

Viscosity B coefficient and apparent molar volume studies of electrolytes in aqueous salt solutions at 25°C

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Viscosity and density measurements are reported for aqueous binary solutions involving Me_4NBr , Et_4NBr , Bu_4NBr , CsBr and LiBr in the concentration range of 0.02 to 0.2 m at 25°C. Similar data are obtained for these electrolytes in aqueous NaCl 4 m and KBr 4 m solutions at 25°C. By using the data obtained and the appropriate thermodynamic equations, the parameters like apparent molal volume (ϕ_v) and viscosity B coefficients (B_η) of the electrolytes have been computed. The limiting apparent molar volumes (ϕ_v^0) and B_η coefficients have been used to obtain the transfer parameters ($\Delta\phi_v^0$ and ΔB_η) for different salts. The viscosity B_η coefficients are drastically reduced, in aqueous NaCl solutions while in aqueous KBr they increase profoundly compared to aqueous solutions. These results alongwith volumetric transfer data are discussed in terms of cation-cation hydrophobic interaction and the salting-in and salting-out effects involving structural changes of solvent water.

The viscosity of electrolyte solutions is usually studied to obtain information on ion-solvent interactions¹⁻⁴. In general, the variation of relative viscosity η_r with the molarity, c , or molality, m , can be represented by Jones-Dole equation (1)

$$\eta_r = \eta/\eta_0 = 1 + A_\eta m^{1/2} + B_\eta m \quad \dots (1)$$

where η and η_0 are the viscosity coefficients of the solution and solvent respectively. A_η is a constant depending on the long-range coulombic forces (ion-ion interaction) and B_η is an adjustable parameter which is related to the size of the ions and to the different ion-solvent interaction. The apparent molar volumes at infinite dilution and their variation with concentration for electrolytes also shed light on ion-solvent and ion-ion interactions^{5,6}.

Recently, Holz and Patil⁷ using NMR relaxation and diffusion data have reported the experimental detection of hydrophobic affinity between the solute molecules in ternary solutions involving tetramethylammonium bromide and the other alkali halides. The strength of the hydrophobic cation-cation interaction depends upon the nature of cosolutes like alkali halides. They have also observed that the order of effectiveness in the series of alkali

halides is the same as that of the order given by Hofmeister series for solubilization of biomolecules⁸. In order to verify or to obtain further support from other techniques, we have undertaken the programme of measurements of densities and viscosities of various electrolytes in aqueous binary as well as ternary solutions. We report the results of viscosity and volumes and their analysis for (i) aqueous binary solutions involving LiBr , CsBr , Me_4NBr , Et_4NBr and Bu_4NBr in a concentration range of 0.02 to 0.2 m and (ii) ternary solutions of these electrolytes in 4 m NaCl and 4 m KBr used as a solvent at 25°C.

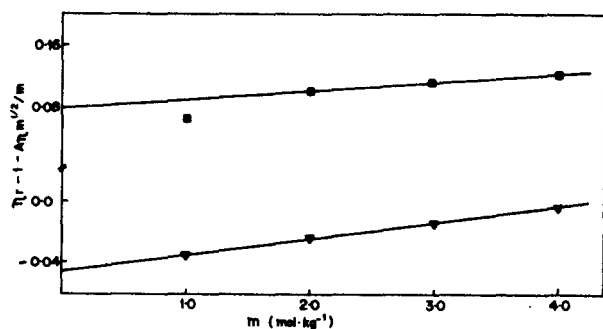
Materials and Methods

All the salts i.e. KBr , NaCl , CsBr , Me_4NBr , Et_4NBr and Bu_4NBr were AR grade (BDH or Fluka) and were dried in a vacuum oven for 10-12 hrs at 110°C or at 60°C and further kept in a vacuum desiccator for several days. Since LiBr is very hygroscopic, its stock solution in water was prepared and the concentration was determined by measuring the density and using the data of Desnoyers *et al.*⁹. All the binary solutions were freshly prepared on a molality basis in triply distilled water. The ternary solutions of electrolytes were prepared by mixing solutes directly in aqueous solu-

Table 1—Values of viscosity A_η and B_η coefficients and apparent molar volumes, (ϕ_v^0) at infinite dilution for various electrolytes in binary aqueous solutions at 25°C

Salt	A_η	B_η expt.	B_η lit.	ϕ_v^0 expt. cm ³ /mol	ϕ_v^0 lit. cm ³ /mol	B_v
NaCl	0.006 ^a	0.08	0.08 ^a	16.6	16.62 ^c	+ve
KBr	0.005 ^a	-0.046	-0.046 ^a	34.8	33.73 ^c	-ve
LiBr	0.0065 ^b	0.105	0.105 ^b	24.9	23.78 ^c	+ve
CsBr	0.0049 ^b	-0.0825	-0.082 ^b	45.8	46.02 ^c	zero
Me ₄ NBr	0.0062	0.080	0.079 ^b	116.2	114.18 ^d	-ve
Et ₄ NBr	0.0069	0.3375	0.339 ^b	174.8	173.85 ^d	-ve
Bu ₄ NBr	0.0081	1.145	1.148 ^b	300.8	300.4 ^d	-ve

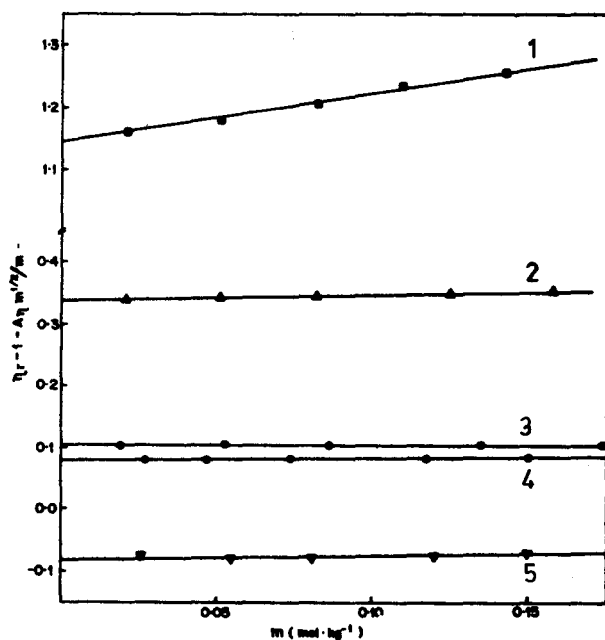
a—Ref. 14, b—ref. 4, c—ref. 15, d—ref. 16

Fig. 1—Plots of $\eta_r - 1 - A_\eta m^{1/2}$ against m for binary electrolyte solutions ▼—KBr and ■—NaCl

tions of 4*m* KBr or 4*m* NaCl in the concentration range of 0.02 to 0.2 aquamolality.

The densities of the solutions were measured with a model DMA 602 digital density meter (Anton Paar). It was calibrated with distilled water and dry air at 25°C and was thermostated with circulating water from a ultrathermostat. The temperature of this water was monitored with a Beckmann thermometer (calibrated against platinum resistance thermometer). The temperature was kept constant at 25 ± 0.02°C. The calibration of the density meter was checked regularly, and the reproducibility of measured density was about ± 5 ppm.

The technique used for viscosity measurements has been the same as that of Kaminisky¹⁰. Thermostatic bath (30 lit) having a window for observation, circulating coil and stirrer was fabricated. The temperature of the bath could be controlled to ± 0.005°C by circulating water from ultrathermostat. Ublehold type viscometers with flow times 400-600 sec. were fabricated using the calibrated

Fig. 2—Plots of $\eta_r - 1 - A_\eta m^{1/2}$ against m for binary electrolytes 1, Bu₄NBr; 2, Et₄NBr; 3, LiBr; 4, Me₄NBr and 5, CsBr

capillaries. Usual care was taken to clean and maintain the viscometers. The reproducible and vertical hanging of the viscometer was controlled by fabricating special levelled stands. The measurements of flow times were made with stopwatch having an accuracy of ± 0.1 sec. Considering the accuracy in time of flow measurements and temperature, the kinematic correction was found to be negligible. The errors due to surface tension and adsorption effects are thought to be negligible. The overall accuracy of the relative viscosity is of the order of ± 0.02%.

Table 2—Values of viscosity A_η and B_η coefficients and limiting apparent molar volumes for various electrolytes in 4*m* KBr and 4*m* NaCl at 25°C. The transfer volumes ($\Delta\phi_v^0$) from water to mixed solutions are also included

Salt	4 <i>m</i> KBr				4 <i>m</i> NaCl				ΔB_η water to 4 <i>m</i> KBr	ΔB_η water to 4 <i>m</i> NaCl
	A_η	B_η	ϕ_v^0 cm ³ /mol	$\Delta\phi_v^0$ cm ³ /mol	A_η	B_η	ϕ_v^0	$\Delta\phi_v^0$		
LiBr	0.0002	0.40	26.4	1.5	0.0002	-0.08	26.8	1.9	+0.295	-0.185
CsBr	0.008	-0.041	46.2	0.4	0.016	0.016	46.1	0.3	+0.042	-0.0985
Me ₄ NBr	0.136	0.116	123.6	7.4	0.072	0.057	107.3	-8.9	+0.037	-0.023
Et ₄ NBr	0.120	0.414	171.0	-3.8	0.274	0.063	167.3	-7.5	+0.075	-0.275
Bu ₄ NBr	0.108	1.470	304.0	3.2	0.702	0.0089	298.3	-2.5	+0.322	-1.136

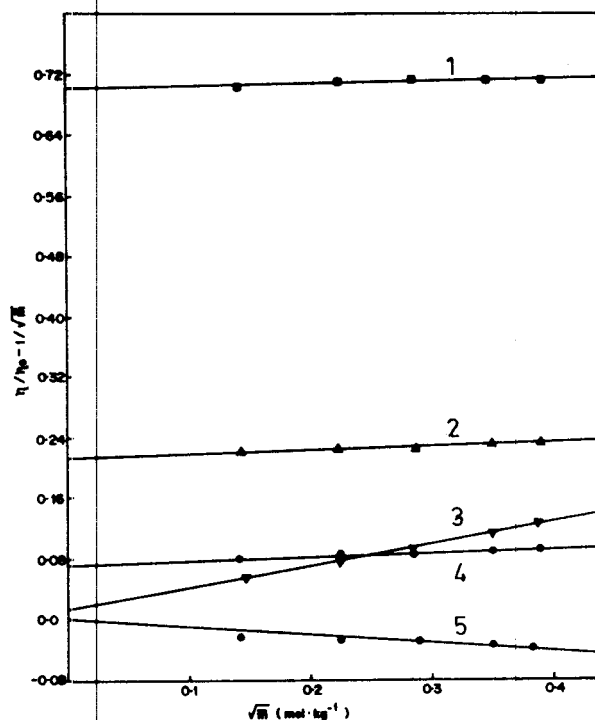


Fig. 3—Plot of $\eta_r - 1/\sqrt{\bar{m}}$ against $\sqrt{\bar{m}}$ for electrolytes in 4*m* NaCl 1, Bu₄NBr; 2, Et₄NBr; 3, CsBr; 4, Me₄NBr and 5, LiBr

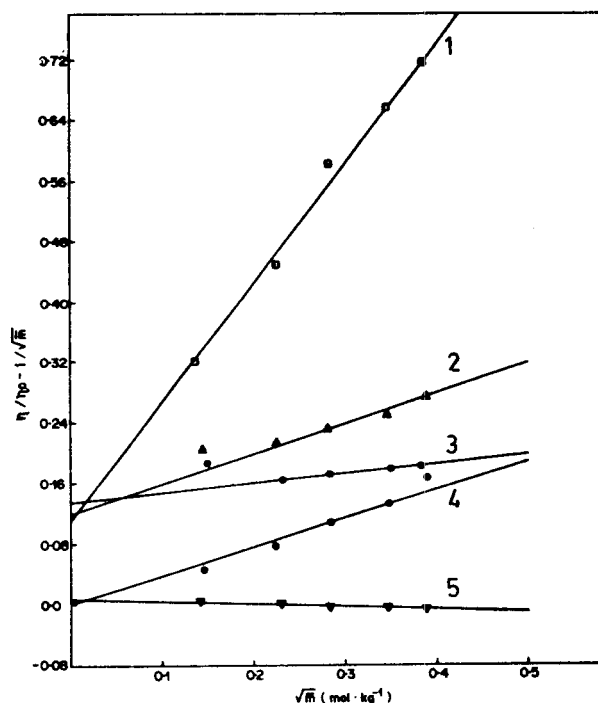


Fig. 4—Plots of $\eta_r - 1/\sqrt{\bar{m}}$ against $\sqrt{\bar{m}}$ for electrolytes in 4*m* KBr 1, Bu₄NBr; 2, Et₄NBr; 3, Me₄NBr; 4, LiBr and 5, CsBr

Results

The relative viscosities η_r which were measured at 25°C for all aqueous solutions of the salts are used to obtain the B_η coefficient of the salts. The $A_\eta m^{1/2}$ term was calculated using the expression given by Falkenhagen and the known conductivity data^{11,12}, and $(\eta_r - 1 - A_\eta m^{1/2})/m$ was plotted against m . The examples of such plots are given in Figs 1 and 2. The B_η viscosity coefficients are obtained from the intercepts. The calculated values for A_η and the derived values for B_η are summarized in Table 1. In general, the present B_η coeffi-

cients are in reasonable agreement with the best literature data^{1,13}.

The relative viscosity data for these salts in 4*m* KBr and 4*m* NaCl solutions were studied as a function of aquamolality (\bar{m}) of the salt[†]. The constants A_η and B_η were found out by plotting $(\eta_r - 1)/\sqrt{\bar{m}}$ against $\sqrt{\bar{m}}$. These plots are shown in Figs 3 and 4 respectively. The values of A_η (intercept) and B_η (slope) for the salts in 4*m* KBr and 4*m* NaCl are collected in Table 2.

[†]Aquamolality is defined as the number of moles of solute in 55.51 moles of mixed solvent.

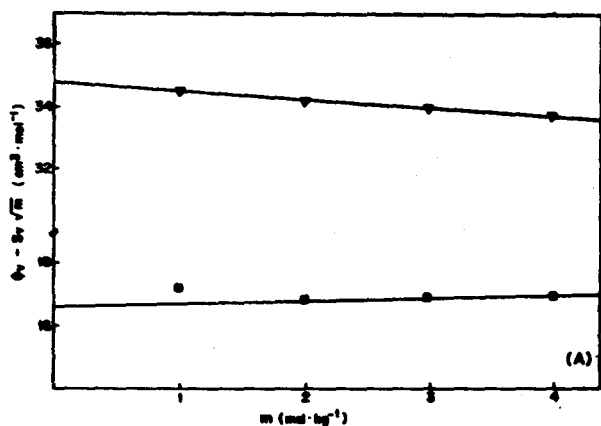


Fig. 5A—Plots $\phi_v - S_v \sqrt{m}$ against m for electrolytes in water. \blacksquare — \blacksquare NaCl and \blacktriangledown — \blacktriangledown KBr

The apparent molal volumes (ϕ_v) were calculated using the density data and the usual equation¹¹. The ϕ_v data for the salts are generally represented by an equation:

$$\phi_v = \phi_v^0 + S_v \sqrt{m} + B_v m = \phi_v^0 + A_v (d_0 \cdot m)^{1/2} + B_v m$$

where ϕ_v^0 is the standard partial molar volume of the electrolyte and $A_v (= 1.86 \text{ cm}^3 \text{ mol}^{-1})$ is the limiting slope of the Debye-Hückel theory in case of binary 1:1 electrolyte solutions. The B_v is an adjustable parameter which takes into account all deviations from the limiting law. For binary solutions, we have plotted $\phi_v - S_v \sqrt{m}$ against m to evaluate ϕ_v^0 , such plots are shown in Fig. 5A and B. The corresponding A_v parameter for ternary solutions has not been evaluated since the variation of the dielectric constant of electrolyte-water mixtures with pressure is not known. Hence for ternary solutions to calculate ϕ_v^0 of electrolyte we preferred to plot ϕ_v values against \bar{m} and smooth extrapolation to infinite dilutions were made. The plots of ϕ_v against \bar{m} for LiBr, CsBr, Me_4NBr , Me_4NBr , Et_4NBr and Bu_4NBr in 4*m* NaCl and 4*m* KBr are shown in Figs 6 and 7 respectively. The ϕ_v^0 values for the electrolytes in binary and ternary solutions are collected in Table 1 and 2 respectively along with the literature data for binary solutions. Since, we have not handled sufficiently dilute solutions, only the sign of B_v parameter was considered and not the magnitudes. The changes in viscosity B_η coefficients (ΔB_η) in transferring the electrolyte from water to 4*m* aq. NaCl and to 4*m* aq. KBr solutions are also collected in Table 2.

Discussion

The interpretation of the sign and magnitude of

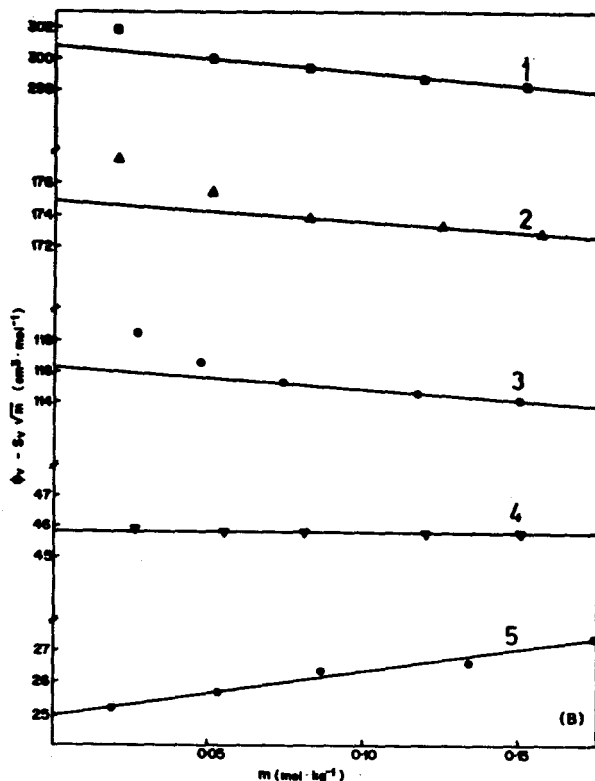


Fig. 5B—Plots of $\phi_v - S_v \sqrt{m}$ against m for electrolytes in water. 1, Bu_4NBr ; 2, Et_4NBr ; 3, Me_4NBr ; 4, CsBr and 5, LiBr

B_η values are well known in literature. The salts NaCl, LiBr, Me_4NBr , Et_4NBr and Bu_4NBr are water-structure making (+ve B_η coefficient) while KBr and CsBr are structure-breaking salts (-ve B_η coefficient). In order to obtain much more subtle information, one has to calculate individual ionic B_η coefficient values and also they should be obtained at different temperatures. The comparison of ϕ_v^0 values obtained in this work shows that they are reasonably in agreement with literature values although we have not extended the measurements to sufficiently low concentrations from where reliable extrapolation to infinite dilution can be made. The negative values of the B_v parameter are usually taken as a support for the water structure making action of the cations i.e. hydrophobic hydration in case of tetraalkylammonium salts.

Critical examination of the data in Tables 1 and 2 reveals that (i) viscosity B_η coefficients for all the salts increase (ΔB_η is +ve) in 4*m* KBr while they get reduced in 4*m* NaCl (ΔB_η is -ve) compared to water. (ii) viscosity A_η coefficients for all the salts in 4*m* KBr as well as in 4*m* NaCl increase from the values in pure water. Comparatively the increase is more pronounced in the case of tetraalkylammonium salts in 4*m* NaCl. (iii) The

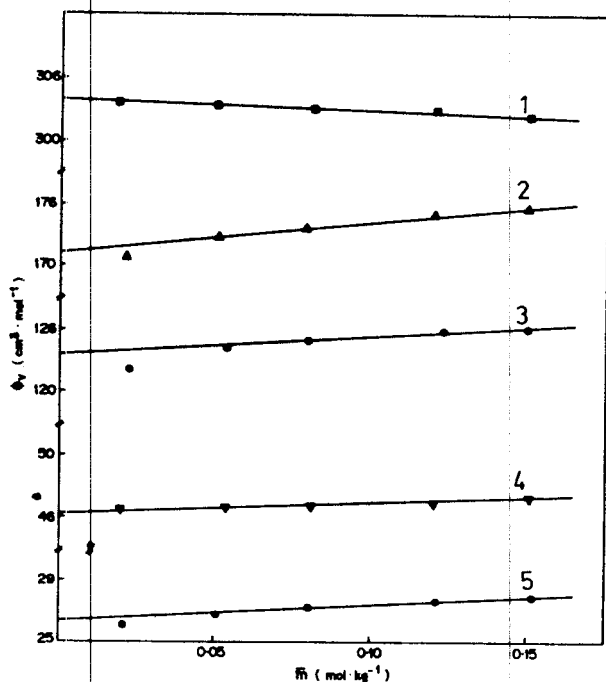


Fig. 6—Plots of ϕ_v^0 against \bar{m} for electrolytes in $4m$ KBr. 1, Bu_4NBr ; 2, Et_4NBr ; 3, Me_4NBr ; 4, CsBr and 5, LiBr

limiting apparent molar volumes (ϕ_v^0) are more in magnitude ($\Delta\phi_v^0 +ve$) in $4m$ KBr except in the case of Et_4NBr while the alkali halides show positive $\Delta\phi_v^0$ and $-ve \Delta\phi_v^0$ in the case of tetraalkylammonium salts in $4m$ NaCl solutions and (iv) the concentration variation of $\phi_{v,s}$ with aquamolalities of the salts (Figs 6 and 7) show that $(d\phi_v^0)/d\bar{m}$ are positive for all the salts except Bu_4NBr .

The results discussed above are highly significant. We cannot offer any quantitative interpretation at this stage but the same can be qualitatively discussed as below: The properties of aqueous NaCl and aqueous KBr solutions are generally interpreted in terms of structure forming and structure breaking action of NaCl and KBr respectively (viscosity of $4m$ aq. NaCl is more than water while it is less than water in the case of aq. KBr solution). The higher B_η coefficient for tetraalkylammonium salts in KBr solutions may be explained on the basis of stronger solute-solute-solvent interaction because of the hydrophobic interactions amongst the non-polar groups. The already structure broken region (for aq. KBr) i.e. B zone water molecules (Frank and Wen model)¹⁷ are getting more ordered because of the tetraalkyl cation-cation interactions resulting in higher B_η coefficient. Similarly, the comparatively high B_η

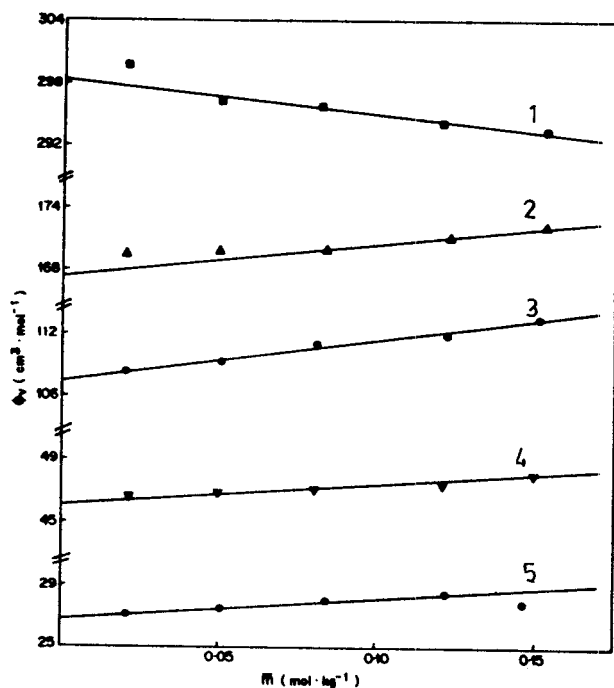


Fig. 7—Plots of ϕ_v^0 against \bar{m} in $4m$ NaCl. 1, Bu_4NBr ; 2, Et_4NBr ; 3, Me_4NBr ; 4, CsBr and 5, LiBr

value in the case of LiBr may result because of the less electrostrictive volume available in solution i.e. the A zone water molecules also get more ordered in such solutions while in case of CsBr , because of the less electrostriction (low charge density of Cs^+ ions) and the structure breaking action of Cs^+ , the B_η coefficient does not get appreciably altered. The higher A_η coefficients observed in the case of tetraalkylammonium salts also point out more cation-cation interaction (solvent separated ion-pairs) i.e. more solvent-solvent interactions (structure making effect), supporting the explanation given earlier. Recently, Bouguerra and Letellier^{18,19} have reported from their studies on limiting apparent molar volumes of these ions in concentrated KCl solutions that for large size cation (R_4N^+), the ϕ_v^0 's are equal to their intrinsic volumes while an increase in ϕ_v^0 in the case of small size cations was attributed to the interaction of cations with water molecules. The trends observed in the case of ϕ_v^0 reported in this work also support the conclusions drawn above. The $+ve \Delta\phi_v^0$ values probably suggest the salting-out effects ($+ve$ volume change). The situation can be compared with a miscellization process. This statement can be further supported by the observed reduction in the slopes of ϕ_v^0 versus m curves in the case of Bu_4NBr solutions and $+ve$ slopes for other salts.

If we propose that in binary solutions NaCl acts as a structure maker (a borderline case), then the observed B_η and A_η coefficient values can be explained easily. The high A_η and very small B_η values mean that ion-ion interactions are increased many fold while the ion-solvent interactions have been reduced to a considerable extent. This happens only for tetraalkylammonium salts but for a structure-breaking salt like CsBr both A_η and B_η coefficients increase meaning increased ion-ion as well as ion-solvent interactions. The volumetric results in aqueous NaCl are also typical and may be explained in a similar way.

Thus, the observed viscosity and volumetric effects are due to the manifestation of ion-ion, ion-solvent and hydrophobic water structure making interaction. In the case of ionic solutions the final interpretation can only be given in terms of the distribution functions in A and B region of the Frank and Wen model, which is a difficult task considering the present rudimentary knowledge of the liquid state.

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