

A Study of Solute-Solvent Interaction of Chloride and Bromide of Barium in Aqueous Dimethyl-formamide (DMF) between 298 and 313 K from Apparent Molal Volume Data

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The apparent molal volume ϕ_v of chloride and bromide of barium in aqueous dimethyl-formamide (DMF) of different compositions (10, 20 and 40 wt %) with different concentrations of electrolytes between 298 and 313 K have been determined from densities data. The data have been analysed using Masson's equation. The limiting apparent molal volumes (ϕ_v^0) and experimental slopes (s_v^*) have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The ϕ_v^0 values are found to be positive and increase with the solvent compositions as well as with temperatures for both the electrolytes. The ϕ_v^0 values are higher for barium bromide while s_v^* values are higher for barium chloride. s_v^* values increase with the rise in temperature and decrease with the increase in DMF in the solvent. ϕ_v^0 values for electrolytes are obtained by extrapolation of curves for zero mole-fraction of DMF *i.e.* for water and they are found to decrease with the rise of temperatures in case of barium bromide. The results have been correlated to the dielectric constant of solvent and viscosity β -coefficient of Jones-Dole equation. The results are in good agreement to the conclusions proposed on the basis of thermodynamic parameters of viscous flow obtained from the method of Nightingale and Benck.

INTRODUCTION

The changes in solvent structures by ions in aqueous^{1,2}, non-aqueous³⁻⁵ and mixed solvent system⁶⁻¹⁴ have been a subject of active interest among physical chemists for more than the last three decades. The subject has been analysed on the basis of both kinetic measurements and thermodynamic data obtained from viscosity, partial molal volume, molal adiabatic compressibility, conductance, electromotive force and spectroscopic examination such data are available in literature for a number of electrolytes and non-electrolytes in both aprotic^{1,2} and dipolar aprotic solvents of medium as well as higher dielectric constants.³⁻⁵ The

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behaviour of ions or electrolytes as a whole in solution has often little effective correlation with the bulk physical properties and those in mixed solvent systems cannot be predicted sometimes even qualitatively on the basis of data in pure components of mixture alone. Solute-solvent interaction makes each mixture effectively a new solvent.¹⁵ Therefore, it is of increasing interest to study the properties of electrolytes and ions in mixed solvent system. Among these aprotic-dipolar aprotic mixtures are of special interest because of their pronounced effect on equilibrium acidities and rate of reactions resulting from very different solvation characteristics of individual components particularly towards nucleophiles.¹⁶ Literature reveals that solute-solvent interaction in such mixed solvent system from partial molal volume data have not been extensively studied. Therefore, in the present investigation, the nature of solute-solvent interaction in a mixture of aprotic solvent water with a dipolar solvent dimethyl formamide (DMF) have been investigated from partial molal volume (ϕ_v) and experimental slope (s_v^*). The present investigation is the continuation of previous works^{11,12} and reports the evaluation of ϕ_v and s_v^* for the same electrolytes in the same solvent composition at temperatures 308 and 313 K. These results provide information to correlate the solvent structures around the ions together with the variation with temperatures and solvent compositions on these structures. These investigations lead to very similar conclusions that have already been proposed from thermodynamic parameters of viscous flow.¹¹⁻¹⁴

EXPERIMENTAL

The experimental procedures for the purification of salts used and DMF together with the preparation of solvent and solution were the same as reported earlier.^{12,13} All solutions of the electrolytes were prepared by weight and conversion molality into molarity were carried out. The densities of solution and solvent were measured by pycnometer as reported earlier.^{12,13} The ranges of concentration were 0.0005 M to 0.2 M.

RESULTS AND DISCUSSION

The apparent molal volumes ϕ_v for electrolytes have been calculated from density data using the equation

$$\phi_v = \frac{M}{\rho_0} - \frac{1000}{c} \left(\frac{\rho}{\rho_0} - 1 \right) \quad (1)$$

where ρ_0 and ρ are the densities of the pure solvent and solution respectively. M is the molecular weight of electrolytes and C is the concentration in molarity scale of the solution.

The apparent molal volume (ϕ_v) has been found to vary linearly with the square root of concentration and the data can be represented by empirical Masson's equation.¹⁷

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \quad (2)$$

where ϕ_v^0 is the limiting apparent molal volume and s_v^* is the experimental slope.

ϕ_v^0 is the measure of solute-solvent interaction and s_v^0 is a measure of solute-solute interaction.

The apparent molal volume ϕ_v^0 at zero concentration and the slope s_v^* for barium chloride and barium bromide between temperature ranges 298 to 313 K are presented in Table-1. These data have been obtained from intercept and slope of the plot of the curves between ϕ_v vs. \sqrt{c} which are found to be linear for the electrolytes under investigated conditions. A typical plot (Fig. 1) drawn between ϕ_v vs. \sqrt{c} for the electrolytes at 298 K shows the applicability of Eq. (2). Dielectric constant of the solvents has also been presented in the table.

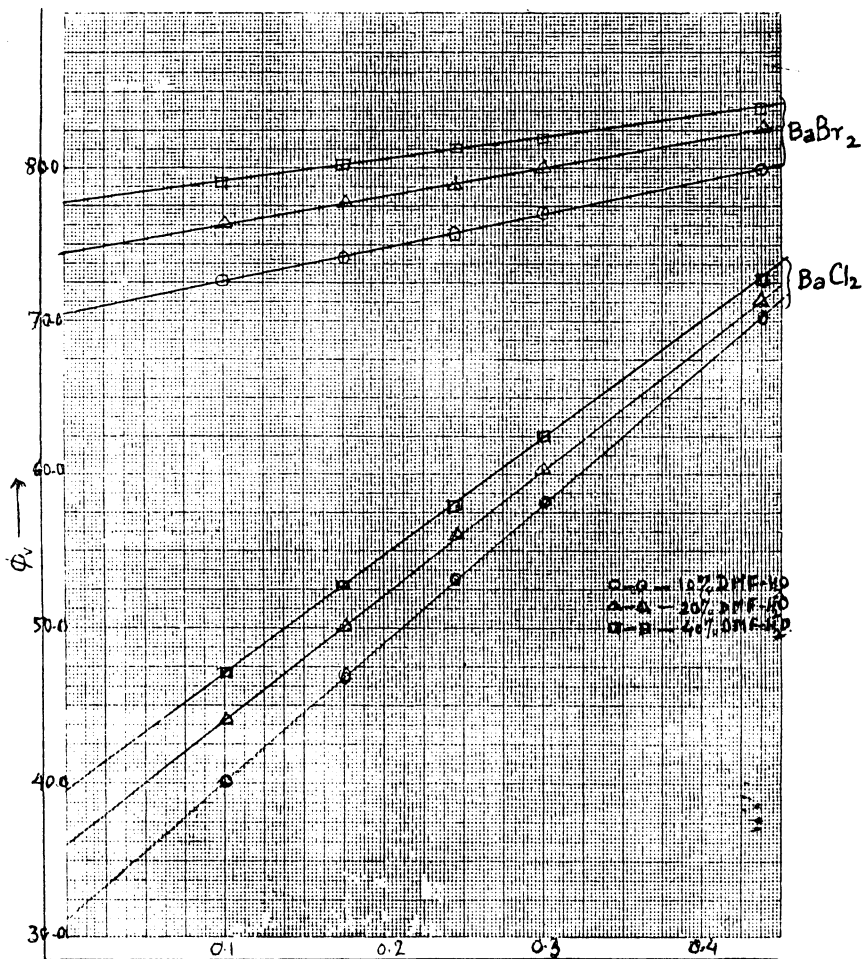


Fig. 1 Plots of ϕ_v vs. \sqrt{c} for BaCl_2 and BaBr_2 solution in different composition of DMF- H_2O mixture at 298 K.

Although the range of concentrations taken into consideration are 0.0005 M to 0.2 M, the apparent molal volumes are found to be linear functions of \sqrt{c} for concentrations greater than 0.009 M. For lower concentrations some of the

deviations seem to be real as equation (2) is valid for concentrated solutions of electrolytes.

TABLE-1
DIELECTRIC CONSTANT OF SOLVENT, LIMITING APPARENT MOLAL VOLUMES
($\phi_v^0 \text{ cm}^3 \text{ mole}^{-1}$) THE EXPERIMENTAL SLOPES ($s_v^x \text{ cm}^3 \text{ L}^{1/2} \text{ mole}^{-3/2}$) FOR
BARIUM CHLORIDE AND BARIUM BROMIDE IN AQUEOUS DIMETHYL
FORMAMIDE (DMF) OF VARIOUS COMPOSITIONS BETWEEN
THE TEMPERATURE 298 AND 313 K.

Temperature (K)	Solvent composition DMF in water % (w/v)	Dielectric constant of solvent ¹⁸	BaCl ₂		BaBr ₂		ϕ_v^0 (BaBr ₂ - BaCl ₂)
			ϕ_v^0	s_v^0	ϕ_v^0	s_v^0	
298 ¹¹	10	76.58	31.34	88.89	70.45	20.33	39.11
	20	74.26	36.25	80.25	74.50	18.00	38.25
	40	69.28	39.50	75.80	77.50	15.00	38.00
303 ¹²	10	75.25	31.90	89.57	70.85	20.91	38.95
	20	72.93	36.88	80.93	75.45	18.96	38.57
	40	68.00	40.25	76.52	78.60	15.98	38.35
308	10	73.92	32.55	90.58	71.35	21.35	38.80
	20	71.67	37.55	81.93	76.40	19.30	38.85
	40	66.82	40.80	77.50	79.65	16.35	38.75
313	10	72.59	33.20	92.11	71.80	21.78	38.60
	20	70.48	38.30	83.45	77.35	19.75	39.05
	40	65.63	41.60	79.00	80.70	16.80	39.10

Both the electrolytes have positive s_v^* value for all solvent compositions. This has been attributed to the fact that in these solvent systems, electrolytes remain completely ionised. There is a presence of strong solute-solute interaction for both the electrolytes but the interaction is stronger in case of barium chloride. The interactions are found to decrease with the increase in DMF content in the system, probably due to the formation of bulkier solvent structure¹³ in presence of large amount of DMF in the solvent as indications of strong amide-water interaction in the mixture has been suggested from NMR data.²⁰ The increase in s_v^* values with the increase in temperature suggests that more and more solute is accommodated in the void space left in packing of large associated solvent molecules and as such enhance the structure of solvent. The stronger solute-solute interaction for barium chloride can also be attributed due to smaller size, high charge density and lesser polarisability of Cl⁻ ion.

The ϕ_v^0 values are positive for both the electrolytes in all solvent compositions and are found to increase with increase in percentage of DMF in the solvent as well as with the rise of temperatures. Curves representing the variation of ϕ_v^0 with dielectric constant of solvent and with temperatures are presented in Fig. 2. These curves are found to be almost linear for both the electrolytes in all solvent

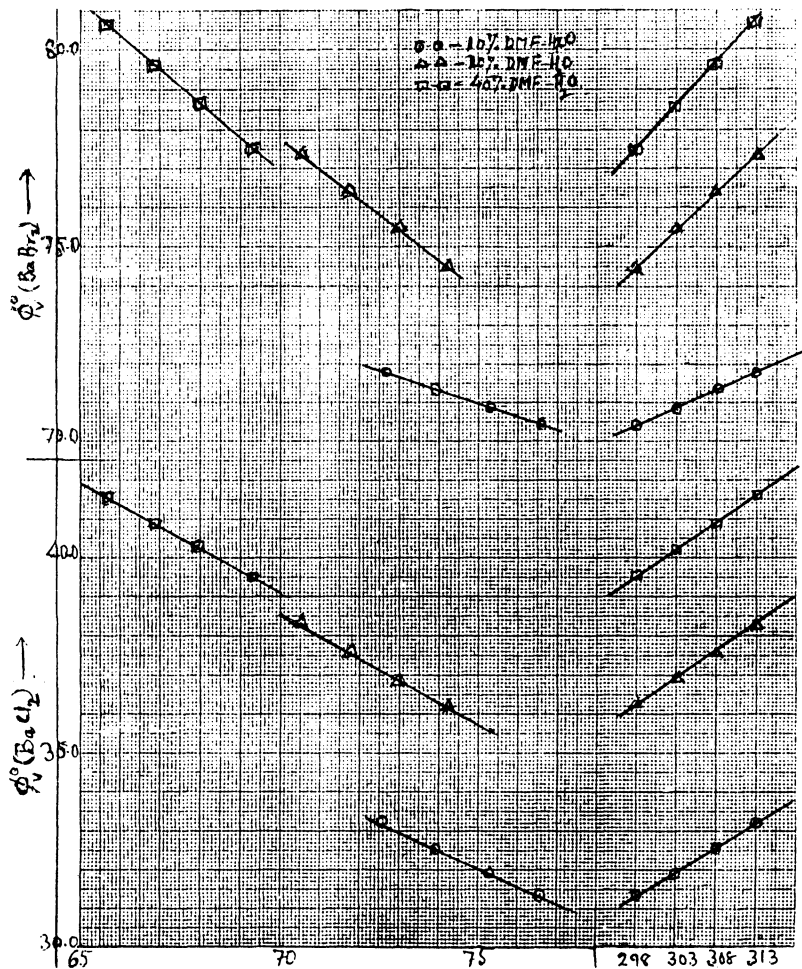


Fig. 2. ϕ_v^0 as a function of Dielectric constant of solvent and temperature for BaCl_2 and BaBr_2 in $\text{DMF-H}_2\text{O}$ mixture.

compositions. ϕ_v^0 decrease with increase in dielectric constant of medium while increase with the rise of temperature.

The curve representing the variation of ϕ_v^0 with the mole-fraction DMF in solvent (Fig. 3), indicates that increase in ϕ_v^0 is more rapid between the mole-fraction 0.027 and 0.058. The variation can be attributed to the degree of solvation. The electrolytes are minimally solvated at higher mole-fraction of DMF in the solvent.

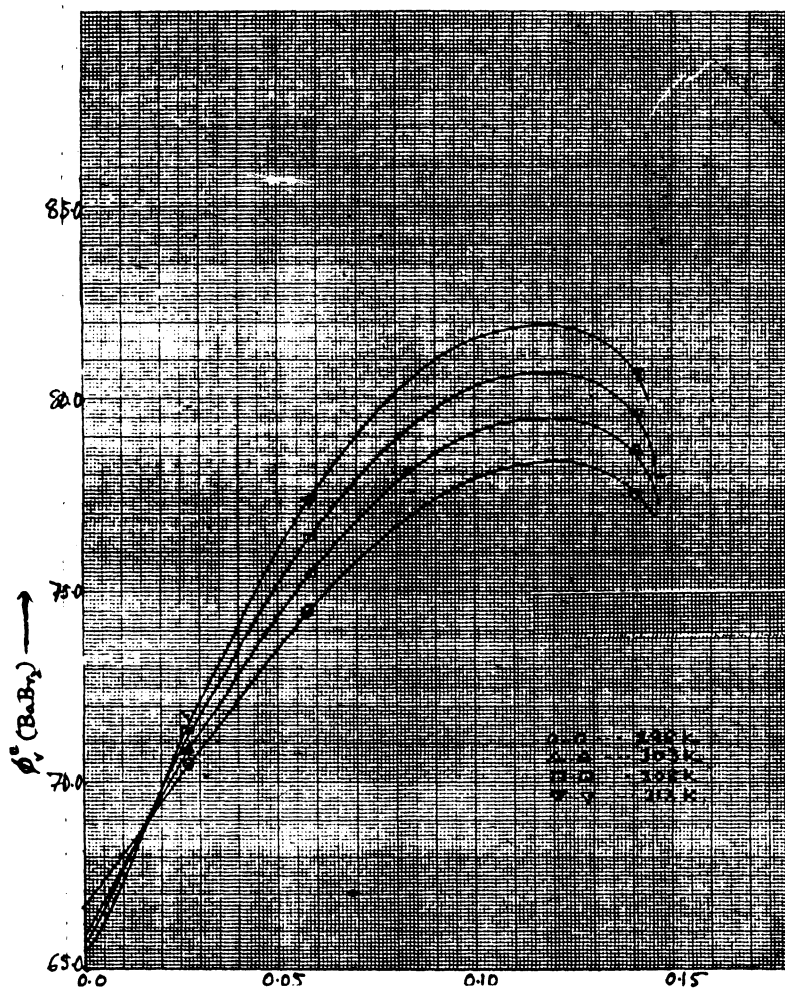


Fig. 3 ϕ_v^0 for BaCl_2 as a function of mole-fraction of DMF in solvent.

From the examination of dielectric constant data, a decrease in dielectric constant from water to mixed solvent suggests a reduction in intermolecular attraction in the medium which leads to an increase in the possibilities of formation of highly structured solvent molecule¹³ resulting from breaking of hydrogen bonded water molecule and increasing possibility of penetration of space between solvent and ions. Thus, there is an increase in cavity-creation effect causing a gradual increase in positive contribution to ϕ_v^0 . It can also be concluded from above observations that limiting apparent molal volume ϕ_v^0 of an electrolyte depends on solvent composition and temperature together with dielectric constant of system which is a function of both of the above two factors. The higher ϕ_v^0 values for barium bromide suggests the presence of stronger solute-solvent interaction in this electrolyte in comparison to that in barium chloride. As the cation in these two halides is the same, so differences observed in ϕ_v^0 can be due

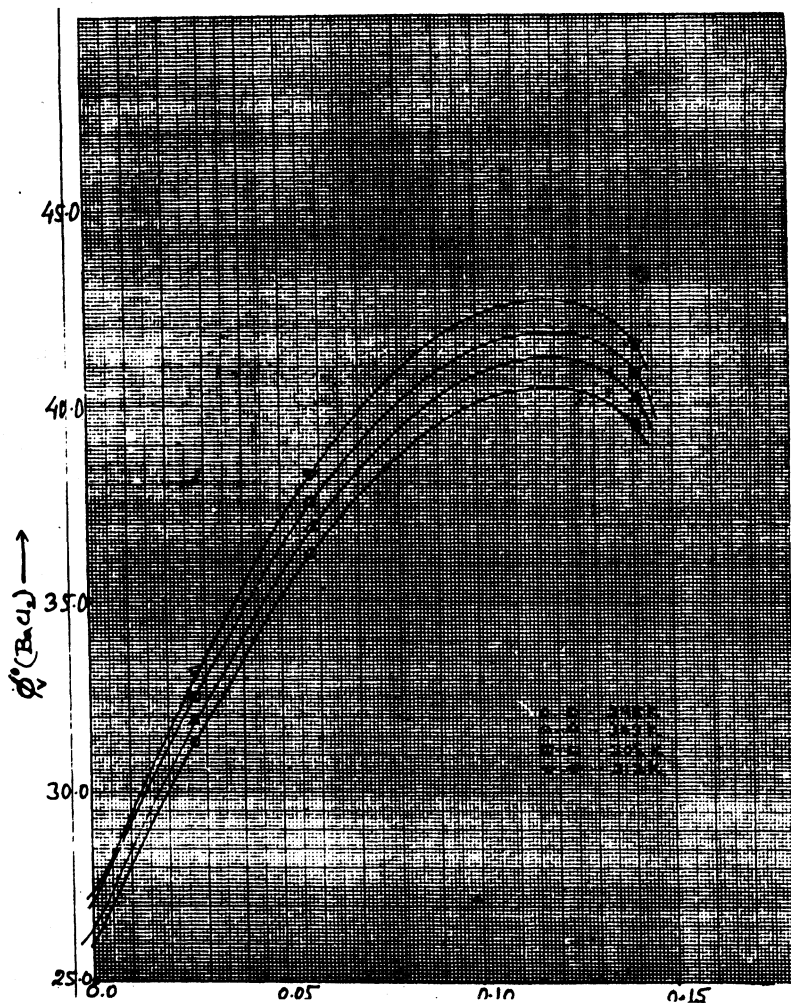


Fig. 4 ϕ_v^0 for BaBr_2 as a function of mole-fraction of DMF in solvent.

only to the difference in the behaviour of chloride and bromide ions. Bromide ion, therefore, is more strongly solvated probably due to larger ionic size, low charge density and larger polarizability effect. Larger anions are considerably more solvated in dipolar aprotic solvent like DMF.¹⁶ Preferential solvation of dipolar aprotic solvent by larger anion may also be responsible for increase in ϕ_v^0 with the rise of temperature as the possibility of free DMF molecule in mixed solvent is large due to thermal agitation at higher temperature. Effects associated with preferential solvation have also been observed for RbCl ¹⁹ in DMF-water system although a strong amide-water interaction is present. Similar effect has also been reported for methanol-dimethyl sulphoxide system²¹ in which there is also strong interaction between the component solvents.²²

The data obtained by extrapolation of curve in Fig. 3 are presented in Table-2 which gives the ϕ_v^0 values of these electrolytes in pure water.

TABLE-2
FOR BaCl₂ AND BaBr₂ IN PURE WATER BETWEEN
TEMPERATURES 298 AND 313 K

Temperature	ϕ_v^0 (BaCl ₂)	ϕ_v^0 (BaBr ₂)
298	26.00	66.25
303	26.50	65.90
308	27.00	65.65
313	27.40	65.45

From examination of the data it is evident that in case of barium chloride ϕ_v^0 values increase while in case of barium bromide, the values decrease with the rise of temperature. The decrease in ϕ_v^0 is in accordance with the view of Parker,¹⁶ who suggested that larger anions are considerably less solvated in aprotic solvent like water. The hydrogen bonded water molecules are broken by thermal agitation at higher temperature and free water molecules produce one less solvated by bromide ion. Penetration of ions in the solvent cosphere is larger causing a decrease in ϕ_v^0 . A similar decrease in ϕ_v^0 is also observed in case of NaI and KI in aqueous solutions and also in ethylene carbonate (EC) above 323 K.⁵ Similar conclusions have already been suggested on the basis of ionic entropy of activation of viscous flow for ions.¹⁴ In aqueous solution ΔS_{ion}^* decreases with the increased ionic size for anion *i.e.*, $\Delta S_{Cl^-}^* > \Delta S_{Br^-}^*$ whereas in the mixed solvent the order is just reversed *i.e.* $\Delta S_{Br^-}^* > \Delta S_{Cl^-}^*$, indicating the reversal of the behaviour of anions. In mixed solvent system, solvent has the most stable transition state around larger anion. It is also evident from curves that at mole-fraction DMF 0.016, the curves of different temperatures coincide at a single point where ϕ_v^0 is 68.9. Under this condition ϕ_v^0 is not affected by temperature and may be regarded as a transition point for solvent structure under the influence of bromide ion.

From the data for ϕ_v^0 (BaBr₂-BaCl₂) at all solvent compositions as well as temperatures, it is evident ϕ_v^0 has an additive character in mixed solvent system which has also been observed by Scott,¹ Krus^{23, 24} and others in aqueous solutions of electrolytes.

Similar informations regarding solute-solvent interaction for the electrolytes in the mixed solvent have already been suggested from viscosity measurements.^{12, 13} The positive A coefficient of Jones-Dole equation²⁵ indicates the presence of strong ion-ion interaction. The higher A-values for barium chloride suggest the presence of stronger ion-ion interaction. A stronger solute-solvent interaction is indicated in barium bromide as it has higher β -coefficient values. A similar trend in variation of β -coefficient values with the mole-fraction of DMF in the solvent and with temperature confirms the similar behaviour of electrolytes in the solvent. Identical conclusions regarding the behaviour of these electrolytes in specified solvent systems within the studied temperature range have already been suggested on the basis of thermodynamic parameters of viscous flow.¹¹⁻¹⁴ The highest ΔS^* for barium bromide in all solvent system as well as for all temperatures, suggests more stable transition state for solvent around bromide ion.

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