

## Viscosity studies of aqueous mixed electrolyte solutions

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Relative viscosity studies of ternary aqueous mixed electrolyte solutions for the systems KBr-NaBr, KBr-Bu<sub>4</sub>NBr, NaCl-NaBr and NaCl-Bu<sub>4</sub>NBr at various constant ionic strengths with varying electrolyte mole fractions ( $y$ ) at 25°C are reported. The data are used to calculate viscosity  $B$ -coefficients of the total electrolyte as a function of solute mole fraction. The excess viscosity  $B$ -coefficients ( $B^{Ex}$ ) have been calculated and found to be distinctly positive for all the systems studied. The variation of  $B^{Ex}$  with  $y$  and the magnitudes have been explained in terms cation-cation, anion-anion interactions and the specific structural interactions with solvent water.

In recent years, the studies of thermodynamic properties of aqueous mixed electrolyte solutions using the Mayer-McMillan theory as developed by Friedeman have been found to be useful in understanding the specific ion-ion interactions in solution<sup>1,2</sup>. The thermodynamic properties such as, changes in free energy of mixing ( $\Delta_m G^E$ ), heat of mixing ( $\Delta_m H^E$ ), volume of mixing ( $\Delta_m V^E$ ) and compression of mixing ( $\Delta_m \beta^E \cdot V$ ) in electrolyte solutions involving common anions and cations like tetraalkylammonium salts have clearly established the concept of cation-cation interactions leading to hydrophobic interactions in aqueous solutions<sup>3-6</sup>. However, such studies are lacking as far as the transport properties like viscosity are concerned. The validity of the Jones-Dole viscosity equation and the additivity concept for ionic-viscosity  $B$ -coefficients had been examined by Wu for electrolytic mixtures involving simple salts like LiCl-KCl and LiCl-NaCl<sup>7</sup>.

The present work is a part of studies on the influence of salts on the association of hydrophobic species in aqueous solutions. This problem under investigation is closely connected with the effect of salting-out of hydrophobic particles. The influence of salts on aqueous solutions of macromolecules like lipids, nucleic acids, peptides and proteins is of great importance in applied chemistry and biochemistry. These salt effects are of a complicated nature. There are combined contributions of interactions of cations and anions with nonpolar and

with polar groups, specific interactions and combined salting-in and salting-out effects. In this connection we thought that the study of transport properties like viscosity may furnish important information about the salt effects on the association behaviour of simple model systems.

In our earlier studies we have discussed the viscosities of aqueous binary and ternary electrolytic solutions<sup>8</sup>. We report in this paper the relative viscosities in aqueous solutions involving mixed electrolytes (KBr-NaBr, KBr-Bu<sub>4</sub>NBr, NaCl-NaBr and NaCl-Bu<sub>4</sub>NBr) at constant 0.2, 0.5 and 1.0 ionic strengths as a function of mole fraction of one of the electrolyte. The  $B$ -coefficient of the electrolytes obtained are used to calculate excess  $B$ -coefficient ( $B^{Ex}$ ). These are examined to understand the above mentioned structural interactions in solution phase.

### Materials and Methods

All the salts i.e. KBr, NaCl, NaBr and Bu<sub>4</sub>NBr were AR grade (BDH or Fluka) which were used after drying in a vacuum oven at 110°C or at 60°C for 10 to 12 hours. All the binary solutions were prepared in triply distilled water on molality basis. The ternary solutions of electrolytes were prepared by mixing the solute directly with weighed amount of water such that the ionic strength could be kept constant (0.2, 0.5 or 1.0). The mole fraction of the solute ( $y$ , accuracy  $\pm 0.002$ ) i.e. the fraction of ionic strength due to the electrolyte in the mixture of two electrolytes was varied in the range of 0 to 1.0 mole fraction. All the weighings were made on a Mettler balance ( $\pm 0.05$  mg).

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The densities of the solutions were measured with a model DMA 602 digitale density meter (Anton-Paar) at  $25 \pm 0.02^\circ\text{C}$ . The reproducibility of the density values was of the order of  $\pm 5$  ppm. The viscosity measurements were carried out using ubbelohde viscometers (efflux time 472 and 621 s for water at  $25 \pm 0.02^\circ\text{C}$ ). The kinetic energy and surface tension corrections were neglected. The reflux time was measured to  $\pm 0.1$  s and the overall accuracy of the relative viscosity is of the order of  $\pm 0.05\%$ . The details regarding density and viscosity set-ups and measurements can be found in our earlier publication<sup>8</sup>.

**Results**

The relative viscosity data ( $\eta/\eta_0$ ) for the systems KBr-NaBr, KBr-Bu<sub>4</sub>NBr, NaCl-NaBr and

NaCl-Bu<sub>4</sub>NBr are shown as a function of ionic strength fraction of the second component at various total ionic strength in Figs 1a, 1b, 2a and 2b respectively.

The relative viscosity of binary electrolyte solutions is generally discussed in terms of equations of Jones and Dole

$$\eta/\eta_0 = 1 + A\sqrt{I} + BI \quad \dots (1)$$

where  $I$  is the molal ionic strength and  $A$  and  $B$  coefficients all related to ion-ion and ion-solvent interaction. It is well known that  $B$  has the property of additivity<sup>9</sup>. It has also been suggested that the additivity rule for the  $B$ -coefficient can be extended to multicomponent mixtures.

If we rearrange Eq. 1 as,

$$\frac{(\eta/\eta_0) - 1}{\sqrt{I}} = A + B\sqrt{I} \quad \dots (2)$$

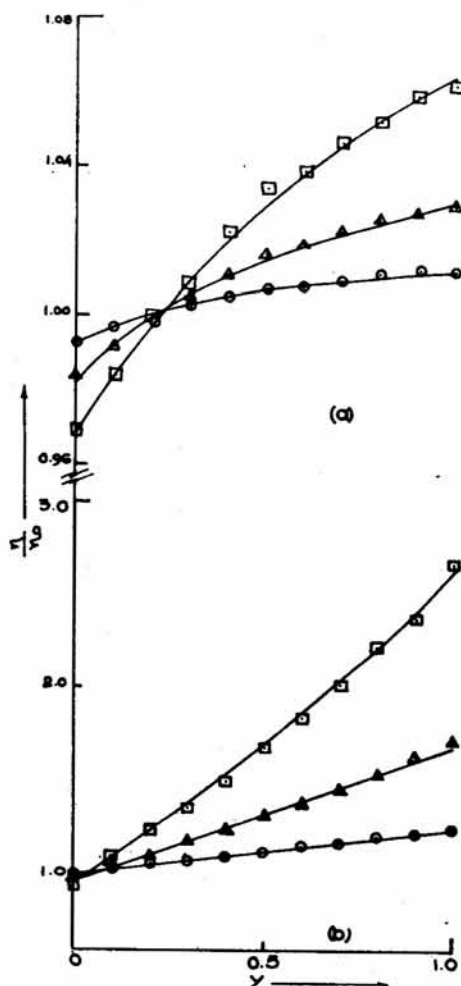


Fig. 1—Plots of  $\eta/\eta_0$  against  $\gamma$  (fraction of ionic strength due to an electrolyte in a mixture of two electrolytes AX and BX) of mixed electrolytes in water at  $25^\circ\text{C}$ .

- (a) KBr + NaBr:  $\circ-\circ$   $I=0.2$  mol/kg H<sub>2</sub>O,  $\Delta-\Delta$   $I=0.5$  mol/kg H<sub>2</sub>O and  $\square-\square$   $I=1.0$  mol/kg H<sub>2</sub>O.
- (b) KBr + Bu<sub>4</sub>NBr:  $\circ-\circ$   $I=0.2$  mol/kg H<sub>2</sub>O,  $\Delta-\Delta$   $I=0.5$  mol/kg H<sub>2</sub>O and  $\square-\square$   $I=1.0$  mol/kg H<sub>2</sub>O

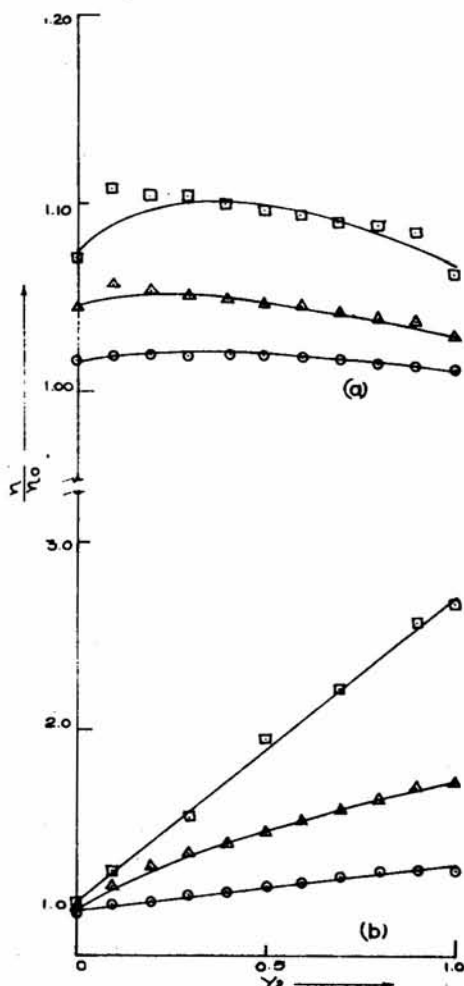


Fig. 2—Plots of  $\eta/\eta_0$  against  $\gamma/₂$  of mixed electrolytes in water at  $25^\circ\text{C}$

- (a) NaCl + NaBr:  $\circ-\circ$   $I=0.2$  mol/kg H<sub>2</sub>O,  $\Delta-\Delta$   $I=0.5$  mol/kg H<sub>2</sub>O and  $\square-\square$   $I=1.0$  mol/kg H<sub>2</sub>O.
- (b) NaCl + Bu<sub>4</sub>NBr:  $\circ-\circ$   $I=0.2$  mol/kg H<sub>2</sub>O,  $\Delta-\Delta$   $I=0.5$  mol/kg H<sub>2</sub>O,  $\square-\square$   $I=1.0$  mol/kg H<sub>2</sub>O

one can calculate the  $A$  and  $B$  coefficients. In our mixed electrolyte systems, we have plotted the function  $[(\eta/\eta_0) - 1]/\sqrt{I}$  against  $\sqrt{I}$  for a given value of  $y$  but having different ionic strengths. Such representative plots are shown in Figs 3 and 4 for aqueous solutions of KBr-NaBr and KBr-Bu<sub>4</sub>NBr respectively. The other two systems follow the same trend. The  $A$ -coefficients (intercepts) were found to be small in magnitude while the  $B$ -coefficients (for mixture of electrolytes) were obtained from the slope values.

It seemed reasonable that values of  $B$  for mixtures of electrolytes could be obtained from the values for the individual components; thus for a mixture of two electrolytes:

$$B_{\text{Cal}} = y_A \cdot B_A + y_B \cdot B_B \quad \dots (3)$$

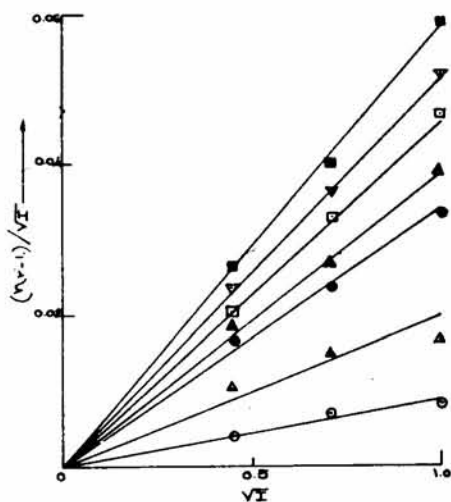


Fig. 3—Plots of  $(\eta/\eta_0 - 1)/\sqrt{I}$  against  $\sqrt{I}$  of KBr + NaBr in water at 25°C ( $\eta/\eta_0$  is denoted as  $\eta_r$ )  $\circ$ - $\circ$   $y=0.3$ ,  $\Delta$ - $\Delta$   $y=0.4$ ,  $\bullet$ - $\bullet$   $y=0.5$ ,  $\blacktriangle$ - $\blacktriangle$   $y=0.6$ ,  $\square$ - $\square$   $y=0.7$ ,  $\nabla$ - $\nabla$   $y=0.8$ , and  $\blacksquare$ - $\blacksquare$   $y=0.9$

where  $y_i$  is the ionic strength fraction and  $B_i$ , the linear coefficient of Eq. 1. The individual  $B$ -coefficient values for the salts in binary single electrolyte in water solutions were obtained from our previous work<sup>8</sup>. The excess  $B$ -coefficient values were computed using Eq. 4 given below:

$$B^{\text{Ex}} = B_{\text{Obs}} - (y_A \cdot B_A + y_B \cdot B_B) \quad \dots (4)$$

The values of  $B$  and  $B^{\text{Ex}}$  coefficients at different ionic strength fractions for all the studied systems are collected in Tables 1 and 2 respectively.

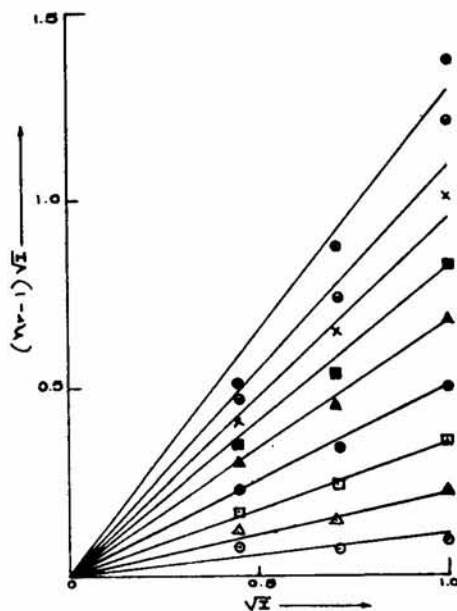


Fig. 4—Plots of  $(\eta/\eta_0 - 1)/\sqrt{I}$  against  $\sqrt{I}$  of KBr + Bu<sub>4</sub>NBr in water at 25°C  $\circ$ - $\circ$   $y=0.1$ ,  $\Delta$ - $\Delta$   $y=0.2$ ,  $\square$ - $\square$   $y=0.3$ ,  $\bullet$ - $\bullet$   $y=0.4$ ,  $\blacktriangle$ - $\blacktriangle$   $y=0.5$ ,  $\blacksquare$ - $\blacksquare$   $y=0.6$ ,  $\times$ - $\times$   $y=0.7$ ,  $\ominus$ - $\ominus$   $y=0.8$  and  $\otimes$ - $\otimes$   $y=0.9$

Table 1—Values of viscosity  $B$ -coefficient at 25°C and at various ionic strength fractions

System	$B$ -coefficient									
	$y=$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
KBr-Bu <sub>4</sub> NBr		0.118	0.236	0.363	0.509	0.669	0.827	0.926	1.009	1.254
KBr-NaBr		—	—	0.0095	0.0205	0.029	0.039	0.0468	0.052	0.0515
NaCl-Bu <sub>4</sub> NBr		0.360	0.55	0.625	0.769	0.938	1.044	1.177	1.311	1.40
NaCl-NaBr		0.110	0.106	0.1025	0.0975	0.0957	0.092	0.086	0.084	0.076

Table 2— $B^{\text{Ex}}$  values of different fractions of ionic strength for different systems

System	$B^{\text{Ex}}$									
	$y=$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
KBr-Bu <sub>4</sub> NBr		0.0449	0.0438	0.0517	0.0786	0.1195	0.1584	0.1383	0.1022	0.2281
KBr-NaBr		—	—	0.0279	0.0297	0.0290	0.0298	0.0284	0.0244	0.0197
NaCl-Bu <sub>4</sub> NBr		0.1735	0.257	0.626	0.263	0.3255	0.3250	0.3515	0.379	0.3615
NaCl-NaBr		0.0334	0.0328	0.0327	0.0311	0.0327	0.0324	0.0298	0.312	0.0266

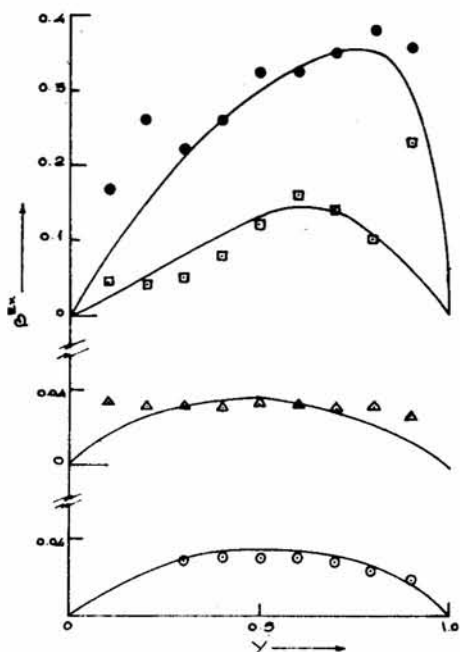


Fig. 5—Plots of  $B^{Ex}$  against  $y$  of mixed electrolytes in water at 25°C

(a)  $\circ-\circ$  KBr-NaBr, (b)  $\triangle-\triangle$  NaCl-NaBr, and (c)  $\square-\square$  KBr-Bu<sub>4</sub>NBr,  $\bullet-\bullet$  NaCl-Bu<sub>4</sub>NBr

### Discussion

The variation of  $B^{Ex}$  coefficient with ionic strength fraction are shown in Figs 5a to 5c for the studied systems. The examination of the Tables and Figures indicates that  $B^{Ex}$  values are positive for all the combinations studied. For the systems KBr-NaBr and NaCl-NaBr the  $B^{Ex}$  are small indicating the similar type of ion-solvent interactions. This is quite expected as both the electrolytes involved are alkali halides and differ only in terms of charge density. The small charge density differences between  $K^+$  and  $Na^+$  ions show quite a symmetrical variation in  $B^{Ex}$ , while the comparatively large volume differences between  $Cl^-$  and  $Br^-$  ions seem to cause almost constant positive  $B^{Ex}$  at all the ionic fractions studied. This also suggests that anion-anion interaction, although small, are not negligible.

The  $B^{Ex}$  values for KBr-Bu<sub>4</sub>NBr and NaCl-Bu<sub>4</sub>NBr systems are comparatively high and show skewness towards Bu<sub>4</sub>NBr rich region. Wood *et al.*<sup>10,11</sup> have reported such a skewness in the case of heat of mixing data for the mixtures without a common ion. These observations indicate that in these mixtures cation-cation ( $Bu_4N^+ - Bu_4N^+$ ) interactions are significant as well as cause more structural stabilization of solvent water obstructing its flow properties. Patil and Mehta<sup>12</sup> have drawn si-

milar conclusions from excess compressibility data for the ternary solutions involving tetraalkylammonium salts. The process of aggregation of alkyl groups in electrolytic solutions has been experimentally proved by nuclear magnetic relaxation rate and diffusion studies by Holz and Patil<sup>13</sup>. The  $B^{Ex}$  behaviour for the two systems, thus also indicates salting-out of the ions containing nonpolar groups. However, to draw definite conclusions from the behaviour of  $B^{Ex}$  one has to study more combinations of mixed electrolytes as well as solutions having higher ionic strengths. The viscosity properties are markedly dependent on the translational as well as rotational properties of the groups involved in the molecule in a given medium. The hindrance to these motions either through the aggregation of the nonpolar groups (hydrophobic association) or interaction of the polar groups with solvent causes increase in viscosity and hence in  $B$ -coefficient of the salt. Thus our results reported here point out that viscosity  $B^{Ex}$  coefficient may yield important information about the subtle structural interactions in aqueous solutions.

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