Journal of Thermal Analysis, Vol. 52 (1998) 991-996

ENTHALPIES OF DILUTION FOR AQUEOUS SOLUTIONS OF 3:1 ELECTROLYTES: VARIATION WITH TEMPERATURE

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Abstract

The enthalpies of dilution of aqueous solutions of $[Co(en)_3]Cl_3$ and $[Co(tn)_3Cl_3$ (where en=1,2-diaminoethane, and tn=1,3-diaminopropane) were measured at 278.15 K up to 1 mol kg^{-1}, using a large isoperibolic calorimeter, with the 'long-jump' method. Relative apparent molar enthalpies, L_Φ, were extracted via an empirical equation relating L_Φ and molality. These new values were compared with previous results at 298.15 K on the same aqueous systems. Theoretical predictions were satisfied, but an unexpectedly broad divergence was found for such close temperatures. A tentative explanation is put forward.

Keywords: aqueous electrolyte, enthalpy of dilution, hydrophobic interaction, isoperibolic calorimetry

Introduction

The precise determination of enthalpies of dilution for dilute electrolyte aqueous solutions is rather difficult. Direct investigation in the most dilute region ($m<10^{-4}$ mol kg^{-1}) is an almost unattainable task requiring calorimetric apparatus capable of measuring small temperatures changes of a millionth of a degree or better. An alternative, indirect, approach in that dilute range of concentration is achieved by the less ambitious 'long-jump' calorimetric method (semi-concentrated initial aqueous solutions and diluted final ones). On this basis, we have designed an isoperibolic calorimeter with a large vessel containing pure water and a relatively small cell for the initial solution samples [1].

The scarce precise experimental data to be found in the literature largely refer to 298.15 K. The limited reports available at other temperatures usually cover the

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1418-2874/98/ $ 5.00
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range 293–373 K. In this contribution, we report enthalpies of dilution, at 278.15 K, for two aqueous 3:1 systems, $[Co(en)_3]Cl_3$ and $[Co(tn)_3]Cl_3$ (en=1,2-diaminoethane; tn=1,3-diaminopropane), previously investigated at 298.15 K [2, 3].

Increasing experimental difficulties are caused by the temperature lowering, such as technical problems or the noticeable diminution of solubility. Fortunately, our efforts were compensated by the unexpectedly broad divergence observed between these rather close temperatures.

Experimental

The complex salts were prepared, purified and analysed as previously [4, 5]. Both salts were powdered and dried to constant mass in a vacuum oven. Initial aqueous solutions of the dried compounds in freshly prepared purified water (Millipore, Milli-Q) were made up by mass.

Measurements were carried out with a constant-environment home-made calorimeter described in detail elsewhere [1, 2]. The cylindrical calorimeter vessel held an initial volume of pure water of about 825 cm^3 and then thin-walled glass ampoules contained some 10 cm^3 of semi-concentrated solution. The isothermal jacket of the calorimeter, a cylindrical can of stainless steel, was immersed in a stirred-water bath with its temperature regulated to within ±0.0005 K over a 10 h period by means of a proportional electronic controller of heating; a refrigerated circulator supplied the adequate constant cooling power.

The corrected temperature rise, ΔT_{corr}, was obtained following the treatment developed by Brunetti, Prosen and Goldberg [6]. Equation (1) was fitted to the time quartz thermometer data (t, θ) during the initial and final rating periods:

$$\theta = \theta_\infty - (\theta_\infty - \theta_0)\exp[-k(t - t_0)] \quad (1)$$

where θ_∞ is the convergence temperature, k is the calorimeter heat leak modulus or cooling constant ($\cong 6\cdot 10^{-5}$ s^{-1}) and θ_0 is the temperature at time t_0, any selected time in the rating period used. The parameters k and θ_∞ were obtained from simultaneous resolution of Eq. (1) for both the initial and the final rating periods, by using a non-linear least squares procedure. Finally, the measured quartz thermometer temperature rise, $\Delta\theta$, was related to the actual observed temperature rise, ΔT.

The molar enthalpy of dilution, at the mean dilution temperature, was calculated from

$$\Delta_{dil}H = \frac{-\bar{\varepsilon}\Delta T_{corr}}{N} \quad (2)$$

where $\bar{\varepsilon}$ is the average of the initial and final electrical energy equivalents and N is the number of solute moles.

The experimental results for $\Delta_{\mathrm{dil}}H$ were fitted to the equation

$$\Delta_{\mathrm{dil}}H(m_i \rightarrow m_f) = L_\Phi(m_f) - L_\Phi(m_i) \tag{3}$$

by using a least squares technique where the relative apparent molar enthalpy, $L_\Phi(m)$, is given by

$$L_\Phi(m) = A_{\mathrm{DH}}m^{1/2} + \sum_{i=1} B_i m^{(i+1)/2} \tag{4}$$

where A_{DH} is the Debye-Hückel limiting slope and the coefficients B_i are extracted from the numerical fitting.

Results and discussion

Dilution experiments for aqueous solutions of $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ and $[\mathrm{Co(tn)_3}]\mathrm{Cl_3}$ at 278.15 K are shown in Figs 1 and 2, where plots of the $L_\Phi(m)$ curves of fitting are drawn against $m^{1/2}$. Also shown are the experimental values for the initial mo-

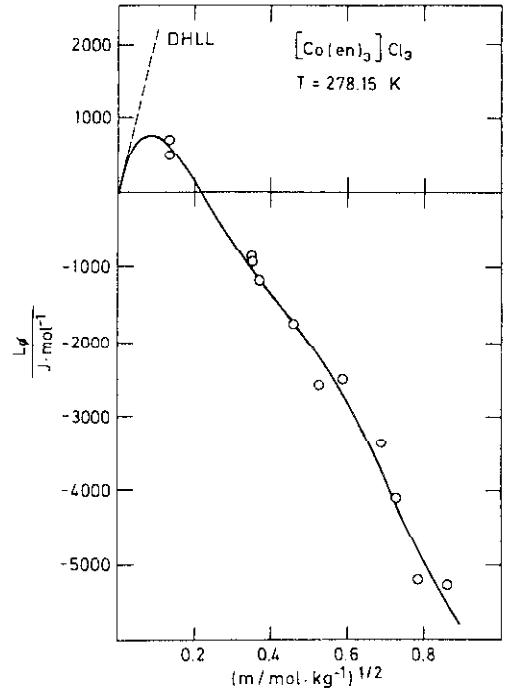

Fig. 1 Enthalpy of dilution of aqueous $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$, plotted as L_Φ *vs.* $m^{1/2}$. The solid line represents the fitting curve. The broken line denotes the Debye-Hückel limiting law (DHLL) at 278.15 K. Open circles are experimental relative apparent molar enthalpy data corresponding to initial molalities $L_\Phi(m_i)$

lalities with the following convention: the vertical distance from the geometrical symbols to the $L_\Phi(m)$ curves is obtained from the deviation between $\Delta_{dil}H$ (experimental) and $\Delta_{dil}H$ (calculated) and fully assigned to the $L_\Phi(m_i)$. The $L_\Phi(m_f)$ points are assumed to lie exactly on the fitting curve and for clarity are not displayed, since their values for $m^{1/2}$ are very close, ranging from 0.014 to 0.095 (mol $\text{kg}^{-1})^{1/2}$ in the positive slope branch of the curves.

The selected polynomials, with the imposed positive first coefficient A_{DH}, ensure an initial increasing trend, as theoretically and experimentally presumed, and prevent a systematic bias upwards or downwards for the $L_\Phi(m)$ curves.

Our previous papers relating to 298.15 K showed the first reported 3:1 electrolyte systems, which exhibited a pronounced maximum when $L_\Phi(m)$ was plotted *vs.* $m^{1/2}$. This behaviour is typical of the hydrophobic 1:3 ionic solutes $K_3[Fe(CN)_6]$ or $Na_3[Fe(CN)_6]$ and opposite to the steady rise of $L_\Phi(m)$ characteristic of the strongly hydrated trivalent cations such as the Al^{3+}, Ga^{3+} or rare earth cations [1–3]. This similar qualitative behaviour is found again for $[Co(en)_3]Cl_3$ and $[Co(tn)_3]Cl_3$ at 278.15 K, as shown in Figs 1 and 2.

Figure 3 provides a comparison between our results at 278.15 K and 298.15 K for the aqueous system $[Co(en)_3]Cl_3$. We wish to emphasize the broad divergence

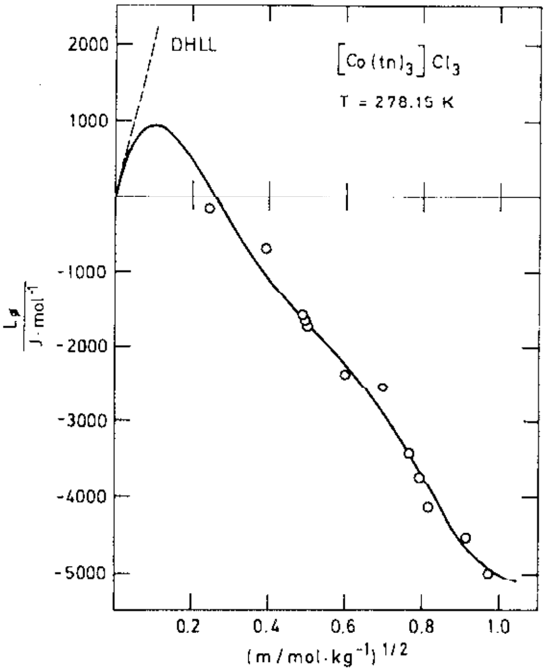

Fig. 2 Enthalpy of dilution of aqueous $[Co(tn)_3]Cl_3$, plotted as L_Φ *vs.* $m^{1/2}$. The solid line represents the fitting curve. The broken line denotes the Debye-Hückel limiting law (DHLL) at 278.15 K. Open circles are experimental relative apparent molar enthalpy data corresponding to initial molalities $L_\Phi(m_i)$

found between these rather close temperatures. All the theories relating to the primitive model predict a lowering in $L_\Phi(m)$ at constant molality when the temperature is reduced, but the effect reported here is astonishingly large. Thus, the Debye-Hückel limiting law, expressed as $L_\Phi(m)=A_{DH}m^{1/2}$, provides a 27% reduction in the slope factor A_{DH}, which is clearly insufficient to justify the deep diminution in $L_\Phi(m)$. Thus, the non-electrostatic part of the solute–solvent interaction is responsible for this trend; as mentioned earlier, $[Co(en)_3]^{3+}$ and $[Co(tn)_3]^{3+}$ behave as hydrophobic cations and this tendency produces a magnified contribution when the temperature is lowered and the structure of the solvent is naturally reinforced. Finally, it must be borne in mind that pure water exhibits a well-known minimum in density near 277 K, reflecting the complex arrangement of water molecules that is greatly influenced by the presence of hydrophobic species efficient in promoting additional strengthening of the solvent structure [7].

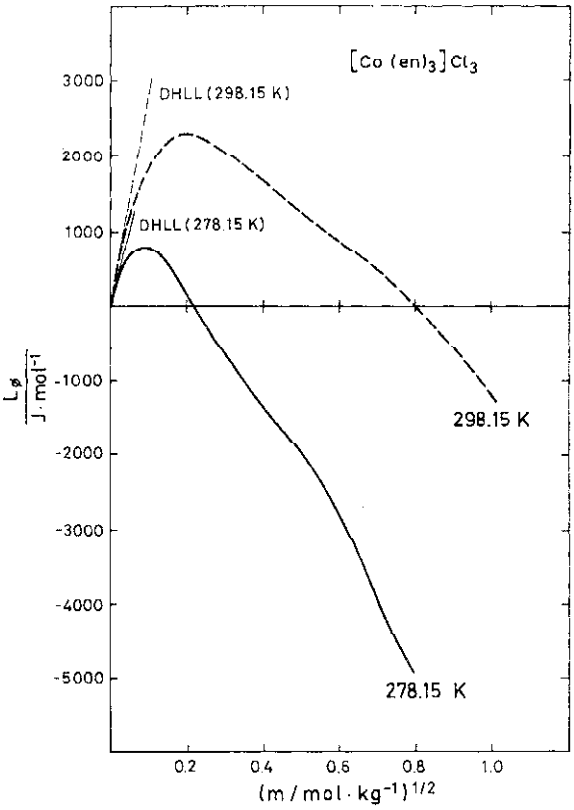

Fig. 3 Variation of relative apparent molar enthalpy $L_\Phi(m)$, as a function of $m^{1/2}$, using temperature as a parameter for the aqueous system $[Co(en)_3]Cl_3$. The coarse solid and broken lines represent the corresponding fitting curves at 278.15 K and 298.15 K. The thin solid and broken lines denote the Debye Hückel limiting slopes (DHLL) at the same temperatures