Densities and Apparent Molal Volumes of Aqueous KCl–CaCl₂ Mixtures at 298.15 K

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Densities of aqueous KCl–CaCl₂ mixtures are reported at 298.15 K and ionic strengths from 0.5 to 4.5 mol kg⁻¹. Mean apparent molal volumes calculated from experimental densities are analyzed by using Pitzer's equations. Densities predicted by Pitzer's equations are in good agreement with experimental data. Addition of binary mixing parameters in Pitzer's equations brings a remarkable improvement in prediction. Excess volumes of mixing obtained are positive.

Introduction

The recently developed Pitzer theory (*1*) has proved to be a very powerful working tool for predicting various thermodynamic properties like activity, osmotic coefficients, enthalpies, and heat capacities of single and mixed aqueous electrolyte solutions (*2*). However, Pitzer's equations have not been vigorously tested on the volume properties of such solutions due to lack of adequate experimental data on concentrated mixtures. Kumar et al. (*3*) and Kumar and Atkinson (*4*) have recently shown the applicability of this formalism in predicting volume properties of aqueous NaCl–CaCl₂ system at various ionic strengths and temperatures.

We now present our experimental results on densities of aqueous KCl–CaCl₂ mixtures at the ionic strengths of 0.5, 1.5, 3.0, and 4.5 mol kg⁻¹ at 298.15 K and analyze them in light of Pitzer's equations.

Experimental Section

Relative densities ($\Delta d = d - d_0$) were measured with a vibrating tube densitometer (Metlar Paar). d and d_0 (0.997 047 g cm⁻³ at 298.15 K) are the densities of mixture and pure water, respectively. The method and calibration were discussed earlier (*3–5*). Solutions were made by mass dissolved in deionized water. Mixtures prepared at constant ionic strengths but for different compositions (ionic strength fraction) were prepared by appropriate combinations of KCl and CaCl₂ solutions. The ionic strength fraction of CaCl₂ (y_B) is given by

$$y_B = 3m_B/(m_A + 3m_B)$$

where m_A and m_B are the molalities of KCl and CaCl₂ in the mixture. Thermostat bath was maintained to ±0.005 K and relative densities were precise to ±3 ppm.

KCl and CaCl₂ were used without further purification. Both the salts were oven-dried. Concentrations of solutions were determined by gravimetric method as silver chloride.

Data Treatment

Details of Pitzer's equation and the method of calculations are given in detail elsewhere (*4*). We summarize only the necessary equations for immediate use.

Pitzer's equation for apparent molal volume can be given as

$$\phi_V = \phi_V{}^0 + \nu|Z_M Z_X|\frac{A_V}{2b} \ln (1 + bI^{1/2}) + 2\nu_M\nu_X RT [mB_{MX}{}^V + m^2(\nu_M\nu_X)^{1/2}C_{MX}{}^V] \quad (1)$$

where

$$B_{MX}{}^V = \left(\frac{\partial\beta^{(0)}}{\partial P}\right)_T + \left(\frac{\partial\beta^{(1)}}{\partial P}\right)_T\left(\frac{2}{\alpha^2 I}\right)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (2)$$

$$C_{MX}{}^V = \left(\frac{\partial C^\phi}{\partial P}\right)\bigg/ 2 \quad (3)$$

$\nu = \nu_M + \nu_X$, $R = 83.1441$ cm³ bar mol⁻¹ K⁻¹, and $\alpha = 2.0$, $b = 1.2$. A_V is the Pitzer–Debye–Hückel slope and has a value of 1.874 cm³ kg¹/² mol⁻³/² at 298.15 K. $\phi_V{}^0$ is the partial molar volume of salt at infinite dilution.

The apparent molal volume of an ion in a mixture can be estimated as

$$\phi_{Vi} = \phi_{Vi}{}^0 + \frac{Z_i A}{2b} \ln (1 + bI^{1/2}) + RT\sum_j B_{ij}m_j + \frac{RT}{2|Z_i|^{1/2}}\sum_j C_{ij}m_j{}^2|Z_i|^{1/2} \quad (4)$$

ϕ_{Vi} then, using usual relationship, yields the apparent molal volume of Jth salt in mixture as

$$\phi_{VJ} = \sum_i \nu_i\phi_{Vi} \quad (5)$$

which in turn calculates theoretical mean apparent molal volumes $\phi^*{}_V$ as

$$\phi^*{}_{V_{calcd}} = \frac{\sum_J m_J\phi_{VJ}}{\sum_J m_J} \quad (6)$$

The densities of a mixture can be calculated as

$$d_{calcd} = \frac{1000 + \sum_J m_J M_J}{1000/d_0 + \sum_J m_J\phi_{VJ}} \quad (7)$$

where M_J is molecular weight of salt J. $\phi^*{}_V$ calculated from eq 6 can be compared with those obtained from experimental densities as

$$\phi^*{}_{V_{exptl}} = \frac{1000(d_0 - d_{exptl})}{\sum_J m_J d_{exptl} d_0} + \frac{\sum_J m_J M_J}{d_{exptl}\sum_J m_J} \quad (8)$$

Densities obtained from eq 7 can easily be compared with the experimental values. The mixing term, θ^V, arising due to the possible interactions between like charge ions like K⁺ and Ca²⁺ can be calculated by

$$\theta_{K^+Ca^{2+}} = \frac{(\phi^*{}_{V_{exptl}} - \phi^*{}_{V_{calcd}})(m_A + m_B)}{RTm_Am_B(\nu_A + \nu_B)} \quad (9)$$

ν_A and ν_B are the number of ions per mole of KCl and CaCl₂,

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Table I. Experimental Relative Densities (Δd) and Mean Apparent Molal Volumes (ϕ^*_V) of Aqueous KCl–CaCl2 at 298.15 K

y_B	$\Delta d \times 10^3$, g·cm^3	ϕ^*_V, cm^3·mol^{-1}
	I = 0.5 mol·kg^{-1}	
0.0000	22.725	28.413
0.1438	21.605	28.035
0.3138	20.282	27.456
0.4673	19.097	26.729
0.5983	18.070	25.956
0.7394	16.973	24.776
0.9038	15.698	22.660
1.0000	14.948	20.787
	σ^a = 0.021 × 10^{-3} g·cm^{-3}	
	σ^{*a} = 0.012 × 10^{-3} g·cm^{-3}	
	I = 1.5 mol·kg^{-1}	
0.0000	64.861	29.373
0.0798	63.168	29.213
0.1532	61.621	29.040
0.2008	60.611	28.918
0.2952	58.592	28.654
0.3493	57.431	28.481
0.4229	55.848	28.213
0.5439	53.291	27.629
0.6630	50.768	26.867
0.7771	48.342	25.898
0.8543	46.702	25.026
0.9495	44.689	23.572
1.0000	43.612	22.593
	σ = 0.112 × 10^{-3} g·cm^3	
	σ^* = 0.047 × 10^{-3} g·cm^{-3}	
	I = 3.0 mol·kg^{-1}	
0.0000	121.289	30.411
0.0997	117.571	30.282
0.1853	114.432	30.121
0.2973	110.209	29.902
0.4175	105.772	29.548
0.5083	102.431	29.195
0.6111	98.630	28.694
0.7099	94.944	28.084
0.8122	91.110	27.239
0.9220	87.084	25.886
1.0000	84.168	24.575
	σ = 0.258 × 10^{-3} g·cm^{-3}	
	σ^* = 0.101 × 10^{-3} g·cm^{-3}	
	I = 4.5 mol·kg^{-1}	
0.0000	171.032	31.197
0.0575	168.337	31.124
0.1638	163.330	30.962
0.2495	159.302	30.791
0.3771	153.316	30.451
0.4483	149.962	30.212
0.5517	145.102	29.770
0.6498	140.499	29.215
0.7632	135.162	28.350
0.8551	130.840	27.382
0.9444	126.658	26.081
1.0000	124.040	25.022
	σ = 0.482 × 10^{-3} g·cm^{-3}	
	σ^* = 0.197 × 10^{-3} g·cm^{-3}	

$^a \sigma$ = standard deviation in Δd without θ^V; σ^* = standard deviation in Δd with θ^V.

respectively. $\phi^*_{V_{calcd}}$ is given by eq 6. Details of the equation can be found elsewhere (4).

Pitzer's equation for calculating ϕ_{VI} in a mixture is

$$\phi_{VI} = \text{right-hand side of eq 4} + RT\sum_k \theta_{ik} m_k \quad (10)$$

where i and k are ions of identical charges.

Results and Discussion

Table I reports the relative densities (Δd) as a function of y_B, at the ionic strengths of 0.5, 1.5, 3, and 4.5 mol·kg^{-1} and

Table II. Pitzer Coefficients for KCl and CaCl2 at 298.15 K

salt	ϕ_V^0	$(\partial\beta^{(0)}/\partial P)_T \times 10^5$	$(\partial\beta^{(1)}/\partial P)_T \times 10^5$	$(\partial C^\phi/\partial P)_T \times 10^6$	σ, cm^3·mol^{-1}
KCl, 0–4.5 m	26.91	1.55	−0.11	−2.74	0.02
CaCl2, 0–7.4 m	18.53	1.56	−104.81	−0.088	0.30

Table III. Parameters of Eq 13 Correlating ΔV^{ex} and y_B

I, mol·kg^{-1}	v_0	v_1	v_2	σ, cm^3·mol^{-1}
0.5	0.0802	−0.0317	0.0135	0.002
1.5	0.7220	−0.1039	−0.2213	0.004
3.0	2.276	−0.0999	0.0309	0.003
4.5	4.251	−0.0905	−0.1254	0.002

at 298.15 K. It also lists the experimental ϕ^*_V as computed by using eq 8.

Pitzer coefficients for pure electrolyte solutions were obtained by using eq 1, 2, and 3 by nonlinear least-squares method. Density data on pure KCl solution were taken from Romankiw and Chou (6). Pitzer coefficients for CaCl2 solutions were taken from our earlier reported work (4). Table II lists these coefficients for these salts along with the standard deviation of fit. ϕ_V^0 obtained for both the salts are in good agreement with literature values (7). Incidentally, the fit for aqueous CaCl2 is relatively poor and the reasons for the relatively poor fit due to structural changes in the solutions are discussed in detail by Phutela and Pitzer (8).

Calculations for the mixtures were performed through eq 4–7 by using the Pitzer coefficients given in Table II. Standard deviations of fit σ are given at the end of each ionic strength in Table I. For instance, one can estimate the density of a mixture of y_B = 0.51 at I = 3 to 0.02%. In general, the densities can be predicted with fairly good accuracy.

In the above discussion, only cation–anion interactions have been considered dominant and the interactions between K$^+$ and Ca^{2+} are neglected. $\theta_{K^+Ca^{2+}}$ calculated by eq 9 varies linearly with ionic strength and has the functional form

$$\theta_{K^+Ca^{2+}} = 5.780 \times 10^{-7}I - 1.039 \times 10^{-7} \quad (11)$$

It was therefore difficult to assume a single value of this parameter for this ionic strength range. We (9) recently suggested $\theta_{K^+Ca^{2+}}$ = 9.1 × 10^{-6} from 8.3 to 9.6 mol·kg^{-1} in brines. $\theta_{K^+Ca^{2+}}$ calculated at I = 9.6 mol·kg^{-1} by using eq 11 yields a lower value, indicating its nonlinear behavior at higher ionic strengths.

Use of mixing terms gives a remarkable improvement in the density fit. The standard deviations listed at the end of Table I indicate this fact. As compared to earlier predictions, one now can estimate Δd with standard deviations of 0.05 × 10^{-3} in dilute mixture (I = 0.5 mol·kg^{-1}) and 0.12 × 10^{-3} upto I = 4.5 mol·kg^{-1}. Excess volumes of mixing ΔV^{ex} were computed by the relation

$$\Delta V^{ex} = \phi^*_{V_{exptl}}\sum_J m_J - \sum_J m_J\phi_{VJ} \quad (12)$$

where ϕ_{VJ} is apparent molal volume of single electrolyte solution at the ionic strength of mixture.

ΔV^{ex} thus calculated are shown in Figure 1 as a function of y_B at various ionic strengths and are fitted to the equation

$$\Delta V^{ex} = y_B(1 - y_B)[v_0 + v_1(1 - 2y_B) + v_2(1 - 2y_B)^2] \quad (13)$$

Figure 1 however does not show ΔV^{ex} at I = 0.5 as they are extremely small numbers. Table III lists parameters v_0, v_1,
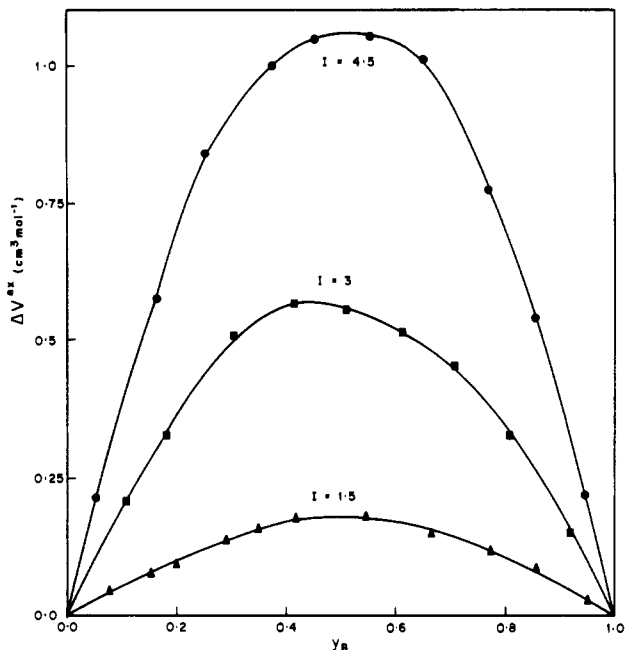
Figure 1. Excess volume of mixing (ΔV^{ex}) vs. y_B for aqueous KCl–CaCl$_2$ at 298.15 K.

and v_2 along with the standard deviation of fit.

In summary, it is shown that densities of aqueous electrolyte mixtures like KCl–CaCl$_2$–H$_2$O can be accurately predicted by the Pitzer's equation.

Use of mixing parameters helps in improving the estimation of densities. However, an attempt should be made to treat binary mixing terms independent of ionic strengths. This will help us in limiting the number of parameters necessary for predicting the density of such ternary mixtures.

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Vapor–Liquid Equilibrium for 1-Naphthol/Methanol and Naphthalene/Methanol Mixtures at Elevated Temperatures and Pressures

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Vapor and liquid equilibrium compositions have been measured for binary 1-naphthol/methanol and naphthalene/methanol mixtures at 248, 276, and 307 °C over a range of pressures from approximately 1.3 MPa to the respective mixture critical pressures. Mixture critical pressures are obtained by observation of critical opalescence within the view cell.

Introduction

The development of new processes for the conversion of nontraditional hydrocarbon resources to useful products will depend to a large extent on the availability of accurate chemical and physical property data. As part of our research program to study fundamental equilibrium phase behavior related to such conversion processes, we are measuring vapor–liquid equilibrium compositions for mixtures of model coal-derived compounds with dense fluids, such as methanol and water, at elevated temperatures and pressures. These data are of particular interest for coal conversion processes which use dense fluids as extractive solvents.

In this paper we report experimental results for two binary mixtures: 1-naphthol/methanol and naphthalene/methanol.

The flow technique used for measuring equilibrium compositions has been described previously (1). Compositions are determined by sampling coexisting fluid phases, and phase behavior, such as critical phenomena, can be observed directly through a view cell. The apparatus is rated for temperatures as high as 425 °C and pressures up to 30 MPa.

Chao and co-workers have used a similar experimental technique to measure vapor–liquid equilibrium compositions for model coal-derived compounds with compressed gases (hydrogen, carbon dioxide, methane, nitrogen) at elevated temperatures and pressures (2–4). However, these investigations did not include naphthalene (mp = 80 °C) and 1-naphthol (mp = 95 °C), which are solids at ambient temperatures. Schneider and co-workers have used a synthetic experimental technique to determine the coexistence curves and critical curves for related water/hydrocarbon binary mixtures at elevated temperatures and high pressures (50–200 MPa). A limited number of measurements have been made for vapor–liquid equilibrium naphthalene/water mixtures (5).

Experimental Section

A flow technique is used to facilitate sampling at elevated pressures and to minimize thermal degradation of the hydro-