Table III. C_p Ratio for the CH_4-CO_2 Mixture at 325.2 K

press., bar	C_{PHP}/C_{P1atm} exptl	C_{PHP}/C_{P1atm} SRK	press., bar	C_{PHP}/C_{P1atm} exptl	C_{PHP}/C_{P1atm} SRK
6.89	1.021	1.023	37.92	1.147	1.149
10.34	1.033	1.035	41.37	1.164	1.166
13.79	1.046	1.047	44.81	1.180	1.184
17.24	1.060	1.060	48.26	1.198	1.202
20.68	1.073	1.074	51.71	1.216	1.221
24.13	1.087	1.088	55.16	1.235	1.241
27.58	1.102	1.102	58.60	1.255	1.261
31.02	1.116	1.117	59.98	1.263	1.269
34.47	1.132	1.133	62.05	1.275	1.282

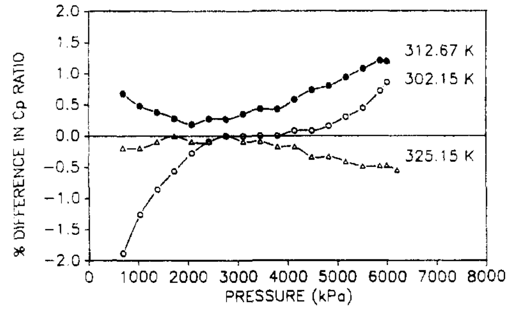

Figure 2. Percentage difference between experimental and SRK-predicted C_p ratios.

the C_p ratio was greater for a lower temperature isotherm.

The uncertainty in the data is approximately 0.6% over most of the pressure range. Only at heat-capacity ratios less than about 1.05 does the uncertainty in temperature-difference measurements lead to larger overall uncertainties.

Discussion

For purposes of comparison, the C_p ratios of the test mixture were calculated by applying the Soave-Redlich-Kwong (SRK) EOS (*10*) to the rigorous thermodynamic equation

$$C_p = C_p{}^* - \left(R + T\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \right) - T\int_V^{\infty} \left(\frac{\partial^2 P}{\partial T^2}\right)_V \mathrm{d}V \quad (3)$$

The mixing rules suggested by Soave (*10*) were used along with one temperature-independent binary interaction parameter in the attractive term. The value ($k_{ij} = 0.0933$) was obtained from a compilation by Knapp et al. (*11*) based on vapor-liquid equilibria (VLE).

The expressions given by Reid et al (*12*) for the ideal-gas heat capacity, $C_p{}^*$, of methane and carbon dioxide were combined according to the mole fractions of each to give $C_p{}^*$ for the mixture. This value was set equal to $C_{p_{1atm}}$, as required in eq 2, without correction.

The results of the SRK calculations are shown in Tables I-III and in Figure 2. The difference plot shows that agreement with the experimental results is quite good. At the lowest pressures, where the precision of the experimental data is poorest because the C_p ratio is near unity, the differences result from scatter in the experimental data. At high pressures the agreement is excellent and within experimental error for much of the pressure range even though a k_{ij} based on VLE data was used for the heat-capacity predictions. Regression of these experimental heat-capacity data for a special k_{ij} would result in a fit that is well within experimental error even at 62 bar. However, the preferred procedure for fitting any equations of state and mixing rules would be the regression of P-V-T and VLE data along with the heat-capacity data (*13*).

Registry No. CH_4, 74-82-8; CO_2, 124-38-9.

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Mixture Densities of Aqueous KCl with NaCl up to Ionic Strength 4.5 mol kg^{-1} and at 298.15 K

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The experimental density differences, Δd, are reported for aqueous mixtures of KCl with NaCl at 298.15 K from the constant ionic strength, I, 0.5-4.5 mol kg^{-1} of water. The results are fitted to the equations derived by Patwardhan and Kumar (equivalent to Young's rule) and by Pitzer. The interactions between Na^+ and K^+, as shown by the excess volumes, ΔV_m, are very small.

Introduction

In continuation of our work on the volume properties of concentrated electrolyte mixtures (*1*, *2*), we now present the experimental density differences for aqueous KCl-NaCl at 298.15 K. Wirth (*3*) and Millero and Sotolongo (*4*) have also reported the densities of this system, but their measurements were restricted to the ionic strength, I, of 1.5 mol kg^{-1} of water. This article reports the experimental density differences, Δd, for this system at constant I = 0.5, 1, 2, 3, and 4.5 mol kg^{-1}, ranging from pure KCl to pure NaCl solutions.

Experimental Section

Both KCl and NaCl from BDH (AR Grade), dried in an oven, were directly used for preparing the stock and starting solutions.

Table I. Experimental Density Differences, Δd (g cm^{-3}), for Aqueous KCl-NaCl at 298.15 K

y_{NaCl}	$10^3\Delta d$, g cm^{-3}	y_{NaCl}	$10^3\Delta d$, g cm^{-3}
	$I = 0.5$ mol kg^{-1}		
0.0000	22.721	0.5253	21.350
0.0466	22.582	0.6462	21.041
0.1522	22.321	0.7626	20.702
0.2886	21.967	0.8731	20.434
0.3919	21.705	1.0000	20.102
	$I = 1$ mol kg^{-1}		
0.0000	44.294	0.5731	41.309
0.1098	43.720	0.6533	40.892
0.2135	43.182	0.7825	40.219
0.3454	42.490	0.9021	39.599
0.4653	41.860	1.0000	39.083
	$I = 2$ mol kg^{-1}		
0.0000	84.472	0.5951	78.874
0.1283	83.260	0.7114	77.770
0.2395	82.208	0.8398	76.560
0.3537	81.148	0.9128	75.884
0.4902	79.854	1.0000	75.060
	$I = 3$ mol kg^{-1}		
0.0000	121.265	0.5710	113.986
0.1435	119.430	0.6995	112.349
0.2957	117.499	0.8531	110.384
0.4098	116.045	1.0000	108.519
	$I = 4.5$ mol kg^{-1}		
0.0000	171.039	0.8530	160.220
0.1341	188.809	0.7789	158.141
0.2594	166.749	0.9132	155.908
0.3995	164.420	1.0000	154.473
0.5114	162.561		

Solutions were made by dissolving a definite mass in deionized water. The concentrations of solutions were determined by gravimetric method using $AgNO_3$ solution.

The density differences ($\Delta d = d - d_0$) were measured with a Paar densimeter with a precision of $\pm 3 \times 10^{-6}$ g cm^{-3}. d and d_0 are the densities of solution and pure water (0.997 047 g cm^{-3} at 298.15 K), respectively. The constant temperature thermostat bath was maintained to ±0.005 K. The methods of calibration and experimentation are discussed elsewhere (*5*).

Results and Discussion

Table I lists the measures Δd values as a function of ionic strength fraction of NaCl ($y_{NaCl} = m_{NaCl}/I$; m = molality) at constant I's of 0.5, 1, 2, 3, and 4.5 mol kg^{-1} of water. The earlier measurements of Wirth (*3*) could not be compared, as his data were neither at constant ionic strength nor at constant ionic strength fraction. Millero and Sotolongo (*4*) measured densities at $I = 1.5$ mol kg^{-1}. Our data, when interpolated to 1.5, gave good agreement with their data.

Mean apparent molal volumes, ϕ^*_V, of mixtures can be calculated by using the relation

$$\phi^*_V = M_T/d - [10^3(d - d_0)/dd_0\sum_J m_J] \qquad (1)$$

where

$$M_T = \sum_J m_J M_J / \sum_J m_J$$

M_J and m_J are the molecular weight and molality respectively of dissolved Jth electrolyte.

The mixture densities, d, can be easily fitted to the equation of Patwardhan and Kumar (*6*). Their basic equations for activity and osmotic coefficients of aqueous mixed electrolyte solutions (*7*) account for the interactions between the ions of opposite charges and neglect any interactions due to like charge ions. Thus, their equations follow the famous Young's rule (*8*). Their equation for estimating density of mixture is

$$d = \sum_J (10^3 y_J + m_J M_J)/(\sum_J (10^3 y_J + m_J M_J)/d_J{}^0) \qquad (2)$$

$d_J{}^0$ is density of Jth electrolyte at the ionic strength of mixture.

The average standard deviation of fit for Δd by using eq 2 from $I = 0.5$ to 4.5 mol kg^{-1} is 0.085×10^{-3} g cm^{-3}.

The author has demonstrated the applicability of the Pitzer theory (*9*) in predicting the densities of electrolyte mixtures (*1*, *2*). After the pure electrolyte Pitzer parameters are obtained, the approach of the mixture calculations is essentially a Young's rule (*8*) approach. Thus, with the use of Pitzer parameters for aqueous KCl (*2*) and aqueous NaCl (*10*), one obtains almost the same standard deviations of fit as obtained by the use of eq 2. The system of the Pitzer equations and method of calculations are discussed in our earlier work (*1*, *2*).

The excess volumes of mixing, ΔV_m, may be obtained as

$$\Delta V_m = \phi_V \sum_J m_J - \sum_J \phi_{VJ}{}^0 m_J \qquad (3)$$

ΔV_m can be easily fitted to the equation (*11*)

$$\Delta V_m = y_{NaCl}(1 - y_{NaCl})I^2[v_0 + v_1(1 - 2y_{NaCl})] \qquad (4)$$

Equation 4 is analogous to the equation for correlating ΔH_m or ΔG_m with RTh_0, RTh_1 or RTg_0 and RTg_1 parameters of heats and free energy of mixing respectively (*12*). In eq 4, v_0 and v_1 indicate the binary (Na^+, K^+) and ternary (Na^+, K^+, Cl^-) interactions.

The value of v_0 was found to be constant with I and was 0.0420 ± 0.0037 from $I = 0.5$ to 4.5 mol kg^{-1} of water. This small magnitude indicates very weak interactions between Na^+ and K^+ ions, which is also supported by heats of mixing data (*12*). The ternary interaction parameter v_1 was negligible for this system.

In the Pitzer theory (*9*), the binary mixing term θ_{ik}^V used in the volumetric equation is the pressure derivative of binary mixing term θ_{ik} of the activity coefficient expression. θ_{ik}^V ($i = K^+$, $k = Na^+$), which can be obtained from the equation discussed in our earlier work (*1*, *2*), is related with v_0 of eq 4. The relationship between θ_{ik}^V and v_0 as simplified for the mixtures of 1–1 electrolytes with common ion is

$$\theta_{ik}^V = v_0/2RT \qquad (5)$$

where $R = 83.1441$ cm^3 mol bar^{-1} K^{-1} and T is in kelvin. The value of $\theta_{K^+Na^+}^V$ thus is $8.47 \pm 0.07 \times 10^{-7}$.

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7.

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