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Mixtures of 1-1 Electrolytes: Densities and Excess Volumes of Aqueous NaCl—NaBr Solutions at 25 °C

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The relative densities and excess volumes of mixing are reported for the system consisting of aqueous NaCl and NaBr at 25 °C at constant ionic strengths of 0.5, 1, 2, 3, and 4 mol kg^{-1} of water. The measurements of densities are precise to $3 \cdot 10^{-6}$ g cm^{-3}. The densities, apparent molal volumes and excess volumes are analysed with the virial coefficients approach with excellent accuracy. The excess volumes are positive throughout.

(Keywords: Aqueous mixed electrolytes; Aqueous NaCl—NaBr; *Virial coefficients approach; Densities, Apparent molal volumes; Excess volumes of mixing; Binary mixing term)*

Mischung von 1:1-Elektrolyten: Dichten und Excess-Volumina von wäßrigen NaCl—NaBr-*Lösungen bei 25 °C*

Die relativen Dichten und Excess-Volumina der Mischung werden für das System wäßriges NaCl—NaBr bei 25 °C und einer konstanten Ionenstärke von 0.5, 1, 2, 3 und 4 mol kg^{-1} Wasser berichtet. Die Dichtemessungen haben eine Genauigkeit von $3 \cdot 10^{-6}$ g cm^{-3}. Die Dichten, die effektiven molalen Volumina und die Excess-Volumina werden von der Virialkoeffizienten-Methode ausgezeichnet wiedergegeben. Die Excess-Volumina sind durchwegs positiv.

Introduction

As a part of our program on *PVT* properties of mixed electrolytes, we [1] recently presented densities and excess volumes of mixing of aqueous NaCl—KCl up to the ionic strength of 4 mol kg^{-1}. The results were treated with the mixing rule proposed by *Patwardhan* and *Kumar* [2, 3].

The present article describes experimental measurements on the relative densities of aqueous NaCl—NaBr mixtures at 25 °C and at constant ionic strength of 0.5, 1, 2, 3, and 4 mol kg^{-1} of water. The excess volumes of mixing are calculated using the values of mean apparent molal volumes. The densities, apparent molal volumes and excess volumes are discussed in terms of the virial coefficient approach of *Pitzer* [4].

Experimental

The relative densities [$\Delta d = d - d_0$; where d and d_0 are the densities of solution and pure water respectively] were measured with a *Paar* vibrating tube densitometer [5]. The densitometer was calibrated with the densities of pure water [6] and of NaCl solutions [7]. The temperature of the thermostat bath was maintained to ± 0.005 K and the densities were precise to $\pm 3 \cdot 10^{-6}\,\mathrm{g\,cm^{-3}}$.

Both NaCl and NaBr (Baker Analysed) were recrystallized before use. The stock solutions were prepared by dissolving a definite mass in deionized water. The concentrations were determined gravimetrically. The mixtures were prepared by mixing appropriate quantities of parent solutions as $y = m/I$; where y and m refer to ionic strength fraction and molality respectively and $y_A + y_B = 1$. In this study, subscripts A and B refer to NaCl and NaBr respectively.

Theory and Working Equations

The virial coefficients approach of *Pitzer* [4] is based on the analysis of single electrolyte solution data, and the virial coefficients thus obtained from such analysis are then used for estimating the mixture properties. The virial equations for apparent molal volume, φ_V, as modified for 1-1 electrolyte are

$$\varphi_V = \varphi_V^\circ + \frac{A_V}{b}\ln(1 + b I^{1/2}) + 2 m RT \beta^{(\circ)V} + m^2 RT C^{\varphi V} \tag{1}$$

φ_V° is the apparent molal volume at infinite dilution. A_V is the *Debye-Hückel* limiting slope, $1.874\,\mathrm{cm^3\,kg^{1/2}\,mol^{-3/2}}$, value taken at 25 °C and 1 bar pressure. $R = 83.1441\,\mathrm{cm^3\ bar\ mol^{-1}\,K^{-1}}$, $b = 1.2$ and ionic strength $I = \frac{1}{2}\sum_i m_i z_i^2$. In Eq. (1), $\beta^{(\circ)V}$ and $C^{\varphi V}$ are the virial coefficients for cation-anion interactions and are defined as

$$\beta^{(\circ)V} = (\partial \beta^{(\circ)}/\partial P)_T \tag{2}$$

$$C^{\varphi V} = (\partial C^{\varphi}/\partial P)_T \tag{3}$$

$\beta^{(\circ)}$ and $C^{\varphi V}$ terms in Eq. (2) and (3) are originally the virial coefficients indicating the interactions between opposite charged ions, derived from the free energy of an electrolyte solution [4].

The apparent molal volume of an ion in mixture, $\varphi^*_{V_i}$, considering the interactions between $\mathrm{Na^+}$—$\mathrm{Cl^-}$ and $\mathrm{Na^+}$—$\mathrm{Br^-}$ is given as

$$\varphi^*_{V_i} = \varphi^\circ_{V_i} + \frac{A}{2b}\ln(1 + b I^{1/2}) + RT\sum_j \beta^{(\circ)V}_{ij} m_j + 0.5\,RT\sum_i C^{\varphi V} m_j^2 \tag{4}$$

The estimated mean apparent molal volume of mixture, $\varphi^*_{V_{cal}}$ can be obtained as

$$\varphi^*_{V_{cal}} = \sum_J m_J \varphi_{VJ} / \sum_J m_J \tag{5}$$

with

$$\varphi_{VJ} = \sum_i \nu_i \varphi^*_{V_i} \tag{6}$$

The relationship between the estimated density, d_{cal} and $\varphi^*_{V_{cal}}$ is

$$d_{cal} = (1\,000 + \sum_J m_J M_J)/(1\,000/d_0) + \sum_J m_J \varphi_{VJ} \tag{7}$$

where M_J is the molecular weight of an electrolyte.

The experimental densities, d_{exp}, may be converted to experimental mean apparent molal volumes, $\varphi^*_{V_{exp}}$, by the relationship

$$\varphi^*_{V_{exp}} = \frac{1\,000\,(d_0 - d_{exp})}{\sum_J m_J d_{exp} d_0} + \frac{\sum_J m_J M_J}{d_{exp} \sum_J m_J} \tag{8}$$

The like charge ion-interactions (Cl^-—Br^- in this case) can be accommodated by appending an additional term $RT \sum_k \theta^V_{Cl^- Br^-} m_k$ to Eq. (4). Thus, the revised Eq. (4) should account for the interactions both between the ions of opposite and similar charges.

The values of $\theta^V_{Cl^- Br^-}$ as modified for this system are calculated as

$$\theta^V_{Cl^- Br^-} = \Delta \varphi^*_V (m_A + m_B)/2\,RT m_A m_B \tag{9}$$

where $\Delta \varphi^*_V = \varphi^*_{V_{exp}} - \varphi^*_{V_{cal}}$ and $\varphi^*_{V_{cal}}$ is obtained from Eq. (5).

Results and Discussion

The experimental relative densities, Δd, are listed in Table 1 as a function of y_B at $I = 0.5$, 1, 2, 3, and 4 mol kg^{-1} from pure NaCl to pure NaBr solutions. In order to fit the mixture data by the equations outlined above, the virial coefficients for pure NaCl and NaBr were taken from elsewhere [8, 9], where they were obtained using a non-linear least-squares technique. The values of $\beta^{(o)V}$ were $12.34 \cdot 10^{-6}$ and $9.09 \cdot 10^{-6}$ for NaCl and NaBr, respectively. The values of $C^{\varphi V}$ were $-1.29 \cdot 10^{-6}$ and $-1.00 \cdot 10^{-6}$ for NaCl and NaBr, respectively. The φ_V versus m fits for both the electrolytes were excellent throughout.

The virial coefficients related to the interactions between opposite charged ions, when applied to Eq. (4) give the estimated φ^*_V and d. The deviations, δ (experimental-calculated) obtained for Δd are listed in Table 2. The δ values are systematically negative, suggesting the importance of

Table 1. *Experimental relative densities* (Δd) *as a function of* y_B (B = NaBr) *for the system* NaCl—NaBr *at 25 °C*

y_B	$\Delta d \cdot 10^3$ g cm^{-3}	y_B	$\Delta d \cdot 10^3$ g cm^{-3}
$I = 0.5$		$I = 3$	
0	20.102	0	110.384
0.1795	23.415	0.1925	130.118
0.4010	27.501	0.4201	153.407
0.6195	31.528	0.6007	171.801
0.8122	35.077	0.7995	191.958
1	38.533	1	212.273
$I = 1$		$I = 4$	
0	39.083	0	139.793
0.2045	46.584	0.1953	166.280
0.4077	54.035	0.4111	195.443
0.5952	60.903	0.6125	222.553
0.8080	68.690	0.8015	247.859
1	75.713	1	274.393
$I = 2$			
0	75.060		
0.1895	88.591		
0.3895	102.847		
0.6078	118.380		
0.8129	132.934		
1	146.193		

Table 2. *Deviations,* δ *(experimental-calculated) of fits for densities of aqueous* NaCl—NaBr *systems at 25 °C as obtained by virial coefficients approach*

Ionic strength I/mol kg^{-1}	$\delta \cdot 10^6$ g cm^{-3} without $\theta^V_{\mathrm{Cl^-Br^-}}$	$\delta \cdot 10^6$ g cm^3 with $\theta^V_{\mathrm{Cl^-Br^-}}$
0.5	5	3
1	32	5
2	101	7
3	214	8
4	324	10
average $\delta \cdot 10^6$	135	7

interactions between ions of like charges. This is demonstrated later. Similarly, the calculations can be accomplished with the mixing term, $\theta^V_{\text{Cl}^-\text{Br}^-}$ and the results are reported in Table 2. One notes that the average δ values are reduced approximately by 20 times with the use of $\theta^V_{\text{Cl}^-\text{Br}^-}$ term. In other words, for example, one can estimate the density of 61.25% (NaBr) mixture of aqueous NaCl—NaBr of $I = 4\,\text{mol}\,\text{kg}^{-1}$ with an accuracy of $380 \cdot 10^{-6}\,\text{g}\,\text{cm}^{-3}$ without the use of $\theta^V_{\text{Cl}^-\text{Br}^-}$ term and with $7 \cdot 10^{-6}\,\text{g}\,\text{cm}^{-3}$ with the use of the $\theta^V_{\text{Cl}^-\text{Br}^-}$ term. Thus, the use of a mixing term brings a remarkable improvement in the predictive capability of the virial coefficient approach and removes systematic δ values. The values of $\theta^V_{\text{Cl}^-\text{Br}}$ [as obtained in this study by Eq. (9)] can be expressed as a function of ionic strength I. One can conveniently assume a straight line relation, expressed by

$$\begin{aligned}\theta^V_{\text{Cl}^-\text{Br}^-} &= \theta^{(\text{o})V} - \theta^{(1)V} \\ &= 3.51 \cdot 10^{-6} - 0.35 \cdot 10^{-6} I \qquad (10)\end{aligned}$$

with a standard deviation of fit $0.08 \cdot 10^{-6}$.

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

$$\Delta V_m = \varphi^{\ddagger}_V \sum_J m_J - \varphi'_{V,A} m_A - \varphi'_{V,B} m_B \qquad (11)$$

where $\varphi'_{V,A}$ is the apparent molal volume of pure electrolyte A at the ionic strength of the mixture, with similar definition for $\varphi'_{V,B}$.

The values of ΔV_m, which are positive throughout and at all the ionic strengths, can be easily represented by [10]

$$\Delta V_m = y_A y_B I^2 v_0 \qquad (12)$$

with v_0, *Friedman* interaction parameter, indicating the interactions between two similar charge ions (Cl^-, Br^-). The values of v_0, thus obtained are 0.162, 0.160, 0.132, 0.115, and 0.102 at $I = 0.5$, 1, 2, 3, and $4\,\text{mol}\,\text{kg}^{-1}$, respectively. These values may be represented by a straight line relation to ± 0.004 units with the equation

$$v_0 = 0.176 - 0.0192 I \qquad (13)$$

Since θ^V and v_0 both indicate the extent of binary interactions, one can establish their relationship. Using the definition of ΔV_m from Eq. (11) and substituting this for $\Delta\varphi^{\ddagger}_V$ in Eq. (9), and using Eq. (12) one obtains after simplification

$$\theta^V_{\text{Cl}^-\text{Br}^-} = v_0/2\,RT \qquad (14)$$

The positive ΔV_m values are supported by the magnitude and sign of heats of mixing (ΔH_m data reported by *Wood* and *Smith* [11]). For example, both ΔV_m and ΔH_m increase by four times, if the ionic strength changes from 0.5 to $1\,\text{mol}\,\text{kg}^{-1}$.

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