Fig 4.17 Contributions to uncertainty of log K from ΔC_p°(Born) ($\mp$20% of ω Values).

Chapter 5

THERMODYNAMICS OF NTA(aq) : APPARENT AND STANDARD PARTIAL MOLAR HEAT CAPACITIES AND VOLUMES OF $Na_2HNTA(aq)$, $Na_3NTA(aq)$ AND NaCuNTA(aq).

5.1. Introduction

The many applications of the organic chelating agent nitrilotriacetic acid (NTA) include its use in aqueous solution at ambient and moderately high temperatures for dissolving metal oxides and scales, in the cleaning of power station boilers, decontamination of radioactive nuclear reactor coolant system components, and the cleanup of heavy metals from contaminated soil. To model the chemical processes that occur in such applications, and to develop a basic understanding of complexation reactions occurring at elevated temperatures, it is essential to develop a thermodynamic data base for the complexation equilibria and hydrolysis reactions of NTA. However, many of the applications involve temperatures considerably higher than 25°C for which there are no equilibrium constants available. Equilibrium constants for high temperature solutions can be calculated by combining known stability constants and enthalpies of complexation at 25°C from the literature with standard partial molar heat capacities and volumes, as outlined in Chapter 2. However, no values of $C_{p,\phi}$ and V_{ϕ} for NTA and its complexes have been reported in the literature.

This chapter describes the determination of apparent molar heat capacities and volumes of $Na_2HNTA(aq)$, $Na_3NTA(aq)$ and NaCuNTA(aq). The measurements were made as a function of molality in Picker flow microcalorimeters and vibrating tube densimeters at temperatures from 10 to 55°C. The partial molar properties were also treated by a simple Born model to derive the temperature dependence of standard partial molar properties for NTA at very high temperatures. The results are used to calculate temperature dependent parameters for the equilibria between $HNTA^{2-}(aq)$, $NTA^{3-}(aq)$, and the complexes of NTA with $Cu^{2+}(aq)$.

5.2. Experimental

Standard solutions of NaCl were prepared by mass after drying the salt (BDH certified, ACS) at 110°C for about 24 hours, and used without further purification. All stock solutions were prepared from nanopure water with a final resistance of 17 MΩ cm or greater. Aldrich ("certified 99+%") reagent grade nitrilotriacetic acid disodium salt Na_2 HNTA was dried at 55°C for seven days until the samples reached constant weight. The stock solutions of $Na_2HNTA(aq)$ were prepared by mass from the salt without further purification.

The stock solutions of $Na_3NTA(aq)$ were prepared by mass from Aldrich certified 99+% reagent grade nitrilotriacetic acid, trisodium salt monohydrate ($Na_3NTA \cdot H_2O$) without further purification. The hydration number was determined to be 1.020 ± 0.010 by drying to constant weight at 135°C. The calculations are based on the stoichiometric formula ($Na_3NTA \cdot 1.00\ H_2O$).

The salt NaCuNTA was synthesized from Aldrich Certified $Cu(OH)_2$, and Aldrich Certified Na_2HNTA, both without further purification, by the same method used for Na_2H_2EDTA. Briefly, 678.12 g aqueous solution of 0.79318 mol kg^{-1} Na_2HNTA. was added to an excess amount (1160.99g) of $Cu(OH)_2$, stirred and heated at 70°C for about 24 hrs. The excess solid $Cu(OH)_2$ was removed by filtration, and the aqueous NaCuNTA was crystallized by a method derived from Vogel(1989). In this method, ethanol (95%) was slowly added to the liquid phase until a precipitate appeared. After filtering off the precipitate and discarding it, an equal volume of ethanol was added dropwise to the filtrate over a period of several hours with vigorous stirring. Ethanol was again added continuously to precipitate more NaCuNTA. The blue green crystalline product was washed with ethanol and then recrystallized again by the same procedure. The recrystallized product was dried in bulk in an oven (5 days at 80°C) and was then used to prepare the stock solution. The loss of mass after vacuum dehydration at 135°C confirmed the number of waters of hydration which is 1.467. The stock solution of NaCuNTA(aq) was prepared by mass from the NaCuNTA·(1.467)H_2O salt without further purification.

All apparent molar properties measured were corrected for a very slight heat loss by the method described by Desnoyers et al. (1976). The heat loss factor was obtained daily by measuring the apparent molar heat capacity and relative density of the standard NaCl solution. All the heat loss factors are presented in Appendix I.

The densities of all solutions were measured relative to water with a Sodev-03D vibrating tube densimeter equipped with platinum cells. The cells were calibrated daily with water and a standard solution of sodium chloride. The heat capacities were measured relative to water with a Picker flow microcalorimeter, Sodev Model CP-C, also equipped with platinum cells. Temperature was controlled with a Sodev Model CT-L bath and measured with a thermistor set in a well deep in the coolant circuit. The density and specific heat capacity of water and NaCl solution from 10 to 55°C were taken from the compilation by Archer and Wang(1990).

5.3. Results

5.3.1. Experimental Apparent Molar Properties

Tables 5.1, 5.2 and 5.3 list the experimentally determined relative densities ($d-d_w^\circ$) and heat capacity ratios [$c_p d/(c_{pw}^\circ d_w^\circ)-1$] for all of the aqueous solutions at each temperature. The experimental parameters and the corresponding values of V_ϕ and $C_{p,\phi}$ for Na_2HNTA (aq), Na_3NTA (aq) and NaCuNTA (aq) are tabulated in Tables 5.1, 5.2 and 5.3. Values for d_w° and c_{pw}° were taken from the compilation by Hill (1990), and these are listed in Table 3.2.

5.3.2. Relaxation Contributions to Heat Capacities of Mixed Electrolyte Solutions

The interpretation of the apparent molar properties of Na_2HNTA (aq) is somewhat complicated by chemical equilibrium effects. Stoichiometric solutions contain small concentrations of the ions $HNTA^{2-}$ (aq) and H_2NTA^- (aq), which form according to the equilibria

$$HNTA^{2-}(aq) \rightleftharpoons NTA^{3-}(aq) + H^{+}(aq) \qquad (5.1)$$

and

$$HNTA^{2-}(aq) + H^{+}(aq) \rightleftharpoons H_2NTA^{-}(aq) \qquad (5.2)$$

The experimental apparent molar heat capacities, $C_{p,\phi}(Na_2HNTA,aq)$, are considered to be the sum of the contribution of each species in solution according to Young's rule, plus an additional term to correct for the shift in the degree of dissociation caused by the "chemical relaxation" effect (Barbero et al., 1983; Mains et al., 1984; Woolley and Hepler, 1977), as discussed in Sections 2.2.4 and 2.2.5. The expression is

$$\begin{aligned} C_{p,\phi}^{exp}(Na_2HNTA,aq) &= (1-\alpha-\beta)C_{p,\phi}(HNTA^{2-},aq) + \alpha\, C_{p,\phi}(NTA^{3-},aq) \\ &\quad + \beta\, C_{p,\phi}(H_2NTA^{-},aq) + (\alpha-\beta)C_{p,\phi}(H^{+},aq) \qquad (5.3) \\ &\quad + 2\, C_{p,\phi}(Na^{+},aq) + C_{p,\phi\alpha}^{rel} + C_{p,\phi\beta}^{rel} \end{aligned}$$

Here, α and β are the degree of dissociation to form NTA^{3-} (aq) and H_2NTA^{-} (aq), respectively. The chemical relaxation contributions are given by

$$C_{p,\phi\alpha}^{rel} = \overline{\Delta H_1}\ (\partial\alpha/\partial T)_m \quad (5.4)$$

$$C_{p,\phi\beta}^{rel} = -\overline{\Delta H_2}\ (\partial\beta/\partial T)_m \quad (5.5)$$

Further, in dilute solutions that are only slightly dissociated

$$(\partial\alpha\ /\ \partial T)_m = \alpha\ \Delta H^\circ_1\ /\ (2RT^2) \quad (5.6)$$

$$(\partial\beta\ /\ \partial T)_m = \beta\ -\Delta H^\circ_2\ /\ (RT^2) \quad (5.7)$$

where $\Delta H_1°$ and $\Delta H_2°$ refer to the enthapy of ionization to form $H_2NTA^-(aq)$ and $NTA^{3-}(aq)$ from $HNTA^{2-}(aq)$. Martell and Smith (1982) list critically compiled values of log K = - 9.46 for reaction 5.1 and log K = 2.48 for reaction 5.2 at 0.1 mol kg^{-1} ionic strength, from which we calculated the values for α and β, which are all of the order 2 - 4×10^{-4}. These are presented in Appendix II. These values for α and β were used with enthalpy data for reactions 5.2 and 5.3 from the compilation by Martell and Smith, (1982) which are $\Delta H^\circ = 19.25$ kJ mol^{-1} and 0.837 kJ mol^{-1}at ionic strength equal to 0.1 respectively, to calculate $C_{p.\phi\alpha}^{rel}$ and $C_{p.\phi\beta}^{rel}$. These are also summarized in Appendex II, along with the final values for the species $C_{p.\phi}$ (2 Na^+ + $HNTA^{2-}$, aq). Assuming $\Delta H = \Delta H^\circ = \Delta H$ (0.1m), the relaxation contributions are all of the order of 1×10^{-2} J K^{-1} mol^{-1}. The relaxation contributions to the heat capacity of Na_2HNTA (aq) are tabulated in Table 5.4.

Similar calculations for the relaxation contribution to $C_{p.\phi}$ (Na^+ + $CuNTA^-$, aq) were carried out for the equilibria

$$CuNTA^-\ (aq)\ =\ NTA^{3-}\ (aq)\ +\ Cu^{2+}\ (aq) \tag{5.8}$$

$$CuNTA^-\ (aq)\ +\ NTA^{3-}\ (aq)\ =\ Cu(NTA)_2^{4-}(aq) \tag{5.9}$$

The values of α' and β', are the degree of dissociation to form Cu^{2+} (aq) and $Cu(NTA)_2^{4-}$ (aq), respectively. Using the values of log K and ΔH° from the compilation by Christensen and Izatt (1983), values for α' and β', and the relaxation contributions to the heat capacities were calculated and are summarized in Appendix II. These chemical relaxation contributions are less than 0.1 J K^{-1}

mol^{-1} and are also negligible.

For Na_3NTA (aq), only one equilibrium

$$NTA^{3-}\,(aq) + H_2O \rightleftharpoons HNTA^{2-}\,(aq) + OH^{-}(aq) \tag{5.10}$$

was considered. The expression for apparent molar heat capacities is

$$\begin{aligned} C_{p,\phi}^{\exp}\,(Na_3NTA,aq) &= (1-\alpha')\, C_{p,\phi}^{sp}\,(Na_3NTA,aq) \\ &\quad + \alpha'\, C_{p,\phi}^{sp}\,(Na_2HNTA,aq) \\ &\quad + \alpha'\, C_{p,\phi}^{sp}\,(NaOH,aq) + C_{p,\phi}^{rel} \end{aligned} \tag{5.11}$$

where α' is the degree of dissociation to form $HNTA^{2-}$(aq) and OH^- (aq). From the expression above, values for the species $C_{p,\phi}$ [$3Na^+$(aq) + NTA^{3-}(aq)] were calculated, these are listed in Table 5.5. Taking $pK_w = 13.999$ as the "best" value at 25°C (Olofsson and Hepler, 1975), the value of the equilibrium constant for reaction 5.10 is $\log K = (9.65 - 13.999) = -4.349$. The degree of dissociation to form $HNTA^{2-}$ (aq), α', and the relaxation contributions to the heat capacities are calculated and summarized in Table 5.5. The correction to $C_{p,\phi}$ for speciation ranges from 1 to 8 J K^{-1} mol^{-1}.

The effect of partial dissociation on V_ϕ is much less pronounced, in part because there is no contribution from chemical relaxation.

Apparent molar properties of strong electrolytes can be represented to moderate concentrations by the Guggenheim form of the extended Debye-Hückel equation, Equation 2.24 (Hovey et al., 1989; Millero, 1979). Figures 5.1 to 5.6 present the apparent molar properties of $Na_2HNTA(aq)$, $NaCuNTA(aq)$ and $Na_3NTA(aq)$ after subtracting the Debye-Hückel limiting law and chemical relaxation contributions. Values for the Debye-Hückel limiting slopes were taken from the compilation by Archer and Wang (1990).

5.3.3. Standard Partial Molar Properties.

Table 5.6 presents the standard partial molar volumes and heat capacities for aqueous Na_2HNTA (aq), Na_3NTA (aq) and NaCuNTA (aq), obtained by fitting Equation 2.24 to the experimental values of apparent molar properties from 10 to 55 °C.

The temperature dependence of Y_ϕ°, B_Y and C_Y was represented by the *three parameter* expression used in previous studies (Holmes and Mesmer, 1983; Tremaine et al., 1986), presented in Chapter 3 as Equation 3.13. The fitted values for the standard state properties and the adjustable constants were determined by a non-linear least squares analysis of the data in our study, using the Marquardt-Levenberg algorithm in the commercial software SigmaPlot© with temperature and molality as the independent variables. Because the uncertainties for $C_{p,\phi}$ and V_ϕ are larger at lower molalities, a statistical weight of 5 to 10 percent was given to the apparent molar property data for molalities below 0.1 mol kg^{-1}. The standard state and excess parameters are tabulated in Table 5.7, 5.8, and 5.9.

Because no other experimental data for V° and C_p° for $Na_2HNTA(aq)$, $NaCuNTA(aq)$, and $Na_3NTA(aq)$ have been reported, it was assumed that *statistical and systematic errors for* $Na_2HNTA(aq)$ *are the same as those for* $Na_2H_2EDTA(aq)$, which we estimated as $(2\sigma + 6)$ J K^{-1} mol^{-1} for C_p° and $(2\sigma + 0.43)$ cm^3 mol^{-1} for V°. For $NaCuNTA(aq)$ and $Na_3NTA(aq)$, it was assumed that the statistical and systematic errors are the same as those for *NaCuEDTA(aq)*, which were estimated as $(2\sigma + 14)$ J K^{-1} mol^{-1} for C_p° and $(2\sigma + 5.00)$ cm^3 mol^{-1} for V° .

For $Na_2HNTA(aq)$, the statistical errors for C_p° from the isothermal fits are $2\sigma = 4.46, 16.38, 14.2, 19.92$, and 63.34 J K^{-1} mol^{-1} at 10, 15, 25, 40, 55°C. For V° the statistical errors are $2\sigma = 0.46, 1.18, 0.44, 0.62$ and 0.60 cm^3 mol^{-1} at 10, 15, 25, 40, and 55°C respectively.

For NaCuNTA(aq), the statistical errors for C_p° are $2\sigma = 35.88, 47.52, 47.14$, and 23.98 J K^{-1} mol^{-1} at 10, 25, 40, 55°C respectively. For V° statistical errors are $2\sigma = 5.96, 0.14, 3.02$, and 0.20 cm^3 mol^{-1} at 10, 25, 40, and 55°C respectively.

For Na_3NTA(aq), the statistical errors for C_p° are $2\sigma = 117.38, 11.02, 84.10$, and 44.94 J K^{-1} mol^{-1} at 10, 25, 40, 55°C respectively. For V° statistical errors are $2\sigma = 1.50, 0.26, 1.20$, and 1.10 cm^3 mol^{-1} at 10, 25, 40, and 55°C respectively.

Values for the conventional single-ion properties of $HNTA^{2-}$(aq), NTA^{3-}(aq) and $CuNTA^-$(aq) are tabulated in Table 5.10.

5.4. Discussion

5.4.1. Temperature Dependence of Standard Partial Molar Properties

The Helgeson-Kirkham-Flowers semi-theoretical equation (Helgeson and Kirkham, 1974, 1976; Helgeson et al., 1981; Shock et al., 1992) have provided a means by which low-temperature stand-state thermodynamic properties of aqueous ions can be extrapolated to higher temperatures. The "HKF equation of state" has been used with success to extrapolate the standard partial molar properties of aqueous electrolytes to temperatures as high as 300°C (Tremaine et al., 1986). The revised form of the HKF equations are Equations 2.55 - 2.56.

In the HKF equation, the Born coefficient for an electrolyte, ω, can be calculated according to $\omega_j = \omega_j^{abs} - Z_j\, \omega_{H+}^{abs}$, here Z_j is the charge of ion. $\omega_j^{abs} = 6.94657 \times 10^5 \times Z_j^2 / r_{e,j}$, and $\omega_{H+}^{abs} = 2.2539 \times 10^5$ (J mol^{-1}).

It was assumed that the crystallographic radius for NTA complex can be used to calculate the effective radii for all the NTA(aq) species. The crystal structure for the NaCaNTA complex has been reported by Barnett and Uchtman (1979). The crystallographic radius was taken to be the distance between the metal ion (Ca^{2+}) and the outermost oxygen atom of the NTA molecule, plus the van der Waals radius of oxygen to yield $r_{eff} = 4.3162$Å. By assuming that the crystallographic radius of CaNTA complex is equal to the effective radius for the CuNTA complex and the NTA aqueous species $HNTA^{2-}$ (aq) and NTA^{3-}(aq), the effective radius and thus the Born coefficient ω can be calculated. Values of X and Q were taken from the compilations of Helgeson and Kirkham (1974, 1976).

Values of $C_p°$ and $V°$ for aqueous Na_2HNTA, NaCuNTA and Na_3NTA from 10 to 55°C were extrapolated up to 300°C by fitting the parameters in the HKF equations. The results are plotted in Figures 5.7 - 5.12. The parameters for HKF equation for NTA complex and aqueous species are presented in Appendix III.

Table 5.1. Experimental apparent molar volumes (V_ϕ) and heat capacities ($C_{p,\phi}$) of Na_2HNTA(aq) at temperatures from 10 to 55°C.

m mol kg^{-1}	d-d$_w$° g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_p d/(c_{pw}° d_w°)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		10°C		
0.57596	0.073216	100.62	-0.04481	76.64
0.48526	0.062542	99.97	-0.04018	55.04
0.35147	0.046330	98.71	-0.03207	17.95
0.20688	0.027930	97.37	-0.02117	-29.48
0.099213	0.013649	96.21	-0.01115	-72.59
0.072050	0.010017	95.12	-0.008338	-89.84
		15°C		
0.57596	0.072200	102.34	-0.04188	105.75
0.48526	0.061795	101.47	-0.03794	80.99
0.35147	0.045642	100.63	-0.03011	49.55
0.20688	0.027684	98.54	-0.01988	1.76
0.099213	0.013542	97.26	-0.01060	-44.74
0.072050	0.009905	96.64	-0.007941	-60.42
		25°C		
0.57596	0.071053	104.28	-0.03783	143.64
0.48526	0.060717	103.63	-0.03366	127.36
0.35147	0.044936	102.57	-0.02636	102.70
0.20688	0.027086	101.35	-0.01708	70.02
0.099213	0.013229	100.35	-0.009027	34.12
0.072050	0.0096523	100.08	-0.006579	32.68
0.072050	0.0097112	99.26	-0.006525	32.41

Table 5.1 Continued

m mol kg^{-1}	$d-d_w^\circ$ g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_p d/(c_{pw}^\circ d_w^\circ)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		40°C		
0.57596	0.069832	106.32	-0.03405	178.73
0.48526	0.059611	105.82	-0.02969	169.98
0.35147	0.044113	104.81	-0.02305	150.43
0.20688	0.026616	103.50	-0.01464	126.98
0.099213	0.012987	102.65	-0.007861	91.14
0.072050	0.0094921	102.16	-0.005677	91.90
		50°C		
0.57596	0.068769	108.09	-0.03202	198.77
0.48526	0.058724	107.56	-0.02850	185.08
0.35147	0.043377	106.80	-0.02253	162.21
0.20688	0.026194	105.40	-0.01421	141.09
0.099213	0.012787	104.52	-0.008218	80.86
0.072050	0.0093204	104.39	-0.006074	75.12

Table 5.2. Experimental apparent molar volumes (V_ϕ) and heat capacities ($C_{p,\phi}$) of NaCuNTA(aq) at temperatures from 10 to 55°C.

m mol kg^{-1}	d-d$_w^\circ$ g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_p d/(c_{pw}^\circ d_w^\circ)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		10°C		
0.60845	0.098842	102.09	-0.03955	138.51
0.47018	0.078326	100.20	-0.03408	101.82
0.34250	0.057921	99.74	-0.02716	74.28
0.21965	0.037971	98.04	-0.01870	46.31
0.10714	0.018943	96.00	-0.009911	10.57
		25°C		
0.60845	0.097237	104.51	-0.03240	198.90
0.47018	0.076621	103.58	-0.02695	180.49
0.34250	0.056882	102.55	-0.02080	164.65
0.21965	0.037174	101.44	-0.01456	139.50
0.10714	0.018471	100.19	-0.008186	94.75
		40°C		
0.60845	0.095286	107.42	-0.02756	243.74
0.47018	0.075107	106.49	-0.02263	230.32
0.34250	0.055774	105.47	-0.01763	214.36
0.21965	0.036579	103.83	-0.01187	199.56
0.10714	0.018100	103.32	-0.006706	163.91
0.046573	0.0079446	102.71	-0.002690	183.28
		55°C		
0.47018	0.074805	106.78	-0.01857	266.76
0.21965	0.036209	105.11	-0.01090	220.88
0.10714	0.018004	103.79	-0.006191	183.47
0.052750	0.0089719	102.64	-0.002893	192.49

Table 5.3. Experimental apparent molar volumes (V_ϕ) and heat capacities ($C_{p,\phi}$) of Na_3NTA(aq) at temperatures from 10 to 55°C.

m mol kg^{-1}	$d-d_w^\circ$ g cm^{-3}	V_ϕ cm^3 mol^{-1}	$c_pd/(c_{pw}^\circ d_w^\circ)-1$	$C_{p,\phi}$ J K^{-1} mol^{-1}
		10°C		
0.87622	0.12467	118.09	-0.03607	304.59
0.55346	0.083536	114.58	-0.03250	218.56
0.38064	0.059331	112.54	-0.02905	138.03
0.18305	0.029877	108.62	-0.02008	-13.81
0.089197	0.014976	105.60	-0.009928	-28.46
		25°C		
1.1352	0.15254	122.06	-0.03497	362.15
0.87622	0.12233	120.67	-0.03296	329.11
0.55346	0.081440	118.24	-0.02670	277.95
0.38064	0.057741	116.57	-0.02125	242.15
0.18305	0.028914	113.72	-0.01245	183.72
0.089197	0.014420	111.67	-0.006884	139.63
0.070612	0.011490	110.95	-0.005617	127.31
		40°C		
0.87622	0.11692	126.78	-0.02882	372.95
0.55346	0.079637	121.36	-0.02276	319.75
0.38064	0.056376	120.00	-0.01694	303.04
0.18305	0.028249	117.16	-0.009772	257.88
0.089197	0.014067	115.43	-0.004985	242.61
0.070612	0.011213	114.65	-0.003636	258.36
		55°C		
0.87622	0.11913	124.15	-0.02809	363.21
0.55346	0.079176	122.05	-0.02118	332.31
0.38064	0.056047	120.68	-0.01881	281.33
0.18305	0.027511	121.03	-0.009208	283.86

Table 5.4. Contributions of speciation and relaxation to the apparent molar heat capacities of $Na_2HNTA(aq)$'.

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1} mol^{-1}	α $\times 10^4$	$C_{p,\alpha}^{rel} \times 10^2$ J K^{-1} mol^{-1}	β $\times 10^4$	$C_{p\beta}^{rel} \times 10^4$ J K^{-1} mol^{-1}	$C_{p,\phi}-C_{p,tot}^{rel}$ J K^{-1} mol^{-1}
			10°C			
0.57596	76.64	2.103	5.844	2.091	2.197	76.57
0.48526	55.04	2.104	5.847	2.090	2.195	54.98
0.35147	17.95	2.107	5.855	2.087	2.192	17.89
0.20688	-29.48	2.114	5.874	2.080	2.185	-29.54
0.099210	-72.58	2.132	5.925	2.062	2.166	-72.64
0.072050	-89.84	2.146	5.962	2.050	2.153	-89.90
			15°C			
0.57596	105.75	2.265	6.076	2.252	2.284	105.69
0.48526	80.99	2.266	6.079	2.250	2.283	80.93
0.35147	49.55	2.269	6.087	2.247	2.280	49.49
0.20688	1.76	2.276	6.107	2.240	2.272	1.70

Table 5.4. Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1} mol^{-1}	α $\times 10^4$	$C_{p,\alpha}^{rel} \times 10^2$ J K^{-1} mol^{-1}	β $\times 10^4$	$C_{p\beta}^{rel} \times 10^4$ J K^{-1} mol^{-1}	$C_{p,\phi}$-$C_{p,tol}^{rel}$ J K^{-1} mol^{-1}
			15°C			
0.099210	-44.74	2.296	6.160	2.221	2.253	-44.80
0.072050	-60.42	2.310	6.198	2.207	2.239	-60.48
			25°C			
0.57596	143.64	2.606	6.531	2.591	2.455	143.58
0.48526	127.36	2.608	6.535	2.590	2.454	127.30
0.35147	102.70	2.611	6.543	2.587	2.451	102.64
0.20688	70.02	2.620	6.564	2.578	2.443	69.95
0.099210	34.12	2.642	6.620	2.556	2.422	34.05
0.072050	32.68	2.658	6.661	2.541	2.407	32.62
0.072050	32.41	2.658	6.661	2.541	2.407	32.34

Table 5.4. Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1} mol^{-1}	α $\times 10^4$	$C_{p,\alpha}^{rel} \times 10^2$ J K^{-1} mol^{-1}	β $\times 10^4$	$C_{p\beta}^{rel} \times 10^4$ J K^{-1} mol^{-1}	$C_{p,\phi}$-$C_{p,tol}^{rel}$ J K^{-1} mol^{-1}
			40°C			
0.57596	178.73	3.164	7.187	3.146	2.702	178.66
0.48526	169.98	3.166	7.191	3.144	2.701	169.90
0.35147	150.43	3.170	7.200	3.140	2.697	150.36
0.20688	126.98	3.180	7.223	3.130	2.689	126.91
0.099210	91.14	3.206	7.284	3.104	2.666	91.07
0.072050	91.90	3.226	7.327	3.086	2.650	91.82
			55°C			
0.57596	198.77	3.773	7.806	3.752	2.935	198.69
0.48526	185.08	3.775	7.810	3.750	2.933	185.00
0.35147	162.21	3.780	7.820	3.746	2.930	162.13

Table 5.4. Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1} mol^{-1}	α $\times 10^4$	$C_{p,\alpha}^{rel} \times 10^2$ J K^{-1} mol^{-1}	β $\times 10^4$	$C_{p\beta}^{rel} \times 10^4$ J K^{-1} mol^{-1}	$C_{p,\phi}$-$C_{p,tot}^{rel}$ J K^{-1} mol^{-1}
			55°C			
0.20688	141.09	3.792	7.844	3.734	2.920	141.01
0.099210	80.86	3.823	7.909	3.703	2.896	80.78
0.072050	75.11	3.846	7.956	3.682	2.879	75.04

* α and β are the degree of dissociation. The relaxation contributions were calculated by using enthalpy data from Martell and Smith, assuming $\Delta H = \Delta H° = \Delta H(0.1m)$.

Table 5.5 Contributions of speciation and relaxation to the apparent molar capacities of Na_3NTA (aq).

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1}mol^{-1}	α* ×10^2	$\alpha C_{p,\phi}(Na_2\ HNTA)$ J K^{-1}mol^{-1}	$\alpha C_{p,\phi}(NaOH)$ J K^{-1}mol^{-1}	$C_{p,\alpha}{}^{rel}$* J K^{-1} mol^{-1}	$C_{p,\phi}(Na_3\ NTA)$** J K^{-1} mol^{-1}
			10°C			
0.8762	304.59	0.4824	1.13	0.08	1.34	303.51
0.5535	218.56	0.6067	0.84	-0.12	1.69	217.47
0.3806	138.03	0.7311	0.51	-0.37	2.03	136.86
0.1831	-13.81	1.052	-0.28	-1.03	2.92	-15.58
0.08920	-28.46	1.504	-1.22	-1.91	4.18	-29.96
			25°C			
1.1352	362.15	0.6261	-0.53	0.21	1.57	363.18
0.8762	329.11	0.7123	0.15	0.19	1.78	329.33
0.5535	277.95	0.8954	0.79	0.03	2.24	277.37
0.3806	242.15	1.079	0.97	-0.20	2.70	241.29
0.1831	183.72	1.552	0.82	-0.81	3.89	182.65

Table 5.5. Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1}mol^{-1}	α* $\times 10^2$	$\alpha C_{p,\phi}(Na_2HNTA)$ J K^{-1}mol^{-1}	$\alpha C_{p,\phi}(NaOH)$ J K^{-1}mol^{-1}	$C_{p,\alpha}^{rel}$* J K^{-1} mol^{-1}	$C_{p,\phi}(Na_3NTA)$** J K^{-1} mol^{-1}
			25°C			
0.08920	139.63	2.215	0.36	-1.62	5.55	138.40
0.07061	127.31	2.487	0.18	-1.93	6.23	125.96
			40°C			
0.5535	319.75	1.272	0.83	0.08	2.89	320.02
0.3806	303.04	1.532	1.50	-0.15	3.48	302.85
0.1831	257.88	2.202	1.91	-0.73	5.00	257.37
0.08920	242.61	3.139	1.82	-1.49	7.13	242.77
0.07061	258.36	3.521	1.75	-1.78	8.00	259.53
			55°C			
0.8762	363.21	1.393	-0.55	0.30	2.88	365.67
0.5535	332.31	1.750	1.56	-0.03	3.62	332.98

Table 5.5. Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1}mol^{-1}	α* $\times 10^2$	$\alpha C_{p,\phi}(Na_2\,HNTA)$ J K^{-1}mol^{-1}	$\alpha C_{p,\phi}(NaOH)$ J K^{-1}mol^{-1}	$C_{p,\alpha}^{rel}$* J K^{-1} mol^{-1}	$C_{p,\phi}(Na_3\,NTA)$** J K^{-1} mol^{-1}
			55°C			
0.3806	281.33	2.107	2.41	-0.32	4.36	280.80
0.1831	283.86	3.023	2.89	-0.96	6.25	284.27

* α is the degree of dissociation. The relaxation contributions were calculated by using enthalpy data from Martell and Smith (1982), and assuming $\Delta H = \Delta H^\circ = \Delta H$ (0.1m).

** $C_{p,\phi}$ (NTA^{3-}, aq) = [$C_{p,\phi}$ (Na_3NTA, aq) - α $C_{p,\phi}$ (Na_2HNTA, aq) - α $C_{p,\phi}$ (NaOH, aq) - $C_{p,\phi}^{rel}$] / (1 - α)

Table 5.6. Standard partial molar properties of Na_2HNTA (aq) and NaCuNTA (aq) and Na_3NTA (aq).

t / °C	$V°$ / (cm^3 mol^{-1}) isothermal[1]	$V°$ / (cm^3 mol^{-1}) global fitting[2]	$C_p°$ / (J K^{-1} mol^{-1}) isothermal[1]	$C_p°$ / (J K^{-1} mol^{-1}) global fitting[2]
		Na_2HNTA(aq)		
10	93.67(0.23)	93.3 ± 0.9	-139.81(2.23)*	-143 ± 11*
15	94.11(0.59)	94.9 ± 1.6	-117.07(8.19)*	-99 ± 22 *
25	97.80(0.22)	97.4 ± 0.9	-26.82(7.10)*	-37 ± 20 *
40	99.89(0.31)	99.9 ± 1.1	25.52(9.96)*	7 ± 26 *
55	101.37(0.30)	101.4 ± 1.0	-4.79(31.67)*	9 ± 69*
		NaCuNTA(aq)		
10	94.82(2.98)	91.9 ± 11.0	-9.48(17.94)*	-22 ±50*
25	98.52(0.07)	97.7 ± 5.1	58.87(23.76)*	80 ± 62 *
40	101.02(1.51)	99.9 ± 8.0	152.77(23.57)*	125 ± 61 *
55	101.60(0.10)	99.6 ± 5.2	127.84(11.99)*	133 ± 38 *
		Na_3NTA (aq)		
10	99.86(0.75)	99.6 ± 6.5	-254.19(58.69)*	-214 ± 131*
25	105.57(0.13)	105.3 ± 5.3	24.93(5.51)*	-4 ± 25*
40	108.27(0.60)	109.2 ± 6.2	128.56(42.05)*	132 ± 98 *
55	114.90(0.55)	111.7 ± 6.1	132.92(22.47)*	218 ± 59 *

[1] Values in parentheses listed for the isothermal fits are equal to one standard deviation.

[2] Error limits in $V°$ and $C_p°$ are 2σ(isothermal fit) + estimated uncertainty from systematic errors.

* After the correction of relaxation contribution to the $C_{p,\phi}$

Table 5.7 Standard state and excess property parameters for Na_2HNTA (aq)

	$q_{1,1}$	$q_{1,2}$	$q_{1,3}$
		$C_{p,\phi}$ /(J K^{-1} mol^{-1})	
$C_p°$	4.501×10^3	-1.710×10^5	-9.917
B_C	2.234×10^1	3.985×10^{-1}	—
C_C	3.269×10^3	-2.087×10^1	3.257×10^{-2}
		V_ϕ / (cm^3 mol^{-1})	
$V°$	1.771×10^2	-4.122×10^3	-1.397×10^{-1}
B_V	2.173×10^1	-6.664×10^{-2}	—
C_V	1.326×10^1	-1.105×10^{-1}	2.211×10^{-4}

Table 5.8 Standard state and excess property parameters for NaCuNTA (aq)

	$q_{i,1}$	$q_{i,2}$	$q_{i,3}$
		$C_{p,\phi}$ /(J K^{-1} mol^{-1})	
C_p°	3.655×10^{3}	-1.407×10^{5}	-7.616
B_C	-1.423×10^{3}	5.752	—
C_C	1.669×10^{4}	-1.027×10^{2}	1.551×10^{-1}
		V_ϕ / (cm^3 mol^{-1})	
V°	1.730×10^{2}	-3.758×10^{3}	-1.333×10^{-1}
B_V	2.194×10^{1}	-2.802×10^{-2}	—
C_V	1.090	-2.606×10^{-2}	1.168×10^{-5}

Table 5.9 Standard state and excess property parameters for Na_3NTA (aq)

	$q_{i,1}$	$q_{i,2}$	$q_{i,3}$
		$C_{p,\phi}$ /(J K^{-1} mol^{-1})	
C_p°	3.755×10^3	-2.043×10^5	-6.269
B_C	1.660×10^3	-5.315	—
C_C	7.230×10^2	-6.244	1.260×10^{-2}
		V_ϕ / (cm^3 mol^{-1})	
V°	1.963×10^2	-5.276×10^3	-1.416×10^{-1}
B_V	3.380×10^1	-1.059×10^{-1}	—
C_V	-4.863×10^{-1}	-2.527×10^{-2}	8.490×10^{-5}

Table 5.10. Standard partial molar properties of species: $HNTA^{2-}$ (aq), $CuNTA^-$ (aq), and NTA^{3-}. *

Temp / °C	Na^+(aq)	Cl^-(aq)	$HNTA^{2-}$ (aq)	$CuNTA^-$(aq)	NTA^{3-}(aq)
			C_p°/ $JK^{-1}mol^{-1}$		
10	21.8	-148.4	-186 ± 11	-66 ± 50	-258 ± 131
25	42.2	-126.6	-121 ± 21	-5 ± 62	-88 ± 26
40	52.8	-115.5	-99 ± 26	20 ± 61	27 ± 98
55	49.5	-111.7	-90 ± 69	34 ± 38	119 ± 59
			V° / cm^3 mol^{-1}		
10	-2.21	17.15	97.7 ± 1.0	96.4 ± 11.0	104.0 ± 6.5
25	-1.27	17.89	99.9 ± 1.0	100.3 ± 5.2	107.9 ± 5.3
40	-0.44	17.91	100.8 ± 1.1	100.8 ± 8.0	110.0 ± 6.2
55	0.12	17.81	101.2 ± 1.1	99.3 ± 5.2	111.4 ± 6.1

*C_p° and V° for $HNTA^{2-}$(aq), $CuNTA^-$(aq), and NTA^{3-}(aq) are taken from global fits of C_p° and V° of Na_2HNTA(aq), NaCuNTA(aq) and Na_3NTA(aq) after subtracting the C_p° and V° for Na^+(aq). The values for Na^+(aq) and Cl^-(aq) reported here were taken from Equation 3.7 to Equation 3.12, the uncertainties for those values are ± 0.3 cm mol^{-1} for V° and ± 3 J K^{-1} mol^{-1} for C_p°.

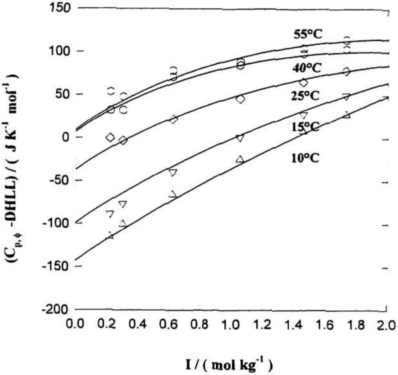

Fig. 5.1. *Apparent molar heat capacities of* Na_2HNTA *(aq), after* subtracting the Debye-Hückel limiting law and the chemical relaxation contributions. The solid line is *the least squares curve fit.*

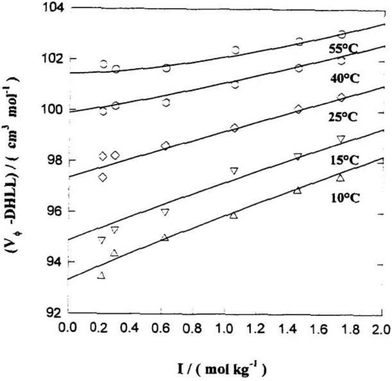

Fig. 5.2. Apparent molar volumes of Na_2HNTA (aq), after subtracting the Debye-Hückel limiting law and the chemical relaxation contributions. The solid line is the least squares curve fit.

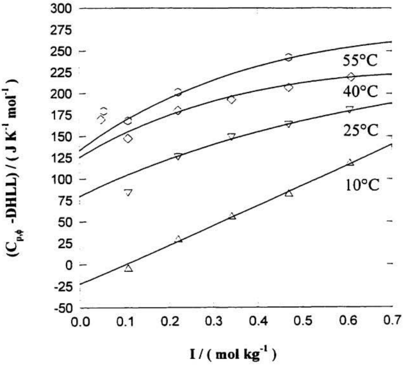

Fig. 5.3. Apparent molar heat capacities of NaCuNTA (aq) solutions, after subtracting the Debye-Hückel limiting law. The solid line is the least squares curve fit to all the experimental data.

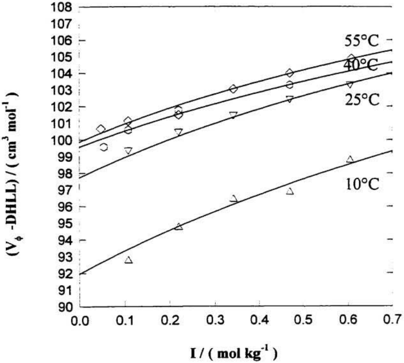

Fig. 5.4. Apparent molar volumes of NaCuNTA (aq), after subtracting the Debye-Hückel limiting law. The solid line is the least squares curve fit to all the experimental data.

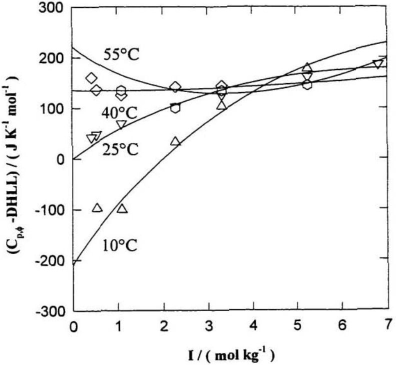

Fig. 5.5. Apparent molar heat capacities of Na_3NTA (aq), after subtracting the Debye-Hückel limiting law and the chemical relaxation contributions. The solid line is the least squares curve fit.

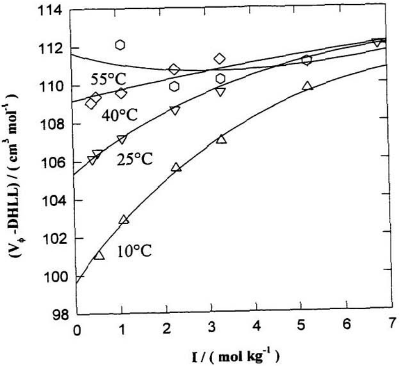

Fig. 5.6. Apparent molar volumes of Na_3NTA (aq), after subtracting Debye-Hückel limiting law and the chemical relaxation contributions. The solid line is the least squares curve fit.

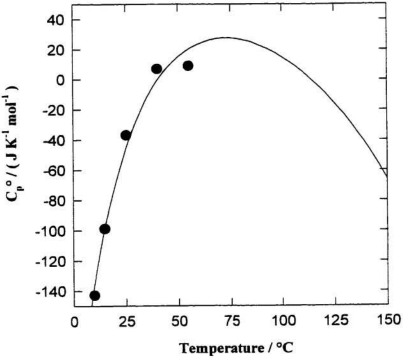

Fig. 5.7. Temperature dependence of standard partial molar heat capacities of Na_2HNTA (aq). The solid line is the least squares curve fit of the HKF equation.

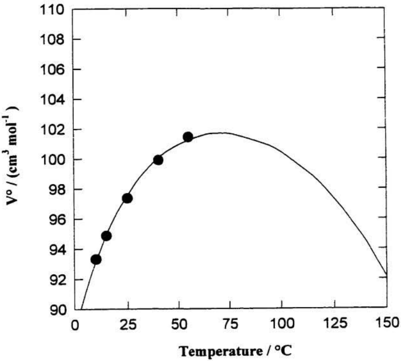

Fig. 5.8. Temperature dependence of standard partial molar volumes of Na_2HNTA (aq). The solid line is the least squares curve fit of the HKF equation.

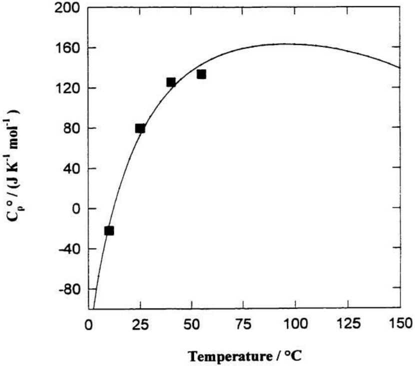

Fig. 5.9. Temperature dependence of standard partial molar heat capacities of NaCuNTA (aq). The solid line is the least squares curve fit of the HKF equation.

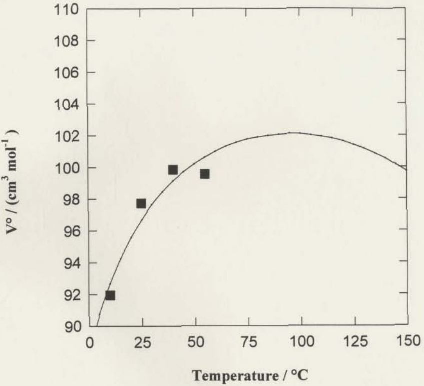

Fig. 5.10. Temperature dependence of standard partial molar volumes of NaCuNTA (aq). The solid line is the least squares curve fit of the HKF equation.

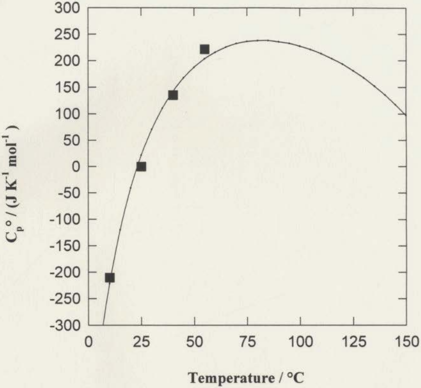

Fig. 5.11. Temperature dependence of standard partial molar heat capacities of Na_3NTA (aq). The solid line is the least squares curve fit of the HKF equation.

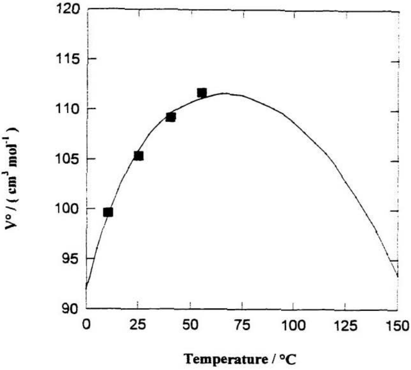

Fig. 5.12. Temperature dependence of standard partial molar volumes of Na_3NTA (aq). The solid line is the least squares curve fit of the HKF equation.

Chapter 6

CONCLUSIONS

The data obtained in this study are the first reported values for the temperature dependance of $C_p°$ and $V°$ for $H_2EDTA^{2-}(aq)$ and $CuEDTA^{2-}(aq)$. The values of $C_p°$ and $V°$ for $HNTA^{2-}(aq)$, $NTA^{3-}(aq)$ and $CuNTA^{-}(aq)$ are the first reported for any NTA species at any temperature. As such they are of fundamental importance for calculations of classical thermodynamic quantities, and as data that can be used to test and /or develop theoretical or semi-theoretical treatments of solute hydration.

The purpose of this work was to provide accurate thermodynamic data that can lead to physical chemical information for these important chelating agents. Mainly, this work involved the measurement and calculation of apparent molar properties, so that the corresponding standard partial molar properties could be obtained. Because of the fundamental relationships between standard partial molar heat capacities, volumes, Gibbs free energies and equilibrium constants, these data are very useful for predicting the temperature and pressure dependence of equilibrium constants for EDTA and NTA complexation reactions. These types of calculations (or more exactly the data used in these calculations) are important for many applications.

One important experimental aspect of this work is the quantitative assessment of the contribution of "chemical relaxation" to the total measured heat capacity of aqueous solutions containing partially dissociated solutes. The observed heat capacities of aqueous solutions containing partially dissociated solutes are higher than expected from the equilibrium molalities of all species present in the solution. Due to the nature of heat capacity measurements (imposed temperature increment), the degree of dissociation of the solute changes with temperature (if there is a finite enthalpy change associated with the dissociation reaction) and thus changes during the course of the experimental measurement. Several treatments of this effect were applied for the aqueous electrolytes and complexes in the present work, the most complicated treatments assessed the contribution of "chemical relaxation" when more than one dissociation reaction was present.

Another result of the present work has been new data for the calculation of the temperature dependence of stability constants. Because the standard partial molar properties for species involved in specific equilibria can be obtained from our study, then the temperature dependence of the standard partial molar properties of those species can be derived by some semi-empirical equation of state, such as the "HKF equation of state". These data can be used to estimate the temperature dependence of stability constants for specific equilibria such as

$$NTA^{3-}\ (aq)\ +\ Cu^{2+}\ (aq)\ =\ CuNTA^{-}\ (aq)$$

by combining them with enthalpy data which are already known. The data for the temperature dependent stability constants for these equilibria are important in thermodynamics, and will be useful in the energy industry and other applications.

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APPENDICES

Appendix I

Heat Leak Correction Factors for NTA species

			ff		
Temp/°C	10	15	25	40	55
$Na_2HNTA(aq)$	1.00830	1.00013	1.01552	1.01053	1.01745
NaCuNTA(aq)	1.00615	—	1.007	1.007	1.02835
$Na_3NTA(aq)$	1.00615	—	1.007	1.007	1.02835

Appendix II

The Chemical Relaxation Effect on NaCuNTA(aq)

Contributions of Speciation and Relaxation to the Apparent Molar Capacities of NaCuNTA (aq).

m mol kg^{-1}	$C_{p,\phi}$-dhll J K^{-1} mol^{-1}	α ×10^{5}	$C_{p,\alpha}{}^{rel}\times10^{3}$ J K^{-1} mol^{-1}	β ×10^{5}	$C_{p\beta}{}^{rel}\times10^{2}$ J K^{-1} mol^{-1}	$C_{p,\phi}$-$C_{p,tol}{}^{rel}$ J K^{-1} mol^{-1}
			10°C			
0.60845	126.46	6.860	3.051	6.859	6.550	126.39
0.47018	90.74	6.860	3.051	6.859	6.550	90.68
0.34250	64.35	6.860	3.051	6.859	6.550	64.28
0.21965	37.86	6.860	3.051	6.859	6.550	37.79
0.10714	4.18	6.860	3.051	6.859	6.550	4.11
			25°C			
0.60845	182.96	5.688	2.281	5.688	4.899	182.91
0.47018	165.85	5.688	2.282	5.688	4.899	165.80

Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1} mol^{-1}	α $\times 10^5$	$C_{p,\alpha}^{rel} \times 10^2$ J K^{-1} mol^{-1}	β $\times 10^5$	$C_{p\beta}^{rel} \times 10^1$ J K^{-1} mol^{-1}	$C_{p,\phi}$-$C_{p,tol}^{rel}$ J K^{-1} mol^{-1}
			25°C			
0.34250	151.52	5.688	2.282	5.688	4.899	151.47
0.21965	128.33	5.688	2.282	5.687	4.898	128.28
			40°C			
0.60845	225.30	4.802	1.746	4.802	3.749	225.26
0.47018	213.38	4.802	1.746	4.801	3.749	213.34
0.34250	199.17	4.802	1.746	4.801	3.749	199.13
0.21965	186.63	4.802	1.746	4.801	3.748	186.60
0.10714	154.13	4.803	1.746	4.801	3.748	154.09
0.04657	176.38	4.805	1.747	4.799	3.747	176.34

Continued

m mol kg^{-1}	$C_{p,\phi}$ J K^{-1} mol^{-1}	α $\times 10^5$	$C_{p,\alpha}^{rel} \times 10^2$ J K^{-1} mol^{-1}	β $\times 10^5$	$C_{p\beta}^{rel} \times 10^1$ J K^{-1} mol^{-1}	$C_{p,\phi}$-$C_{p,tot}^{rel}$ J K^{-1} mol^{-1}
			55°C			
0.47018	247.70	4.117	1.363	4.117	2.927	247.67
0.21965	206.34	4.118	1.363	4.116	2.927	206.30
0.10714	172.46	4.119	1.364	4.115	2.926	172.43
0.05275	184.29	4.120	1.364	4.114	2.925	184.26

1. Here, apparent molar heat capacities are after subtracting Debye-Hückel limiting law.
2. α and β are the degree of dissociation. The relaxation contributions were calculated by using enthalpy data from Martell and Smith, and assuming $\Delta H = \Delta H^\circ = \Delta H$ (0.1m).

Appendix III

Table of Parameters for the HKF Equation

HKF parameters for global fitted standard partial molar properties.

	C_p°		V°	
	c_1	c_2	c_3	c_4
$Cu(ClO_4)_2$ (aq)	209.82	-7.666×10^5	96.89	-1752.90
Na_2H_2EDTA(aq)	513.43	-1.233×10^6	190.71	-2019.32
$Na_2CuEDTA$(aq)	505.52	-1.067×10^6	199.03	-1630.48
Na_2HNTA (aq)	226.02	-7.995×10^5	122.23	-1245.90
NaCuNTA (aq)	268.97	-7.478×10^5	114.94	-1083.51
Na_3NTA (aq)	633.22	-2.056×10^6	145.41	-1909.26