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Enthalpy of dilution of ethanol–$CaCl_2$ solutions at 298.15 K

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Abstract

The enthalpy of dilution of ethanol–$CaCl_2$ solutions was measured at 298.15 K and up to a molality of 2.39 using a Tronac 450–458 isoperibol calorimeter. The experimental data were correlated using the ion interaction model of Pitzer.

INTRODUCTION

In the recent past, extractive distillation with $CaCl_2$ has been proposed for the production of fuel alcohol from dilute fermentation broths [1]. For this purpose, knowledge of the thermodynamic properties of water–$CaCl_2$, ethanol–$CaCl_2$ and water–ethanol–$CaCl_2$ solutions is needed. A knowledge of the enthalpy of dilution data for these systems is also particularly useful. In a previous paper [2], enthalpy of dilution data for water–$CaCl_2$ solutions were reported. In this work, new enthalpy of dilution data for ethanol–$CaCl_2$ solutions at 298.15 K over a concentration range up to 2.39 m are reported. The experimental enthalpy of dilution data were successfully correlated using the ion interaction model of Pitzer [3].

EXPERIMENTAL

Reagent grade $CaCl_2 \cdot 2H_2O$ was dried at 673 K for about 24 hours. Dried $CaCl_2$ and reagent grade ethanol were used to prepare a 2.39 m stock solution. Using the stock solution, six solutions of 2.360, 2.008, 1.501, 1.2, 0.709 and 0.200 m were prepared. The solutions were analyzed by evaporating samples to dryness and further drying at 673 K for about 4 h to constant mass using a platinum crucible.

A Tronac 450–458 isoperibol calorimeter was used to measure the enthalpy of dilution of ethanol–$CaCl_2$ solutions.

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

The measured enthalpies of dilution at 298.15 K are reported in Table 1, where m represents the molality of the solution, subscripts i and f refer respectively to the solution loaded in the reaction vessel and to the final solution, and $\Delta^{\phi}L_e$ and $\Delta^{\phi}L_c$ are the experimental and calculated molal enthalpies of dilution.

Figure 1 shows the calculated and experimental enthalpies of dilution plotted against $m_i - m_f$.

RESULTS AND DISCUSSION

The enthalpies of dilution ΔH_d, reported for the dilution of solution containing 1 mole of solute from m_i to m_f are related to the apparent molal enthalpy ${}^{\phi}L$

$$\Delta H_d(m_1 \rightarrow m_2) = {}^{\phi}L(m_f) - {}^{\phi}L(m_i) \tag{1}$$

where m is the molality, and subscripts i and f refer respectively to the solution loaded in the reaction vessel and to the final solution.

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 concentrations and has proved to be quite reliable.

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

$${}^{\phi}L = \nu\,|Z_m Z_x|\,A_H h(I) - 2\nu_m \nu_x RT^2[mB^L_{mx} + m^2 \nu_m Z_m C^L_{mx}] \tag{2}$$

where

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

and

$$B^L_{mx} = \beta^L_0 + \frac{2\beta^L_1[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]}{\alpha^2 I} \tag{4}$$

A_H is the Debye–Hückel coefficient for enthalpy

$$A_H = -6A_{\phi}RT^2\left(\frac{1}{T} + \left(\frac{\partial \varepsilon_r}{\partial T}\right)_P + \frac{1}{3}\left(\frac{\partial \ln V}{\partial T}\right)_P\right) \tag{5}$$

TABLE 1

Experimental and calculated enthalpy of dilution of ethanol–$CaCl_2$ solutions

m_i in mol kg^{-1}	m_f in mol kg^{-1}	$\Delta^\phi L_e$ in kJ mol^{-1}	$\Delta^\phi L_c$ in kJ mol^{-1}	$\Delta^\phi L_e - \Delta^\phi L_c$ in kJ mol^{-1}	$(\Delta^\phi L_e - \Delta^\phi L_c)/\Delta^\phi L_e \times 100$
0.200	0.191	−0.0358	−0.0165	−0.0192	53.82
0.191	0.182	−0.0297	−0.0159	−0.0138	46.46
0.174	0.166	−0.0113	−0.0134	0.0021	−18.38
0.191	0.182	−0.0217	−0.0159	−0.0058	26.83
0.182	0.173	−0.0221	−0.0154	−0.0067	30.37
0.173	0.166	−0.0209	−0.0117	−0.0092	44.04
0.166	0.158	−0.0127	−0.0132	0.0005	−3.68
0.158	0.151	−0.0078	−0.0115	0.0037	−47.25
0.709	0.675	−0.1069	−0.1133	0.0064	−5.97
0.675	0.645	−0.0976	−0.1003	0.0027	−2.82
0.645	0.615	−0.0924	−0.1006	0.0083	−8.93
0.615	0.587	−0.0849	−0.0940	0.0091	−10.68
0.587	0.559	−0.0847	−0.0940	0.0093	−10.99
0.559	0.534	−0.0766	−0.0838	0.0071	−9.33
0.709	0.676	−0.1060	−0.1099	0.0039	−3.72
0.676	0.645	−0.0977	−0.1037	0.0060	−6.10
0.645	0.615	−0.0924	−0.1006	0.0082	−8.83
0.615	0.587	−0.0828	−0.0940	0.0112	−13.51
0.587	0.559	−0.0841	−0.0940	0.0099	−11.81
0.559	0.534	−0.0721	−0.0838	0.0116	−16.14
1.200	1.114	−0.1828	−0.1764	−0.0064	3.52
1.144	1.092	−0.1669	−0.1639	−0.0030	1.79
1.092	1.040	−0.1629	−0.1644	0.0015	−0.92
1.040	0.993	−0.1496	−0.1492	−0.0005	0.30
0.993	0.946	−0.1473	−0.1500	0.0026	−1.77
0.946	0.903	−0.1355	−0.1380	0.0025	−1.83
1.200	1.143	−0.1891	−0.1795	−0.0096	5.07
1.143	1.091	−0.2061	−0.1639	−0.0422	20.45
1.091	1.039	−0.1654	−0.1644	−0.0010	0.58
1.039	0.992	−0.1509	−0.1492	−0.0017	1.12
0.992	0.944	−0.1505	−0.1532	0.0026	−1.75
0.944	0.900	−0.1370	−0.1413	0.0043	−3.10
1.501	1.453	−0.1645	−0.1555	−0.0091	5.51
1.453	1.366	−0.2808	−0.2788	−0.0020	0.72
1.366	1.304	−0.2103	−0.1969	−0.0135	6.40
1.304	1.244	−0.1933	−0.1896	−0.0037	1.93
1.244	1.191	−0.1741	−0.1670	−0.0070	4.04
1.191	1.135	−0.1793	−0.1764	−0.0029	1.63
1.501	1.430	−0.2369	−0.2295	−0.0073	3.10
1.430	1.366	−0.2151	−0.2047	−0.0104	4.82
1.366	1.302	−0.2127	−0.2032	−0.0095	4.48
1.302	1.244	−0.1888	−0.1832	−0.0055	2.93
1.244	1.186	−0.1918	−0.1828	−0.0090	4.72
1.186	1.132	−0.1760	−0.1701	−0.0059	3.36
2.008	1.948	−0.2179	−0.2232	0.0053	−2.43
1.948	1.892	−0.2013	−0.2042	0.0029	−1.46
1.892	1.832	−0.2124	−0.2147	0.0023	−1.08
1.832	1.774	−0.2113	−0.2037	−0.0075	3.57
1.774	1.720	−0.1946	−0.1865	−0.0081	4.15
1.720	1.667	−0.1877	−0.1804	−0.0074	3.93

TABLE 1 (continued)

m_i in mol kg^{-1}	m_f in mol kg^{-1}	$\Delta^\phi L_e$ in kJ mol^{-1}	$\Delta^\phi L_c$ in kJ mol^{-1}	$\Delta^\phi L_e - \Delta^\phi L_c$ in kJ mol^{-1}	$(\Delta^\phi L_c - \Delta^\phi L_c)/\Delta^\phi L_e \times 100$
1.667	1.617	−0.1803	−0.1679	−0.0125	6.92
1.617	1.565	−0.1877	−0.1724	−0.0152	8.12
1.565	1.516	−0.1731	−0.1607	−0.0124	7.16
2.008	1.941	−0.2426	−0.2489	0.0064	−2.62
1.941	1.879	−0.2252	−0.2254	0.0002	−0.07
1.879	1.829	−0.1807	−0.1785	−0.0022	1.22
1.829	1.771	−0.2067	−0.2035	−0.0032	1.54
1.771	1.717	−0.1950	−0.1864	−0.0086	4.42
1.717	1.665	−0.1897	−0.1768	−0.0129	6.78
2.360	2.346	−0.0595	−0.0598	0.0003	−0.50
2.346	2.310	−0.1481	−0.1523	0.0042	−2.83
2.310	2.275	−0.1409	−0.1461	0.0052	−3.69
2.275	2.241	−0.1346	−0.1400	0.0055	−4.08
2.241	2.208	−0.1370	−0.1342	−0.0028	2.03
2.208	2.177	−0.1290	−0.1246	−0.0044	3.43
2.177	2.146	−0.1247	−0.1232	−0.0016	1.27
2.360	2.324	−0.1432	−0.1531	0.0099	−6.91
2.324	2.272	−0.2036	−0.2175	0.0139	−6.83
2.272	2.223	−0.1958	−0.2010	0.0052	−2.66
2.223	2.176	−0.1813	−0.1894	0.0081	−4.49
2.176	2.131	−0.1797	−0.1783	−0.0015	0.81
2.131	2.088	−0.1804	−0.1676	−0.0128	7.11
2.088	2.047	−0.1636	−0.1574	−0.0062	3.82
2.047	2.007	−0.1564	−0.1514	−0.0050	3.22
2.007	1.969	−0.1487	−0.1418	−0.0068	4.61
2.390	2.376	−0.0589	−0.0605	0.0016	−2.67
2.376	2.339	−0.1466	−0.1583	0.0117	−7.96
2.339	2.304	−0.1395	−0.1477	0.0082	−5.89
2.304	2.270	−0.1332	−0.1416	0.0084	−6.28
2.270	2.236	−0.1356	−0.1398	0.0042	−3.08
2.236	2.204	−0.1277	−0.1299	0.0022	−1.74
2.204	2.172	−0.1235	−0.1284	0.0049	−3.95
2.390	2.353	−0.1418	−0.1591	0.0174	−12.25
2.353	2.301	−0.2016	−0.2199	0.0183	−9.09
2.301	2.251	−0.1939	−0.2074	0.0135	−6.97
2.251	2.204	−0.1794	−0.1914	0.0120	−6.66
2.204	2.158	−0.1779	−0.1841	0.0062	−3.49
2.158	2.114	−0.1786	−0.1732	−0.0054	3.04
2.114	2.072	−0.1620	−0.1627	0.0007	−0.45
2.072	2.032	−0.1549	−0.1527	−0.0021	1.39
2.032	1.993	−0.1472	−0.1468	−0.0004	0.25

A_ϕ is the Debye–Hückel coefficient for the osmotic coefficient

$$A_\phi = \frac{1}{3}\left(\frac{2\Pi N_A \rho_s}{1000}\right)^{1/2}\left(\frac{e^2}{\varepsilon_r kT}\right)^{3/2} \tag{6}$$

N_A is the Avogadro constant, ρ_s is the density of the solvent, ε_r is the relative permittivity of pure solvent, k is the Boltzmann's constant and e is the elementary charge. A_ϕ and A_H/RT were calculated for ethanol

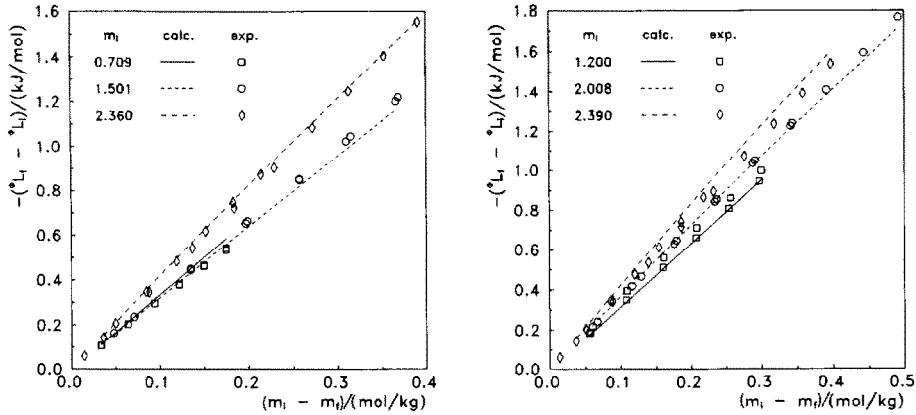

Fig. 1. Experimental and calculated enthalpies of dilution plotted against $m_i - m_f$.

solutions and their values were found to be 2.012 and 8.644 $kg^{0.5}\,mol^{-0.5}$, respectively. $I = 0.5\Sigma_i m_i z_i^2$ 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, and $\nu = \nu_m + \nu_x$.

The terms β_0^L, β_0^L and C_{mx}^L are coefficients related to short-range interaction forces. The best values for the parameters b and α have been found to be 1.2 and 2 [6] for 1–1 and 1–2 electrolytes for aqueous solutions. In this paper, the values of α and b were found together with β_0^L, β_1^L and C_{mx}^L, by fitting experimental data.

The program MINUIT [7] was used to obtain the values of the parameters from a fit of eqn. (1) to the experimental enthalpies of dilution. The standard deviation of the fit was 0.09 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 together with the experimental values for comparison.

TABLE 2

Values of the fitting parameters of eqn. (2)

$\beta_0^L = 1.7669 \times 10^{-3}\,kg\,mol^{-1}\,K^{-1}$	$\alpha = 3.0164\,kg^{0.5}\,mol^{-0.5}$
$\beta_1^L = 8.2665 \times 10^{-2}\,kg\,mol^{-1}\,K^{-1}$	$b = 4.0486\,kg^{0.5}\,mol^{-0.5}$
$C_{mx}^L = -2.3291 \times 10^{-4}\,kg^2\,mol^{-2}\,K^{-1}$	

CONCLUSIONS

New experimental enthalpy of dilution data for the system ethanol–$CaCl_2$ have been determined at 25°C. The experimental data have been successfully correlated using the Pitzer model.

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