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ENTHALPY OF DILUTION OF AQUEOUS $CaCl_2$ AT 298.15 K

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ABSTRACT

The heat of dilution of aqueous solutions of $CaCl_2$ was measured at 298.15 K and up to a molality of 7 using a Tronac 450-458 isoperibol calorimeter. The experimental data were correlated using the ion interaction model of Pitzer.

INTRODUCTION

$CaCl_2$ is a major constituent of natural waters and plays an important role in many biological processes. Therefore an accurate knowledge of the thermodynamic properties of $CaCl_2$ is desirable. However, the current heat of dilution data above 1 m (mol $CaCl_2$/kg H_2O) are of limited accuracy [1].

This paper reports new heat of dilution data for $CaCl_2$ aqueous solutions at 298.15 K over a concentration range up to 7 m. Our new experimental data, together with data for low $CaCl_2$ concentrations [2], were correlated using the ion interaction model of Pitzer and Peiper [3].

EXPERIMENTAL

Four solutions of about 7, 5, 3.5 and 1 m were prepared from reagent grade $CaCl_2 \cdot 2H_2O$ and distilled deionized water. The solutions were analysed by evaporating samples to dryness. The $CaCl_2$ samples were dried at 673 K for about 4 h to constant mass using a platinum crucible. The concentration of the solutions were found to be 7.070, 5.000, 3.518 and 1.032 m. A Tronac 450-458 isoperibol calorimeter was used to measure the heats of dilution of aqueous $CaCl_2$ solutions.

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A weighed amount of solution (or water) was loaded in the reaction vessel; then pre-fixed volumes of water (or solution) were added by means of a 10 ml precision burette (0.05%). The temperature changes in the reaction vessel were measured by means of a thermistor and a Fluka model 8810A digital multimeter, and were recorded by an M24 Olivetti personal computer. The concentration and weight of the resulting solution in the reaction vessel were calculated by using the density data for aqueous $CaCl_2$ solutions [4]. The calorimetric measurements were processed by means of a computer program to obtain the heats of dilution, following the method outlined by Rodante and Onofri [5].

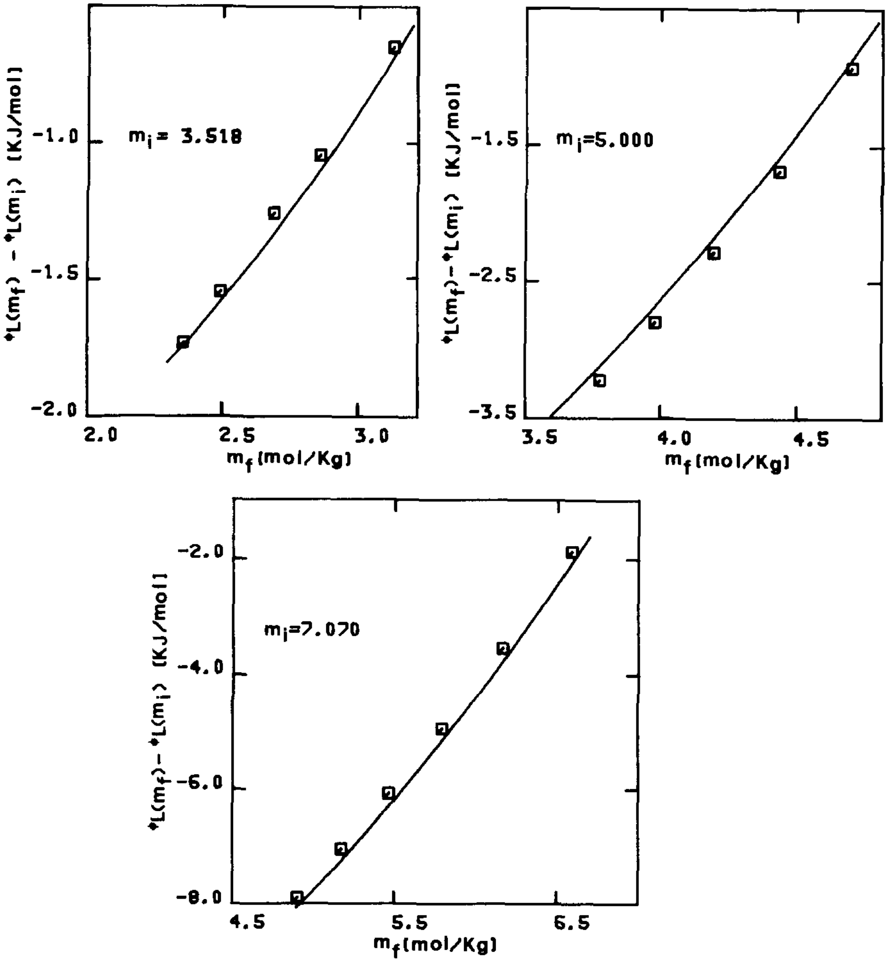

Fig. 1. Experimental and calculated enthalpies of dilution of $CaCl_2$(aq) plotted as the apparent relative enthalpy of the final solution relative to that of the solution initially in the reaction vessel against the final molality.

The measured enthalpies of dilution at 298.15 K are reported in Table 1, where S represents the grammes of solution, subscripts i, a and f refer respectively to the solution loaded in the reaction vessel, to the added solution and to the final solution, and ΔH_e and ΔH_c are the experimental and calculated enthalpies of dilution.

Figure 1 shows the enthalpies of dilution plotted as the apparent relative enthalpy of the final solutions relative to that of the solution initially in the reaction vessel, against the molality of the final solutions, for initial solutions of 3.518, 5.00 and 7.07 m.

RESULTS AND DISCUSSION

The heat of dilution, ΔH^{m}, is related to the apparent molar enthalpy, ${}^{\phi}L$, by the following relation

$$\Delta H^{m} = n_f^{\phi}L(m_f) - n_i^{\phi}L(m_i) - n_a^{\phi}L(m_a) \tag{1}$$

where n represents the moles of $CaCl_2$ in the solution, m is the molality,

TABLE 1

Experimental and calculated enthalpies of dilution of $CaCl_2(aq)$ at 298.15 K

m_i	m_a	m_f	S_i (g)	S_b (g)	ΔH_e (kJ)	ΔH_c (kJ)	$\Delta H_e - \Delta H_c$
1.032	0.000	0.928	80.000	8.035	−0.0049	−0.0049	−0.0000
0.928	0.000	0.839	88.035	8.488	−0.0042	−0.0043	+0.0001
1.032	0.000	0.929	85.020	8.486	−0.0054	−0.0051	−0.0003
0.000	1.032	0.087	90.010	9.254	−0.0125	−0.0118	−0.0007
0.000	1.032	0.097	80.000	9.241	−0.0119	−0.0112	−0.0007
0.097	1.032	0.177	89.241	9.239	−0.0056	−0.0053	−0.0003
1.032	0.000	0.977	95.126	4.835	−0.0027	−0.0030	+0.0003
3.518	0.000	3.128	92.000	8.244	−0.1508	−0.1598	+0.0090
3.128	0.000	2.857	100.245	7.061	−0.0926	−0.0966	+0.0040
2.857	0.000	2.691	107.306	5.036	−0.0494	−0.0536	+0.0042
2.691	0.000	2.492	112.342	6.919	−0.0670	−0.0587	−0.0083
2.492	0.000	2.356	119.261	5.376	−0.0425	−0.0367	−0.0058
5.000	0.000	4.700	100.080	4.112	−0.2989	−0.2806	−0.0183
4.700	0.000	4.433	104.192	4.131	−0.2440	−0.2311	−0.0129
4.432	0.000	4.195	108.322	4.109	−0.1926	−0.1903	−0.0023
4.195	0.000	3.981	112.431	4.130	−0.1647	−0.1600	−0.0047
3.981	0.000	3.788	116.560	4.112	−0.1363	−0.1345	−0.0018
7.070	0.000	6.587	100.000	4.113	−0.7486	−0.8590	+0.1104
6.587	0.000	6.164	104.113	4.133	−0.6607	−0.6909	+0.0302
6.163	0.000	5.792	108.245	4.113	−0.5540	−0.5575	+0.0035
5.793	0.000	5.463	112.358	4.135	−0.4710	−0.4603	−0.0107
5.462	0.000	5.169	116.492	4.112	−0.3856	−0.3796	−0.0060
5.169	0.000	4.905	120.604	4.132	−0.3320	−0.3195	−0.0125

TABLE 2

Values of the fitting parameters of eqn. (2) and 95% confidence limits

$\beta_0^{\mathrm{L}} = 5.6062\times10^{-4} \pm 2.9\times10^{-6}$

$\beta_1^{\mathrm{L}} = 2.6607\times10^{-3} \pm 1.3\times10^{-4}$

$C_{\mathrm{mx}}^{\mathrm{L}} = -7.2278\times10^{-5} \pm 7.2\times10^{-7}$

subscripts i, a and f refer respectively to the solution loaded in the reaction vessel, to the added solution and to the final solution, and ${}^{\Phi}L(m)$ is the apparent molar enthalpy of a solution of molality m.

The measured enthalpies of dilution were correlated using the ion interaction model of Pitzer and Peiper [3]. This model has been successfully used to describe the thermodynamic properties of aqueous solutions over a wide range of temperature and concentration, and has proved to be quite reliable.

The Pitzer equation for the apparent relative molar enthalpy, ${}^{\Phi}L$, is

$${}^{\Phi}L = \nu\,|Z_{\mathrm{m}}Z_{\mathrm{x}}|\,A_{\mathrm{H}}h(I) - 2\nu_{\mathrm{m}}\nu_{\mathrm{x}}RT^2\left[mB_{\mathrm{mx}}^{\mathrm{L}} + m^2\nu_{\mathrm{m}}Z_{\mathrm{m}}C_{\mathrm{mx}}^{\mathrm{L}}\right] \tag{2}$$

where

$$h(I) = \ln(1 + bI^{1/2})/(2b) \tag{3}$$

$$B_{\mathrm{mx}}^{\mathrm{L}} = \beta_0^{\mathrm{L}} + 2\beta_1^{\mathrm{L}}\left[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\right]/(\alpha^2 I) \tag{4}$$

In eqn. (2) A_{H} is the Debye–Hückel slope for enthalpy [6], $I = \frac{1}{2}\,\Sigma_i(m_i Z_i^2)$ is the ionic strength, ν_{m} and ν_{x} are the number of cations and anions in a molecule of solute, Z_{m} and Z_{x} give their respective charges in electronic units, $\nu = \nu_{\mathrm{m}} + \nu_{\mathrm{x}}$, and β_0^{L}, β_1^{L} and $C_{\mathrm{mx}}^{\mathrm{L}}$ are coefficients related to short-range interaction forces. The parameters b and α have fixed values of 1.2 and 2 $\mathrm{kg^{1/2}\ mol^{-1/2}}$ [7] for 1 : 1 and 1 : 2 electrolytes.

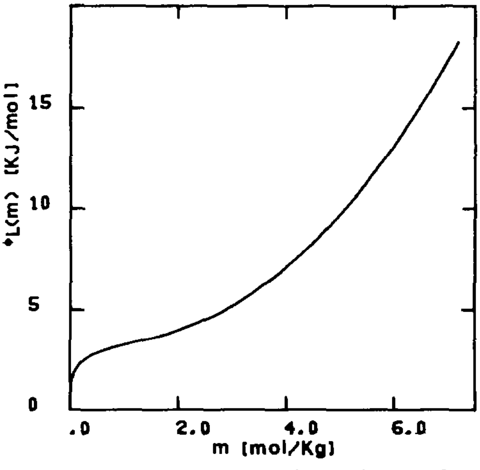

Fig. 2. Apparent relative molar enthalpy of aqueous $CaCl_2$ calculated from eqn. (2).

The program MINUIT [8] was used to obtain the values of the parameters from a fit of eqn. (2) to the experimental enthalpies of dilution. The values of the parameters of eqn. (2) were obtained by fitting the experimental data reported in Table 1 and the data below 0.1 m reported by Lange and Streeck [2]. The standard deviation of the fit was 0.02 kJ. The values of the parameters of eqn. (2) obtained from the fitting are reported in Table 2.

The calculated enthalpies of dilution are reported in Table 1. Figure 2 shows the calculated apparent relative molar enthalpy, ${}^{\phi}L$, as a function of molality.

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