

Solution Densities of Aqueous Potassium Chloride-Barium Chloride Mixtures at 298.15 K & Different Ionic Strengths

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The solution densities of aqueous KCl-BaCl₂ mixtures are reported at 298.15K from ionic strength 0.5 to 4.5 mol kg⁻¹ of water. The negative excess volumes (ΔV_m) obtained from the experimental mean apparent molal volumes are fitted to the Friedman equation. The reliable estimates of the mixture densities can be made by the Young's rule with the addition of the ΔV_m values. In general, the densities can be predicted to within 14 ppm with the use of ΔV_m term as compared to 211 ppm obtained without the use.

Recently, there has been growing interest in the thermodynamic properties of concentrated electrolyte mixtures. Although, a large number of papers have appeared on osmotic and activity coefficients of these mixtures, only a little¹⁻³ has been accomplished as regard their PVT properties in concentrated region. A knowledge of PVT properties is essential in obtaining the pressure dependence of activity coefficients in these solutions. Thus, the present investigation reports the densities and mean apparent molal volumes of aqueous KCl-BaCl₂ mixtures at 298.15K and at ionic strengths of 0.5, 1, 3 and 4.5 mol kg⁻¹ of water. The experimental measurements cover the range from pure KCl to pure BaCl₂ solutions.

Materials and Methods

Both KCl and BaCl₂ (Baker analysed) were recrystallized twice from water before use. The stock and working solutions were prepared by dissolving a definite weight in degassed ion-exchanged water. The concentrations of these solutions were determined gravimetrically using AgNO₃ solution. The mixtures of KCl and BaCl₂ were prepared at constant ionic strength as $Y_{BaCl_2} = 3m_{BaCl_2} / (m_{KCl} + 3m_{BaCl_2})$, where m and Y respectively refer to molality and ionic strength fraction of an electrolyte in mixture and $Y_{KCl} + Y_{BaCl_2} = 1$.

The densities were measured using a Paar vibrating tube densimeter⁴. The relative densities (Δd) were evaluated as the difference between density of solution (d) and that of pure water ($= 0.997047 \text{ gm}^{-3}$ at 298.15K). The densimeter was calibrated with the known densities of water⁵ and NaCl solutions⁶. The temperature of the densimeter was controlled within $\pm 0.005^\circ\text{C}$ and the densities were precise to ± 3 ppm.

Results and Discussion

In Table 1 are reported the relative densities (Δd) as a function of Y_{BaCl_2} for aqueous KCl-BaCl₂ at $I = 0.5, 1, 3$ and 4.5 mol kg^{-1} of water.

Apparent molal volumes, ϕ_v of pure KCl and BaCl₂ solutions were calculated using Eq (1)⁷

$$\phi_v = [10^3(d_0 - d) / m d d_0] + (M/d) \quad \dots (1)$$

where M refers to the formula weight of an electrolyte.

The mean apparent molal volumes in mixtures, ϕ_v^* were obtained using Eq. (2)

Table 1—Experimental Density Differences ($\Delta d / \text{g cm}^{-3}$) as a Function of Y_{BaCl_2} for the System aq. KCl-BaCl₂ at 298.15K

Y_{BaCl_2}	$\Delta d \times 10^3$ g cm^{-3}	Y_{BaCl_2}	$\Delta d \times 10^3$ g cm^{-3}
$I = 0.5 \text{ mol kg}^{-1}$		$I = 3 \text{ mol kg}^{-1}$	
0	22.721	0	121.266
0.1253	23.618	0.1259	127.482
0.2317	24.379	0.2483	133.577
0.3518	25.238	0.3596	139.152
0.4006	25.603	0.4929	145.844
0.5001	26.300	0.6103	151.800
0.6198	27.165	0.7185	157.309
0.7251	27.902	0.8399	163.509
0.8098	28.524	0.9385	168.575
0.9321	29.225	1.0000	171.750
1.0000	29.877		
$I = 1 \text{ mol kg}^{-1}$		$I = 4.5 \text{ mol kg}^{-1}$	
0	44.291	0	171.038
0.1582	46.628	0.1195	180.054
0.3051	48.805	0.2428	189.556
0.4182	50.481	0.3775	199.945
0.4995	51.685	0.4952	209.155
0.6128	53.366	0.6111	218.349
0.7523	55.437	0.7275	227.684
0.8951	57.556	0.8505	237.643
1.0000	59.115	0.9301	244.152
		1.0000	249.950

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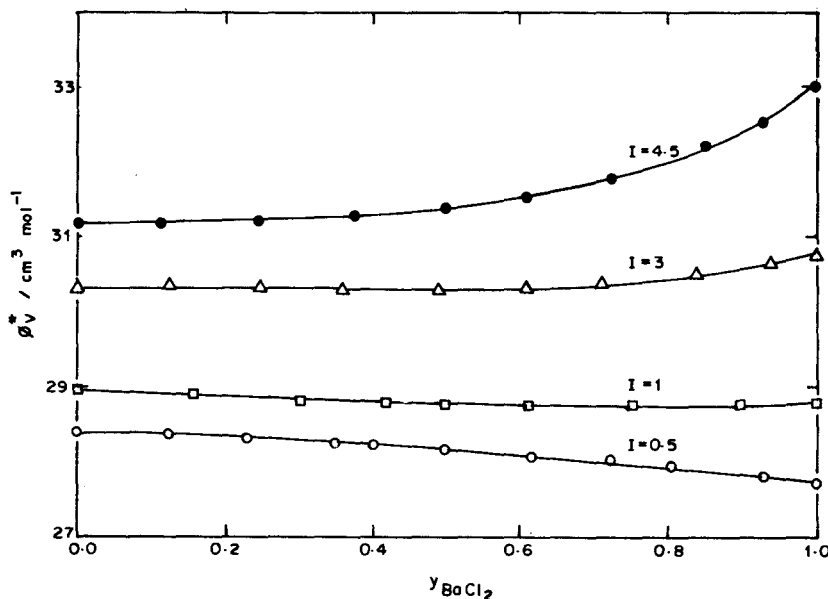


Fig. 1—Experimental mean apparent molal volumes (ϕ_V^*) as a function of Y_{BaCl_2} at different ionic strengths for aq. KCl-BaCl₂

$$\phi_V^* = [10^3(d_0 - d)/m_T d d_0] + (M_T/m_T d) \quad \dots (2)$$

where $m_T = m_{\text{KCl}} + m_{\text{BaCl}_2}$;

$$M_T = (m_{\text{KCl}} M_{\text{KCl}} + m_{\text{BaCl}_2} M_{\text{BaCl}_2}).$$

The values of ϕ_V^* at each ionic strength are plotted as a function of Y_{BaCl_2} in Fig. 1 showing nonlinear variation.

The excess volumes of mixing, ΔV_m were calculated by the expression (3)

$$\Delta V_m = \phi_V^* m_T - \phi'_{V,\text{KCl}} m_{\text{KCl}} - \phi'_{V,\text{BaCl}_2} m_{\text{BaCl}_2} \quad \dots (3)$$

Where ϕ'_V refers to the apparent molal volume of an individual electrolyte solution at the ionic strength of mixture. The ΔV_m values, thus obtained can be fitted to Friedman's equation⁸ (see Eq. 4),

$$\Delta V_m = Y_{\text{BaCl}_2} (1 - Y_{\text{BaCl}_2})^2 [v_0 + v_1 (1 - 2 Y_{\text{BaCl}_2})] \quad \dots (4)$$

where v_0 and v_1 indicate the binary ($\text{K}^+, \text{Ba}^{2+}$) and ternary ($\text{K}^+, \text{Ba}^{2+}, \text{Cl}^-$) interactions respectively. In Fig. 2, the ΔV_m values are plotted against Y_{BaCl_2} , except at $I = 0.5 \text{ mol kg}^{-1}$ because of extremely small ΔV_m values. The ΔV_m values are negative throughout. The plots in Fig. 2 exhibit symmetrical parabola at $Y_{\text{BaCl}_2} = 0.5$. Thus, v_1 in Eq. (4) may be neglected. The values of v_0 obtained from Eq. (4) are -0.122 , -0.178 , -0.272 and -0.528 at $I = 4.5, 3, 1$ and 0.5 mol kg^{-1} of water, respectively with an average standard deviation of fit for ΔV_m to be $0.01 \text{ cm}^3 \text{ kg}^{-1}$ of water.

Wood and Gamkhar⁹ have reported the heats of mixing (ΔH_m) data for this system, and fitted these da-

ta to an equation analogous to Eq. (4) and obtained h_0 and h_1 values similar to v_0 and v_1 . The decrease v_0 with increase in ionic strength is supported by a similar trend in h_0 values reported by Wood and Gamkhar⁹. The magnitude of h_1 is extremely small, thus suggesting negligible triple interactions. A similar situation is found for ΔV_m . In addition, Pitzer and Kim¹⁰ analysed the osmotic and activity coefficient data¹¹ on aq. KCl-BaCl₂ system using their virial coefficient approach. They obtained negative binary mixing and zero ternary terms supporting our ΔV_m results.

The need for considering ΔV_m values in estimating the densities of mixtures can be demonstrated by comparing the experimental densities with those calculated by Eq. (5)

$$d = d_0 (1000 + M_T) / (\phi_{V,\text{est}}^* m_T d_0 + 1000) \quad \dots (5)$$

where

$$\phi_{V,\text{est}}^* = x_{\text{KCl}} \phi'_{V,\text{KCl}} + x_{\text{BaCl}_2} \phi'_{V,\text{BaCl}_2} + \Delta V_m / m_T \quad \dots (6)$$

and $x = m/m_T$

The first two terms on the right hand side of Eq. (6) represent the well known Young's rule¹², which states that no volume change occurs on mixing the solutions of equal ionic strength. The last term on right hand side of Eq. (6) gives the correction term or excess property.

In Eq. (6), $\phi_{V,\text{est}}^*$ can be calculated with and without ΔV_m and so the values of d can be obtained. Table 2 reports the maximum and minimum differences (δ) between experimental and those obtained with and without the use of ΔV_m . One, for example, can see that

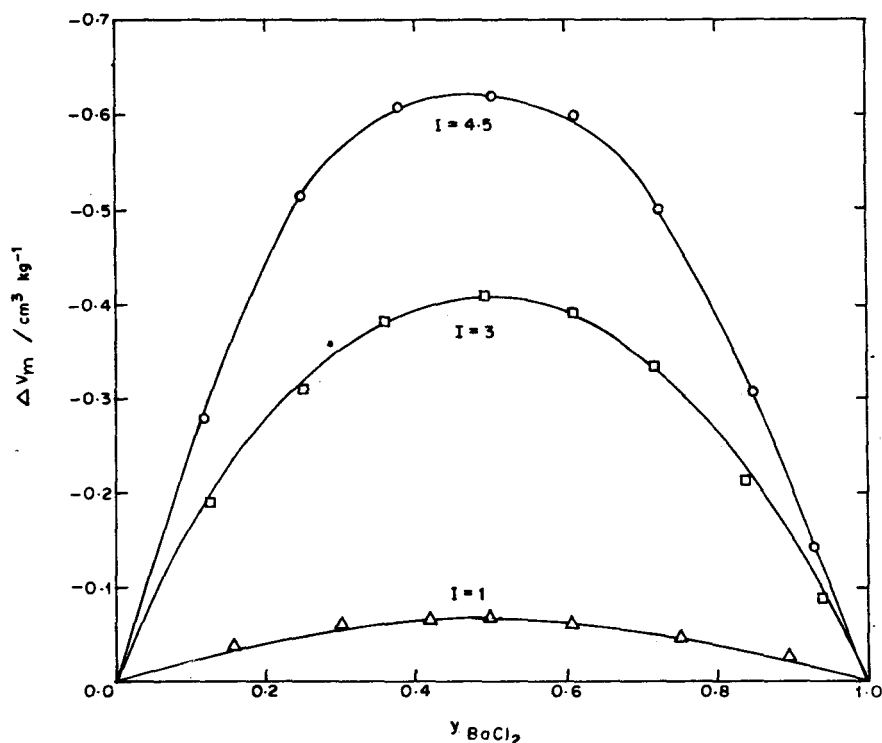


Fig. 2—Excess volumes of mixing ΔV_m as a function of Y_{BaCl_2} at different ionic strengths for aq. KCl-BaCl₂

Table 2—Differences (δ , in ppm) between Experimental Densities and Densities Calculated with and without Addition of ΔV_m to Young's Rule for Aqueous KCl-BaCl₂ at 298.15K

Ionic strength (mol kg ⁻¹)	δ (ppm)			
	Without ΔV_m		With ΔV_m	
	Av.	Max.	Av.	Max.
0.5	12	17	6	9
1	44	61	10	14
3	299	411	18	25
4.5	490	672	21	29

densities at $I = 4.5$ mol kg⁻¹ can be measured to 15 ppm with the use of ΔV_m values as compared to 490 ppm obtained without its use. As an average, the differences δ are 211 ppm at $I = 0.5$ -4.5 mol kg⁻¹ without the use of ΔV_m . These differences are reduced to 14 ppm with the use of ΔV_m .

To summarise, the densities of concentrated mixtures of 1-1 and 2-1 electrolytes can be estimated with the Young's rule¹², combined with the correction term or excess volumes. One notes that the average differ-

ence δ of 14 ppm remains slightly higher than the experimental accuracy.

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