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Mixture Densities and Volumes of Aqueous KCl–MgCl$_2$ up to Ionic Strength of 4.5 mol kg^{-1} and at 298.15 K

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The densities of aqueous KCl–MgCl$_2$ mixtures are measured at 298.15 K and at the ionic strengths of 0.5, 1, 2, 3, and 4.5 mol kg^{-1} water. The excess volumes, ΔV_m, are calculated. It is demonstrated that the ΔV_m terms are very essential in making better estimates of densities (6 ppm with the use of the ΔV_m term as compared to 420 ppm from I = 0.5 to 4.5 mol kg^{-1} without the use of the ΔV_m term) of these concentrated mixtures. A brief discussion for calculating the densities by use of the Pitzer equations is given. The relationship between the Pitzer binary mixing and the Friedman parameters is suggested.

Introduction

As a part of our program on the *PVT* properties of aqueous electrolytes, we (*1*) recently published the densities and apparent molal volumes of aqueous KCl–CaCl$_2$ from ionic strength (I) 0.5 to 4.5 mol kg^{-1} water at 298.15 K. In the present paper we will report on the densities of aqueous KCl–MgCl$_2$ at constant I of 0.5, 1, 2, 3, and 4.5 mol kg^{-1} water and at 298.15 K.

Experimental Section

Both KCl and MgCl$_2$ (Baker Analysed) were recrystallized twice before use. The stock solutions were prepared on a molality basis in deionized water. The molalities of stock and starting solutions were determined by the gravimetric method. The mixtures of KCl and MgCl$_2$ with different compositions at constant I were prepared as $y_B = I_B/(I_A + I_B)$, where subscripts A and B refer to electrolytes KCl and MgCl$_2$, respectively.

The experimental relative densities ($\Delta d = d - d_0$ g cm^{-3}) were measured with a Paar vibrating tube densimeter (*2*). Δd is the difference in density (d) of the solution and that of pure water (d_0, 0.997 047 g cm^{-3} at 298.15 K). The densimeter was calibrated with the known densities of water (*3*) and standard sea water of different salinities (*4–6*). The temperature of the densimeter was controlled to ±0.001 K, and Δd were precise to $\pm 3 \times 10^{-6}$ g cm^{-3}.

Results and Discussion

Table I lists the experimental relative densities (Δd) as a function of y_B at constant ionic strengths. The measurements ranged from pure KCl to pure MgCl$_2$ solutions.

Table I. Experimental Density Differences (Δd, g cm^{-3}) as a Function of y_{MgCl_2} for Aqueous KCl–MgCl$_2$ from 0.5 to 4.5 mol kg^{-1} and at 298.15 K

y_{MgCl_2}	$\Delta d \times 10^3$, g cm^{-3}	y_{MgCl_2}	$\Delta d \times 10^3$, g cm^{-3}
	I = 0.5 mol kg^{-1}		
0.0000	22.721	0.6038	16.570
0.1857	20.821	0.7485	15.109
0.2992	19.678	0.8852	13.701
0.3952	18.692	1.0000	12.541
0.5029	17.605		
	I = 1 mol kg^{-1}		
0.0000	44.294	0.5889	33.290
0.1258	41.940	0.7114	31.012
0.2395	39.828	0.8394	28.603
0.3852	37.093	0.9112	27.270
0.4950	35.044	1.0000	25.616
	I = 2 mol kg^{-1}		
0.0000	84.472	0.6530	61.978
0.1298	80.004	0.7774	57.680
0.2652	75.330	0.9095	53.136
0.3958	70.830	1.0000	50.014
0.5195	66.578		
	I = 3 mol kg^{-1}		
0.0000	121.265	0.6057	92.029
0.1572	113.670	0.7662	84.289
0.3117	106.209	0.9280	76.468
0.4485	99.620	1.0000	72.993
	I = 4.5 mol kg^{-1}		
0.0000	171.039	0.5723	133.301
0.1435	161.569	0.6952	125.194
0.2538	154.282	0.7903	118.899
0.3439	148.369	0.9188	110.459
0.4573	140.894	1.0000	105.103

Our experimental densities for pure KCl solutions are reported at I = 0.5, 1, 2, 3, and 4.5 mol kg^{-1}. Vaslow (*7*) and Gucker et al. (*8*) reported very precise density data on aqueous KCl. Our data agree with those of Vaslow and of Gucker et al. on interpolation to appropriate molalities to within 30×10^{-6} g cm^{-3} with the maximum residual being 95×10^{-6} g cm^{-3}. Interestingly, our data were in excellent agreement (15×10^{-6} g cm^{-3}) with those of Romankiw and Chou (*9*). Similarly, our data compared exceedingly well with the very recent work of Gates and Wood (*10*). However, there are remarkable differences between our data and those of Nickels and Allmand (*11*), Fabuss and Korosi (*12*), and International Critical Tables (*13*) by 992×10^{-6}, 360×10^{-6}, and 250×10^{-6} g cm^{-3}, respectively.

Again our experimental data for pure MgCl$_2$ are in good agreement with the extensive and precise work of LoSurdo et al. (*14*). Our data when compared with their polynomial equations's estimations agreed to within 30×10^{-6} g cm^{-3} with a maximum residual of 87×10^{-6} g cm^{-3}. The present results, however, differ from the values of Phang and Stokes (*15*) by 140×10^{-6} g cm^{-3}. Recently, Isono (*16*) reported density data at round molalities of MgCl$_2$, obtained by using a Weld-type densitometer. The densities measured in the present investigation agree with the values of Isono to within 12×10^{-6} g cm^{-3}. However, it should be mentioned some differences between ours and literature values may be real, as the final ionic strengths of salts and mixtures are rounded off.

Apparent molal volumes ϕ_V of the binary solution were calculated from the densities as

$$\phi_V = [1000(d_0 - d)/mdd_0] + (M/d) \tag{1}$$

where m and M are molality and molecular weight of an electrolyte, respectively.

The mean apparent molal volumes of ternary mixtures, $\phi_V{}^*$, were computed by the relation

$$\phi_V{}^* = [1000(d_0 - d)/m_T d d_0] + (M_T/d) \tag{2}$$

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Table II. Values of v_0 and v_1 Obtained in the Present Work Along with RTh_0 and RTh_1 Values from Wood et al. (*18*) and Wood and Gamkhar (*19*) on ΔH_m of Aqueous KCl-MgCl$_2$ and Aqueous KCl-CaCl$_2$ (*1*) at 298.15 K

I,	KCl-MgCl$_2$				KCl-CaCl$_2$			
mol kg^{-1}	$v_0 \times 10^2$	$v_1 \times 10^2$	RTh_0	RTh_1	$v_0 \times 10^2$	$v_1 \times 10^2$	RTh_0	RTh_1
0.5	57.22	3.05	108	-8	41.28	2.01	70	-5
1	43.81	-0.52	86.7	-4			48.3	-2.8
1.5					32.00	-0.63		
2	37.70	-0.14	54	-3.1			20.5	-1.0
3	34.70	0.38	31.7	-1.5	25.31	0.02	-0.50	-1.9
4.5	31.06	-0.01	17^a	-0.1^a	21.02	-0.01	-22.00^a	-3.0^a

^{a}Extrapolated values to I = 4.5.

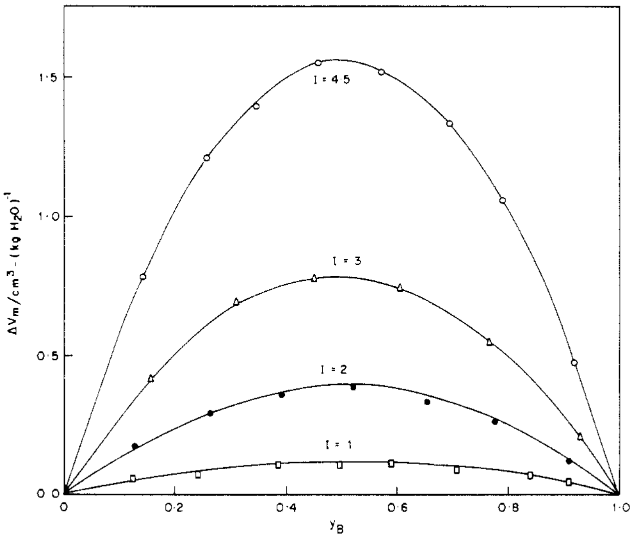

Figure 1. Volume change for mixing ΔV_m, plotted against ionic strength fraction of MgCl$_2$, y_B, at constant ionic strengths of 1, 2, 3, and 4.5 mol kg^{-1} and at 298.15 K.

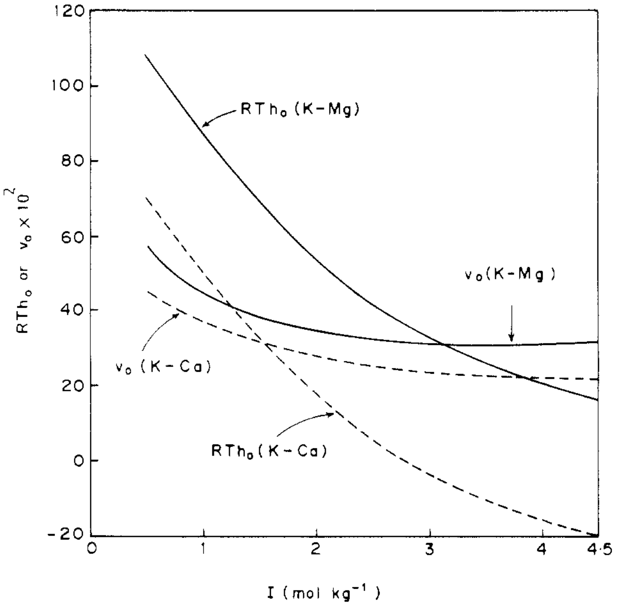

Figure 2. v_0 and RTh_0 terms against I for aqueous KCl-MgCl$_2$ (solid lines) and KCl-CaCl$_2$ (dashed lines) systems at 298.15 K.

Table III. Differences between Experimental and Calculated Densities (ppm) without and with the Addition of ΔV_m Term for Aqueous KCl-MgCl$_2$ System at 298.15 K

I,	average		maximum	
mol kg^{-1}	without	with	without	with
0.5	23	4	28	6
1	57	5	100	15
2	267	7	387	13
3	560	7	768	14
4.5	1193	6	1601	17

where $m_T = m_A + m_B$ and $M_T = (m_AM_A + m_BM_B)/m_T$.

The excess volumes for mixing, ΔV_m, were obtained as

$$\Delta V_m = \phi_V{}^* \, m_T - \phi_V(A)m_A - \phi_V(B)m_B \qquad (3)$$

The values of ΔV_m thus calculated are plotted in Figure 1 as a function of y_B except for I = 0.5 mol kg^{-1} as the ΔV_m values were very small.

The excess volumes, ΔV_m, can be fitted with the equation of Friedman (*17*):

$$\Delta V_m = y_Ay_BI^2[v_0 + v_1(1 - 2y_B)] \qquad (4)$$

where v_0 and v_1 are the indications of binary and ternary interactions due to two like-charge cations (K$^+$, Mg^{2+}) and a three-ion triplet (K$^+$, Mg^{2+}, Cl$^-$), respectively. Table II reports the values of v_0 and v_1 at different ionic strengths.

An examination of Figure 1 shows that ΔV_m vs y_B plots are fairly symmetrical parabolas about y_B = 0.5, showing either no or very little skew.

Wood et al. (*18*) and Wood and Gamkhar (*19*) have reported the heats of mixing ΔH_m for aqueous KCl-MgCl$_2$ and KCl-CaCl$_2$ systems at 298.15 K, fitted their data to the analogous equation for ΔH_m, and reported RTh_0 and RTh_1. Table II also lists values for RTh_0 and RTh_1 for these systems. The values of v_0 and v_1 for the aqueous KCl-CaCl$_2$ system at 298.15 K were obtained from our earlier work (*1*) by refitting the reported ΔV_m data to eq 4. They are also listed in Table II for ready comparison. In Figure 2, v_0 and RTh_0 values are plotted as a function of I for both systems. One can see that v_0 values tend to turn toward high positive values at low ionic strength, e.g., 0.5 mol kg^{-1} of water. The same trend was observed by Wood et al. (*18*) for RTh_0 as shown in the same figure. This nature of the curves is in contrast to the prediction of the theory of Friedman (*17*, *20*) for charge-symmetric mixtures. For charge-symmetric mixtures comparatively flat curves are predicted. It appears that this behavior of RTh_0 or v_0 may be due to the high order limiting law in such mixtures.

Barring the low-concentration data, the magnitude of v_0 decreases slowly with ionic strength. A survey of v_1 terms for both systems shows that the ternary interactions are very weak throughout or are almost negligible. This is again supported by examining the RTh_1 values reported from the school of Wood (*18*, *19*). Another interesting feature is that the slopes for v_0 in both mixtures are almost same, although the sizes of Mg^{2+} and Ca^{2+} differ by about 0.34 Å.

One can demonstrate the need of considering Δv_m by comparing the measured densities with those calculated from

$$d = d_0(1000 + m_TM_T)/(\phi_V{}^*{}_{est}m_Td_0 + 1000) \qquad (5)$$

with

$$\phi_V{}^*{}_{est} = x_A\phi_V(A) + x_B\phi_V(B) + \Delta V_m/m_T \qquad (6)$$

and $x = m/m_T$.

$\phi_V{}^*{}_{est}$ is calculated without and with the ΔV_m term. The differences between experimental and calculated densities with eq 5 without and with the ΔV_m term are summarized in Table III at each ionic strength. The maximum difference is 1601 ppm at $I = 4.5$ mol kg^{-1}, which is reduced to 17 ppm with the use of the ΔV_m term. As an average, the differences are reduced to 6 ppm as compared to 420 ppm with the use of ΔV_m from $I = 0.5$–4.5 mol kg^{-1}.

Recently we (*21*, *22*) have presented a unified approach for predicting the thermodynamic properties of aqueous mixed electrolyte solutions. Our equations did not consider the interactions among ions of like charges and of triplets and were essentially equal to Young's rule (*23*) without the correction term. The equation for estimating the density of a mixture is

$$d = \frac{\sum_J (1000 y_J + m_J M_J)}{\sum_J (1000 y_J + m_J M_J)/d_J{}^0} \qquad (7)$$

where J refers to an electrolyte and $d_J{}^0$ is the density of a constituent single electrolyte solution at the ionic strength of the mixture. The densities estimated by the use of eq 7 are equal to those obtained by eq 5 without the use of the ΔV_m term. Thus, the results quoted in columns 2 and 4 of Table III also apply to the estimations made by eq 7.

We (*1*) have recently used the ion-interaction model of Pitzer (*24*) for estimating the volume properties of aqueous KCl–CaCl$_2$ up to the ionic strength of 4.5 mol kg^{-1}. The pertinent equations and the method of calculations are given in ref *1*; thus, we shall not burden this paper with them. The Pitzer coefficients for the cation–anion pair of pure KCl and MgCl$_2$ were taken from our earlier work (*1*, *25*). For KCl (data fitted to 4.5 *m*), $\beta^{(0)V} = 1.55 \times 10^{-5}$, $\beta^{(1)V} = -0.11 \times 10^{-5}$, and $C^{\phi V} = -2.74 \times 10^{-6}$, and for MgCl$_2$ (data fitted to 5.25 *m*), $\beta^{(0)V} = 1.78 \times 10^{-5}$, $\beta^{(1)V} = -6.38 \times 10^{-5}$, and $C^{\phi V} = -1.82 \times 10^{-6}$. In both cases, the standard deviation of fit was 0.02 cm^{-3} mol^{-1}. It may be noted that the Pitzer equations, when fitted to the data with high concentrations, were found to yield the partial molal volumes at infinite dilution within reasonable accuracy. $\bar{V}^0$ values for KCl (26.91 cm^3 mol^{-1}) and for MgCl$_2$ (14.16 cm^3 mol^{-1}) were in excellent agreement with literature values (*26*).

In our primary mixture calculations with the Pitzer equations, we considered only the interactions between cation and anion. It is important to note that these calculations are essentially a simple Young's rule (*23*) approach. The properties of mixtures are computed from the properties of the individual ions at the same ionic strength, yielding results similar to those quoted in Table III without the use of ΔV_m term.

Pitzer and Kim (*27*) have discussed the interactions of binary (θ_{ik}) and ternary (ψ_{ijk}) nature and treated them as the difference parameters for estimating the activity and osmotic coefficients of aqueous electrolyte mixtures. Their pressure dependences ($\theta_{ik}^V = (\partial \theta_{ik}/\partial P)$ and $\psi_{ijk}^V = (\partial \psi_{ijk}/\partial P)$ can be related to the Friedman parameters v_0 and v_1. We neglect the magnitude of $\psi_{K^+Mg^{2+}Cl^-}$ as this is extremely small, and this decision is guided by the values of ψ_{ijk} listed for such systems in Table I of ref *27*. Following our earlier work (*1*), one may write the binary mixing term $\theta_{K^+Mg^{2+}}$ in terms of ΔV_m as

$$\theta_{K^+Mg^{2+}}^V = \Delta V_m / RT m_{K^+} m_{Mg^{2+}} (\nu_{K^+} + \nu_{Mg^{2+}}) \qquad (8)$$

Using eq 4 and neglecting the v_1 term, one obtains, after simplification, for the mixtures of 1–1 and 2–1 or 1–2 electrolytes

$$\theta_{K^+Mg^{2+}}^V = 1.5 v_0 / RT \qquad (9)$$

Equation 9 correlates v_0 of the Friedman equation to the binary term θ_{ik}^V of Pitzer formalism. It is natural that the plots of θ_{ik}^V vs I will have the same shape as those of v_0 vs I shown in Figure 2.

In a recent work by Phutela and Pitzer (*28*), the ionic strength dependence of binary mixing term for enthalpy ($\theta_{ik}^L = \partial \theta / \partial T$) has been demonstrated considering the limiting law. The same treatment is possible for these pressure-dependent terms and is currently under way (*29*). A preliminary survey of Figure 2 indicates that temperature and pressure dependences of θ_{ik} may exhibit analogous behavior.

In summary, the use of correction term, ΔV_m, is essential in order to make reliable estimates of the densities of such mixtures. The ΔV_m term can also be satisfactorily represented by the Pitzer equations.

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