Volume & Compressibility Changes in Mixed Aqueous Solutions of Potassium Bromide & Tetraethylammonium Bromide at 25°C

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Received 8 July 1985; revised and accepted 30 December 1985

The density and sound velocity data have been obtained for aqueous binary and ternary solutions involving potassium bromide (KBr) and tetraethylammonium bromide (Et₄NBr) as solutes at 25°C in the concentration range of 0.05 to 1.0 m and at constant ionic strength (I)=0.5 and 1.0 in ternary solutions. The deviations in excess volumes of mixing (ΔmV*) and compressibility of mixing (limP,) have been calculated. The ΔmV* values obtained are in agreement with those of Wen and Nara (J phys Chem, 71 (1967) 3907) while limP* values (which are negative) show parabolic behaviour. The excess apparent molal volumes of the salts at negative 0.5 mol fraction whereas the excess apparent molal compressibilities of the salts are almost zero over the entire mol fraction range of solutes indicating the validity of Young's rule. These studies indicate that the compressibility behaviour of KBr and Et₄NBr depends upon the structural interactions of these ions with water. Although ΔmV* values on application of Friedman equation show the presence of cation-cation interactions in such solutions, the ΔmP* values do not point out the hydrophobic (Et₄N⁺ -Et₄N⁺) interaction or alternatively, it can be suggested that such equilibria are not sensitive to pressure effects.

The studies of excess thermodynamic properties of mixed aqueous electrolyte solutions have assumed importance in recent years, since this provide useful information on the interaction of like charge ion and triplet interactions if measurements are made at a constant ionic strength with a common ion. On the basis of Young’s rule, the deviations in heat of mixing (ΔmH*) or volume of mixing (ΔmV*) for many mixed electrolyte aqueous solutions have been explained in terms of specific ion-ion interactions. Wen and Nara using Friedman’s theory and experimental values of ΔmV*, have shown that in the case of mixtures of potassium halides and symmetrical tetraalkylammonium halides, the specific cation-cation interactions are predominant in aqueous solutions. The aqueous solutions of tetraalkylammonium salts have been studied in detail by various physico-chemical techniques because of their importance as hydrophobic solutes. The excess free energy changes (ΔmG*) on mixing solutions of alkali halides and tetraalkylammonium halides have been studied by Wen et al., who observed that in dilute solutions the free energy of interaction between the two large tetraalkylammonium cations is small than that between two alkali metal ions. The small value for tetraalkylammonium cations is due to hydrophobic interaction. Similarly a comparison of ΔmH* and ΔmV* data points out that ΔmH* is largely a measure of the change in the number of hydrogen bonds of water in solution while ΔmV* is a measure of the change in geometrical arrangement of water and ions.

The effect of pressure on ΔmV* can be studied in such systems by making the compressibility studies in binary and ternary solutions. A literature search reveals that such compressibility data for ternary systems involving water, tetraalkylammonium halide salts and alkali halide salts are not available.

In the present work, we have determined the excess adiabatic compressibilities in aqueous solutions containing KBr + Et₄NBr at 25°C and the overall ionic strength I=0.5 and 1.0. We have also examined, if the ΔmV* values for these solutions obtained from direct density measurements agree or not with those obtained by direct mixing of solutions (dilatometry). The validity of Young’s rule for the compressibility has also been tested using the approach of Wirth et al., and apparent compressibility data of the solutes at 25°C.

Materials and Methods

Potassium and tetraethylammonium bromides used were of AR(BDH) grade. These were dried in a vacuum desiccator for several days and then used directly. All the solutions were prepared afresh in doubly distilled water.

The binary aqueous solutions of KBr and Et₄NBr were prepared on molality basis (0.05 to 1.0 m). The mixed electrolyte aqueous solution (i.e. the ternary systems) were prepared by mixing the solutes directly with weighed amount of water such that the ionic strength (0.5 and 1.0) could be kept constant. The mol fraction of the solute Et₄NBr (γ), i.e. the fraction of ionic strength due to the electrolyte Et₄NBr in the...
mixture of two electrolytes (Et₄NBr + KBr) was varied in the range of 0 to 1.0 mol fraction.

All weighings were done on a Mettler balance (+ 0.05 mg). The densities of the solutions were measured directly using a calibrated density bottle (having a standard point thermometer and a side limb with grounded cap for volume adjustment) of volume 25.145 cm³ at 25°C. The necessary buoyancy correction was applied. The density values were reproducible within ± 5 x 10⁻⁵ g/cm³. The density data for aqueous binary solutions agreed very well with the literature data for the same systems (for 1.0 M KBr-H₂O at 25°C, \(d = 1.07771\) g/cm³, lit.\(^8\) \(d = 1.0774\) g/cm³; and for 1.0 M Et₄NBr-H₂O at 25°C, \(d = 1.02973\) g/cm³, lit.\(^9\) \(d = 1.0299\) g/cm³). The compressibilities were determined from sound velocity and density data using the usual Laplace equation. The details about the sound velocity measurements have been given earlier\(^{10}\). The accuracy of the velocity measurements is of the order of ± 0.5 m/sec.

**Results**

The excess volume of mixing (\(\Delta m V^e\)) and excess adiabatic compressibility of mixing (\(\Delta m \beta^e\)) were calculated using the expressions (1) and (2) respectively,

\[
\Delta m V^e = V - [y \cdot V_2 + (1-y) \cdot V_3] \quad \ldots (1)
\]

\[
\Delta m \beta^e = \beta - [y \cdot \beta_2 + (1-y) \cdot \beta_3] \quad \ldots (2)
\]

where \(V, V_2\) and \(V_3\) are the molal volumes of ternary solution and of binary solutions of Et₄NBr and KBr respectively. Similarly \(\beta, \beta_2\) and \(\beta_3\) are the compressibilities of ternary solution and of binary solutions of Et₄NBr and KBr respectively. The variation of \(\Delta m V^e\) and \(\Delta m \beta^e\) as a function of \(y\) is shown graphically in Fig. 1.

The mean apparent molal volume (\(\phi_V\))mix and compressibility (\(\phi_\beta\))mix of a mixture of solutes were determined using expressions (3) and (4):

\[
(\phi_V)_{mix} = \frac{V - 55.51 \times \bar{V}_1^0}{m_2 + m_3} \quad \ldots (3)
\]

\[
(\phi_\beta)_{mix} = \frac{\beta V - 55.51 \times \bar{V}_1^0 \cdot \bar{\beta}_1^0}{m_2 + m_3} \quad \ldots (4)
\]

where \(V\) is volume of solution containing 1000 g of water, \(m_2\) and \(m_3\) are the molalities of Et₄NBr and KBr and \(\beta, \beta_2\) and \(\beta_3\) represent the adiabatic compressibilities of solution and water respectively. The apparent molal compressibilities (\(\phi_K\) and \(\phi_K\)) were calculated using the usual relations\(^{10}\) and their variation with concentration (\(\sqrt{m}\)) is shown in Fig. 2. The accuracy in \(\phi_K\) at the lowest concentration used is of the order of ± 6 cm³ dyne⁻¹ mol⁻¹. The apparent molal volumes (\(\phi_V\) and \(\phi_V\)) data for the salts were obtained from Wen and Saito\(^9\), and Wirth\(^4\). The excess apparent molal

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Fig. 1—Plots of volume changes, \(\Delta m V^e\) (a) and compressibility changes \(\Delta m \beta^e\) (b), on mixing Et₄NBr and KBr in water against the mol fraction (\(y\)) at constant ionic strength (\(\lambda\)) = 0.5 (○ — ○) and 1.0 (Δ—Δ) at 25°C

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Fig. 2—Apparent molal adiabatic compressibility (\(\phi_\beta\)) of EtNBr (\(\phi_K\), a) and KBr (\(\phi_K\), b) as a function of \(\sqrt{m}\) in aqueous binary solutions at 25°C

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636
PATIL & MEHTA: VOLUME & COMPRESSIBILITY CHANGES IN MIXED AQUEOUS SOLUTIONS OF KBr + Et₄NBr

Discussion

Examination of Fig. 2 (curves a and b) reveals that \( q_{JK} \) values are in reasonable agreement with data reported by other workers in the low concentration region. This is also evident from the \( q_{K}^0 \) values for EtNBr [\( q_{K}^0 = -6.5 \times 10^{-10} \text{ cm}^5 \text{ dyne}^{-1} \text{ mol}^{-1} \) (lit.11 5.9 \times 10^{-10} \text{ cm}^5 \text{ dyne}^{-1} \text{ mol}^{-1} )] and for KBr, \( q_{K}^0 = -34.5 \times 10^{-10} \text{ cm}^5 \text{ dyne}^{-1} \text{ mol}^{-1} \) (lit.8 36 \times 10^{-10} \text{ cm}^5 \text{ dyne}^{-1} \text{ mol}^{-1} ) obtained on the basis of linear extrapolation to infinitely dilute concentration. The behaviour of KBr in the high concentration region appears to be rather unusual as it shows a slight variation from linearity in the concentration region of 0.3 to 0.5 \( y \). We do not wish to attach much importance to this observation but such discontinuous slopes for other properties of alkali halides in water have been reported in literature12. It has been suggested by Vaslow13 that in such solutions a transition of the critical type can occur at higher concentrations.

It has been observed that variation of \( \Delta m V^{ex} \) with \( y \) (Fig. 1, curve a) shows a parabolic curve which is in agreement with the previous studies. The present values of \( \Delta m V^{ex} \) are in very good agreement with those reported by Wen and Nara5. Thus, direct density measurements of mixed electrolyte solutions give quite reliable excess volume of mixing.

The \( \Delta m V^{ex} \) goes through a minimum around 0.5 \( y \) and the depth of the minimum increases with increase in ionic strength (Fig. 1, curve b). These results indicate that excess compressibilities of ternary aqueous solutions are negative and their variation is similar to that of \( \Delta m V^{ex} \).

The \( q_{V}^{ex} \) values of the salts also show a parabola having a minimum at 0.5 \( y \) (Fig. 3, curve a) which is similar to that of the \( D \)-parameter (signifies the deviation from Young's rule) used by Wirth et al.3. The values of \( q_{V}^{ex} \) are -0.95 and -3.4 at 0.5 \( y \) for ionic strength =0.5 and 1.0 at 25°C respectively.

If we write, following Wen and Nara5

\[
\frac{q_{V}^{ex}}{I^2} = \frac{V^{ex}(AX) - V^{ex}(BX)}{I^2} = \frac{V_{AA}}{2} + 2V_{AX}
\]

where

\[
V^{ex}(AX) = I_(\varphi_{V}(AX) - \varphi_{V}(AX))
\]

\[
V^{ex}(BX) = I_(\varphi_{V}(BX) - \varphi_{V}(BX))
\]

The \( q_{V}^{ex}/I^2 \) values are found to be -3.8 and -3.4 at 0.5 \( y \) for \( I = 0.5 \) and 1.0 respectively. These values are in excellent agreement with those of Wen and Nara5. The \( q_{V}^{ex} \) values of salts in ternary solutions obtained using Eq. (7) (Fig. 3, curve c) are almost zero over the entire mol fraction region while those calculated using Eq. (6) (Fig. 3, curve b) are slightly negative for KBr and almost zero for Et₄NBr in higher mol fraction ranges in ternary solutions. It is concluded from these observations that the compressibilities of the Et₄NBr-
KBr mixed electrolyte solutions obey the Young's rule fairly well.

The $\Delta m V_{\text{ex}}$ behaviour for this system has been explained by Wen and Nara\(^5\) in terms of cation-cation interactions on the basis of equations derived by Friedman\(^6\). Similar approach can be extended to $\phi_k^c$ by differentiating Eqs (5) and (6) of Wen Nara\(^5\) with respect to pressure and making an assumption that $V_0$ does not vary with $I$

$$\frac{\partial}{\partial P} \Delta m V_{\text{ex}} \left[ P^2y(1-y) \right] = \frac{\partial}{\partial P} \left[ V_0 + \text{rem.} \right]$$

$$= \frac{\partial}{\partial P} \left[ 2V_{AB^*} - V_{AA} - V_{BB^*} + \text{rem.} \right] \quad (11)$$

$$= - \left[ 2\phi_{AB^*} - \phi_{AA^*} - \phi_{BB^*} \right] \quad (12)$$

and

$$\frac{\partial}{\partial P} \left[ \frac{V_{\text{ex}}(AX)}{V_{\text{ex}}(BX)} \right] / P^2$$

$$= \frac{\partial}{\partial P} \left[ V_{AA^*} + 2V_{AX^*} - V_{BB^*} - 2V_{BX^*} + \text{rem.} \right] \quad (13)$$

$$= - \left[ \phi_{AA^*} + 2\phi_{AX^*} - 2\phi_{BB^*} \right] \quad (14)$$

where $A$, $B$ and $X$ represent $\text{Et}_4\text{N}^+$, $\text{K}^+$ and $\text{Br}^-$ respectively.

If $\Delta m \phi_{\text{ex}} \Delta m V_{\text{ex}} = -\phi_k^c = 0$, then from Eq. (12) we get:

$$2\phi_{AB^*} = \phi_{AA^*} + \phi_{BB^*} \quad (15)$$

Similarly from Eq. (14), after substituting the proper values of $\phi_{AX^*}$ and $\phi_{BB^*}$ we get

$$\phi_{AX^*} < \phi_{BB^*} \quad (16)$$

Combining Eqs (15) and (16) we get

$$\phi_{AX^*} > \phi_{AX^*} < \phi_{AX^*}$$

Since the electrostriction for $\text{K}^+$ ion is more than that of $\text{Et}_4\text{N}^+$ ion one can assume:

$$\phi_{K^* \text{K}^*} - \phi_{K^* \text{K}^*} > \phi_{K^* \text{K}^*} - \phi_{K^* \text{K}^*}$$

This suggests that the change in compressibility is comparatively small due to $\text{Et}_4\text{N}^+ - \text{Et}_4\text{N}^+$ interaction in aqueous ternary solutions. It has been suggested that $\text{Et}_4\text{N}^+$ ion is neither a structure breaker nor a structure maker in aqueous solution\(^1\). In the light of this the compressibility behaviour seems to be dependent upon structural interactions in water other than $\text{Et}_4\text{N}^+ - \text{Et}_4\text{N}^+$ interaction. Probably the strength of hydrophobic interaction of $\text{Et}_4\text{N}^+$ is weaker because of less number of non-polar groups in the ion or because of the stronger ion-dipole (ion-solvent) interactions in solution.

Acknowledgement

We thank to Prof D B Muie and Prof R B Kharat, for the facilities and encouragement during this work.

References


