Ion-Solvent Interactions Investigated by Isentropic Compressibility Measurements of Tetraalkylammonium, Copper(I) and Sodium Salts in Binary Mixtures of Acetonitrile and *n*-Butyronitrile at 298.15 K

Dip Singh Gill, Avnesh Kumari, Surinder Kumar Sharma, and Surinder Pal Jauhar

Department of Chemistry, Panjab University, Chandigarh – 160 014, India

Reprint requests to Dr. D. S. G.; Fax: 91-172-2545074; E-mail: dipgill@yahoo.com

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Ultrasonic velocities and densities of binary mixtures of acetonitrile (AN) and *n*-butyronitrile (*n*-BTN) with Bu_4NBPh_4, Bu_4NClO_4, Bu_4NI, Bu_4NBr, Pr_4NBr, Et_4NI, Et_4NBPh_4, $NaBPh_4$, $NaClO_4$ and $CuClO_4$ have been measured in the concentration range 0.0045 – 0.2 mol kg^{-1} over the entire composition range at 298.15 K. Isentropic compressibilities (K_s) and apparent molal isentropic compressibilities ($K_{s,\phi}$) have been calculated. Limiting apparent molal isentropic compressibilities ($K^o_{s,\phi}$) have been evaluated and split into the contribution of individual ions, i. e. into $(K^o_{s,\phi})_\pm$ values. $(K^o_{s,\phi})_\pm$ for Cu^+, Na^+ and Br^- in all cases is negative and large, for Bu_4N^+ and Ph_4B^- positive and large, and for I^- and $ClO_4{}^-$ negative only in AN, and becomes positive in binary mixtures of AN and *n*-BTN for all compositions. The negative $(K^o_{s,\phi})_\pm$ values for Cu^+, Na^+ and Br^- indicate strong ion-solvent interactions involving electrostatic ion-dipole interactions. The large and positive $(K^o_{s,\phi})_\pm$ values for Bu_4N^+ and Ph_4B^- show some special type of ion-solvent interactions (hydrophobic or dispersion interactions) with AN and *n*-BTN. The small negative value changing to a small positive value for I^- and $ClO_4{}^-$ indicates the change of a weak electrostatic ion-solvent interaction to another weak special interaction. A comparison of $(K^o_{s,\phi})_\pm$ for Cu^+ in some solvent systems shows that the ion-solvent interaction behaviour of Cu^+ in AN + *n*-BTN is similar to that in AN + NM, AN + TEP, BN + TEP and PY + TEP mixtures but differs from that observed in AN + DMF and AN + DMSO mixtures.

Key words: Ion-Solvent Interaction; Isentropic Compressibility; Copper(I) Salts; Acetonitrile; *n*-Butyronitrile.

1. Introduction

Ion-solvent interactions have been extensively investigated [1 – 6] in a number of mixed solvents using different techniques. Alkali ions interact with solvent molecules purely through electrostatic forces [7, 8]. Cu^+ and Ag^+ ions interact with nitrile solvents also through a special type of interactions [9 – 11]. Limiting ionic apparent molal isentropic compressibilities $(K^o_{s,\phi})_\pm$ [12 – 14] are important parameters which not only provide the magnitude but also predict the nature of the interactions on the basis of their positive or negative sign. Even hydrophobic interactions, taking place between tetraalkylammonium ions and solvent molecules, can be identified by evaluation of their $(K^o_{s,\phi})_\pm$ values. In the present work, ion-solvent interactions have been measured in some copper(I), sodium and tetraalkylammonium salts by their isentropic compressibilities. AN and *n*-BTN mixtures are selected for these studies, because these solvents have different dielectric constants ($\varepsilon_{AN} = 36.0$, $\varepsilon_{n-BTN} = 24.8$) but similar $-C \equiv N$ groups, and are expected to interact with the ions through a different extent of electrostatic but similar special interactions.

2. Experimental

AN 99.5% and *n*-BTN 99.5% (both E. Merck) were purified as reported in [15]. The purified solvents had the densities 0.77685 and 0.78662 g cm^{-3}, viscosities 0.341 and 0.551 cP, and ultrasonic velocities 1280.8 and 1279.0 m s^{-1}, respectively, which agreee well with the literature values [15].

Copper(I) perchlorate tetraacetonitrile ($[Cu(CH_3CN)_4]ClO_4$) was prepared by the reduction of copper(II) perchlorate hexahydrate by copper powder in warm AN, following the method reported by Hathaway *et al.* [16] and Gill *et al.* [17]. The purity of the complex was checked by its elemental and chemical analysis. Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) (used as reference electrolytes in the present work), anhydrous sodium perchlorate ($NaClO_4$) and tetraethylammonium tetraphenylborate (Et_4NBPh_4) were prepared by the methods given in [18]. $NaBPh_4$, 99.5% (E. Merck), Bu_4NI, Bu_4NBr, Pr_4NBr and Et_4NI (all $>$ 99%, from Fluka) were used as received.

Ultrasonic velocity measurements of the binary mixtures as well as of all salt solutions were carried out at 2 MHz frequency with an ultrasonic time intervalometer (Model UTI-101), manufactured by Innovative Instruments (Hyderabad), using a pulse echo overlap technique. Different concentrations of the salts in AN + *n*-BTN mixtures were prepared by diluting the stock solutions. In all cases the measurements were performed twice. The densities were measured using a precision densitimeter (Anton Paar model DMA-60 with an external measuring cell DMA-602). The absolute accuracy of the sound velocity and density measurements was better than $\pm 2 \times 10^{-4}$ m s^{-1} and $\pm 1 \times 10^{-5}$ g cm^{-3}, respectively, as reported in [13].

3. Results and Discussion

The Physical parameters of the AN + *n*-BTN binary mixtures of varying compositions are reported in Table 1, which shows that density (ρ_o), viscosity (η_o) and ultrasonic velocity (u_o) of all binary mixtures vary over a wide range. The ultrasonic velocities (u) and densities (ρ) of Bu_4NBPh_4, Bu_4NClO_4, Bu_4NI, Bu_4NBr, Pr_4NBr, Et_4NI, Et_4NBPh_4, $NaBPh_4$, $NaClO_4$ and $CuClO_4$ have been measured at different salt molalities (m) in the molality range 0.0045 to 0.2 mol kg^{-1} in AN + *n*-BTN mixtures containing 0, 20, 40, 60, 80 and 100 mol% AN. The isentropic compressibility (K_s) of each electrolyte in each solvent has been calculated by using the relation

$$K_s = \frac{1}{u^2\rho}. \tag{1}$$

The apparent molal isentropic compressibility $(K_{s,\phi})$ of these salts has been calculated using the partial molal volume V_ϕ and the equations

$$V_\phi = \frac{M}{\rho} - \frac{10^3[\rho - \rho_o]}{m\rho\rho_o}, \tag{2}$$

Table 1. Viscosity (η_o), density (ρ_o), permittivity (ε_o), ultrasonic velocity (u_o) and isentropic compressibility (K_s^o) for AN + *n*-BTN mixtures at 298.15 K.

mol% AN	η_o / cP	ρ_o / g cm^{-3}	ε_o	u_o / ms^{-1}	$10^6 K_s^o$ / bar^{-1}
100	0.341	0.77685	36.0	1280.8	78.47
80	0.405	0.78054	33.9	1276.6	78.61
60	0.428	0.78125	32.5	1276.7	78.52
40	0.467	0.78379	30.8	1277.4	78.19
20	0.510	0.78547	28.9	1278.8	77.86
0	0.553	0.78662	24.8	1279.0	77.71

$$K_{s,\phi} = V_\phi K_s + \frac{10^3[K_s - K_o]}{m\rho_o}, \tag{3}$$

where m is the molality and M the molecular mass of the solute. K_s and K_o are the isentropic compressibilities of the solution and the pure solvent, and ρ and ρ_o are the corresponding densities. The plots of $K_{s,\phi}$ versus $m^{1/2}$ were linear in the concentration range studied. The limiting apparent molal isentropic compressibilities $(K_{s,\phi}^o)$ were obtained by extrapolation from the linear plots of $K_{s,\phi}$ versus $m^{1/2}$ by the least squares method using the equation

$$K_{s,\phi} = K_{s,\phi}^o + A_{s,\phi} m^{1/2}. \tag{4}$$

The $K_{s,\phi}^o$ values of the various salts thus obtained are reported in Table 2.

The $K_{s,\phi}^o$ values of these electrolytes are not available for AN + *n*-BTN mixtures. Therefore a comparison of our values could not be made. In pure AN, the $K_{s,\phi}^o$ values for Bu_4NBPh_4 (106.5×10^{-4} cm^3 mol^{-1} bar^{-1}) and for Bu_4NClO_4 (22.6×10^{-4} cm^3 mol^{-1} bar^{-1}) agree within $\pm 2.6 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1} with the values 108.0×10^{-4} cm^3 mol^{-1} bar^{-1} and 20.0×10^{-4} cm^3 mol^{-1} bar^{-1}, respectively [19].

Table 2 shows that the $K_{s,\phi}^o$ values for copper(I) perchlorate and sodium perchlorate are negative and large in AN + *n*-BTN mixtures at all compositions of the solvent mixtures. For Bu_4NBPh_4, Bu_4NClO_4, Bu_4NI, Bu_4NBr, Pr_4NBr, Et_4NBPh_4 except for $NaBPh_4$, $K_{s,\phi}^o$ is mostly positive and large at all compositions. Et_4NI has a negative $K_{s,\phi}^o$ value in AN + *n*-BTN mixtures, which decreases with increase in mol% of *n*-BTN.

For obtaining quantitative information regarding the tendency of each ion to produce structural or solvation effects, the $K_{s,\phi}^o$ values for the salts in Table 2 have been split into contributions of individual ions, *i. e.* into ionic $K_{s,\phi}^o$ values.

As reported in [20–23], the $K_{s,\phi}^o$ values are additive and can be split that way. For that splitting of

Table 2. Limiting apparent molal isentropic compressibilities[a] $(K^{\mathrm{o}}_{\mathrm{s},\phi})$ for some salts in AN + *n*-BTN mixtures at 298.15 K.

	$(K^{\mathrm{o}}_{\mathrm{s},\phi})$ / 10^{-4} cm^3 mol^{-1} bar^{-1}					
	mol% AN					
Salt	100	80	60	40	20	0
Bu_4NBPh_4	106.5	160.0	372.8	373.9	402.1	412.1
Bu_4NClO_4	22.6	108.0	220.5	235.7	249.7	290.8
Bu_4NI	12.0	79.0	184.0	196.0	235.9	295.1
Bu_4NBr	9.4	36.9	135.5	138.0	179.0	268.5
Pr_4NBr	−44.4	−34.0	112.0	123.0	133.0	238.2
Et_4NI	−103.8 (−103.5)[b]	−48.2 (−47.0)[b]	−25.2 (−24.8)[b]	−12.4 (−10.5)[b]	19.9 (19.1)[b]	86.3 (84.7)[b]
Et_4NBPh_4	−9.0	34.0	164.0	167.4	185.3	201.7
$NaBPh_4$	−92.2 (−92.3)[b]	−136.3 (−134.9)[b]	−48.1 (−48.1)[b]	−77.5 (−75.3)[b]	−74.1 (−72.1)[b]	−133.8 (−133.4)[b]
$NaClO_4$	−176.2	−186.9	−200.4	−213.0	−224.5	−254.7
$CuClO_4$	−212.0	−219.9	−250.0	−280.5	−300.4	−351.8

[a] Maximum uncertainity in these values is $\pm 2.6 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}.

[b] These values have been obtained by adding $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ for the respective ions constituting the salts.

Table 3. Limiting ionic apparent molal isentropic compressibilities $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ for some ions in AN + *n*-BTN mixtures at 298.15 K.

	$(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ / 10^{-4} cm^3 mol^{-1} bar^{-1}					
	mol% AN					
Ion	100	80	60	40	20	0
Bu_4N^+	47.8	71.9	167.5	168.0	180.7	185.2
Pr_4N^+	−6.0	1.0	144.0	153.0	134.7	154.9
Et_4N^+	−67.7	−54.1	−41.3	−38.5	−36.1	-25.2
Cu^+	−186.8	−256.1	−303.0	−348.7	−369.4	-457.4
Na^+	−151.0	−223.0	−253.4	−281.2	−293.5	-360.3
Ph_4B^-	58.7	88.1	205.3	205.9	221.4	226.9
I^-	−35.8	7.1	16.5	28.0	55.2	109.9
ClO_4^-	−25.2	36.1	53.0	68.2	69.0	105.6
Br^-	−38.4	−35.0	−32.0	−30.0	−1.7	83.3

$K^{\mathrm{o}}_{\mathrm{s},\phi}$ some approaches in [20] have been utilized. The method already used in AN is based upon $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ for $Ph_4B^- = 0$. This method is not appropriate because Ph_4B^- is large (0.535 nm), even larger than Bu_4N^+ (0.50 nm) [21]. Therefore its contribution to the compressibility cannot be neglected. Millero [22] has split the partial molal volumes of electrolytes into ionic components using Ph_4AsBPh_4 as a reference electrolyte. A similar model in [23], in which it is recommended to use Bu_4NBPh_4 as reference electrolyte to achieve the splitting of the $K^{\mathrm{o}}_{\mathrm{s},\phi}$ values into their ionic contributions $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ with the help of the equations

$$\frac{K^{\mathrm{o}}_{\mathrm{s},\phi}(\mathrm{Bu_4N^+})}{K^{\mathrm{o}}_{\mathrm{s},\phi}(\mathrm{Ph_4B^-})} = \frac{r^3_{\mathrm{c}}(\mathrm{Bu_4N^+})}{r^3_{\mathrm{c}}(\mathrm{Ph_4B^-})} = \left(\frac{5.00}{5.35}\right)^3, \quad (5)$$

$$K^{\mathrm{o}}_{\mathrm{s},\phi}(\mathrm{Bu_4NBPh_4}) = K^{\mathrm{o}}_{\mathrm{s},\phi}(\mathrm{Bu_4N^+}) + K^{\mathrm{o}}_{\mathrm{s},\phi}(\mathrm{Ph_4B^-}). \quad (6)$$

Using (5) and (6), the $K^{\mathrm{o}}_{\mathrm{s},\phi}$ values of Bu_4NBPh_4 were split into contribution of Bu_4N^+ and Ph_4B^- ions. By using these $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values, such values for all other ions have been calculated and are reported in Table 3.

The consistency of the present results can be checked by comparing the experimental $(K^{\mathrm{o}}_{\mathrm{s},\phi})$ values for Et_4NI and $NaBPh_4$ from Table 2 with the $(K^{\mathrm{o}}_{\mathrm{s},\phi})$ values obtained by adding up the $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values for the respective ions constituting the salts. The added up values for Et_4NI and $NaBPh_4$ from Table 3 are written in parantheses in Table 2. Good agreement (within $\pm 2.5 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}) has been observed between the experimental and added up values.

Negative $(K^{\mathrm{o}}_{\mathrm{s},\phi})$ values are generally obtained due to stronger ion-solvent interactions involving electrostatic ion-dipoles, or some special type of interactions, while positive values are obtained mostly for tetraalkylammonium ions due to hydrophobic or dispersive interactions. The results of Table 3 show that the $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values for Cu^+, Na^+ and Br^- are negative. For Cu^+ and Na^+ their magnitude is quite large, but for Br^- it is relatively small. The results indicate that Cu^+ and Na^+ ions have strong ion-solvent interactions as compared to Br^- in all these mixtures. For Cu^+ and Na^+ the extent of ion-solvent interactions increases with increase of the *n*-BTN composition, while but for Br^- it decreases. The $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values for Bu_4N^+ and Ph_4B^- are positive and large at all compositions of the mixtures. These $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values indicate some special type of ion-solvent interaction, which may take place due to hydrophobic dispersion or solvent-solvent interactions. The hydrophobic interaction with increase of the *n*-BTN composition increases due to the increased chain length of *n*-BTN. I^- and ClO_4^- have negative $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values in pure AN, and these values become positive in the *n*-BTN rich region. The magnitude of the $(K^{\mathrm{o}}_{\mathrm{s},\phi})_{\pm}$ values in both these cases is, however, small indicating poor solvation of both these ions in AN + *n*-BTN mixtures.The ion-solvent interac-

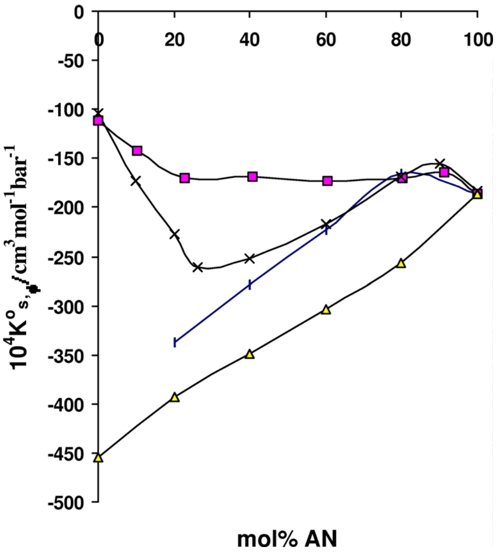

Fig. 1. Plot of $(K^o_{s,\phi})_\pm$ for Cu^+ versus mol% AN in AN + NM (■), AN + DMF (×), AN + DMSO (|), and AN + *n*-BTN (△) mixtures.

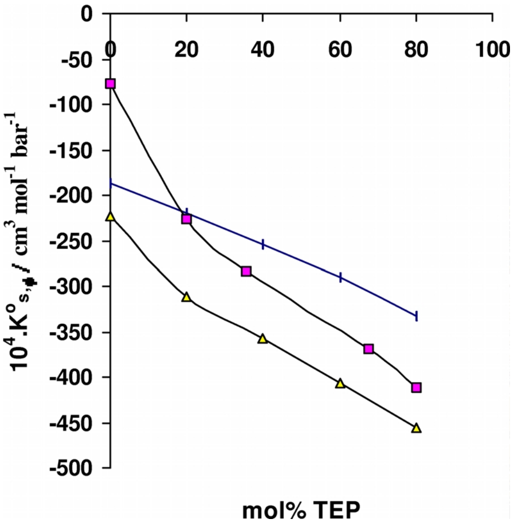

Fig. 2. Plot of $(K^o_{s,\phi})_\pm$ for Cu^+ versus mol% TEP in AN + TEP (|), BN + TEP (■), and PY + TEP (△) mixtures.

tion for these ions changes from weak electrostatic to a special type of interaction in the *n*-BTN rich region. As special interaction of Ph_4As^+ and Ph_4B^- with AN through dispersion forces was also reported by Bose and Kundu [24].

For Et_4N^+ at all compositions and for Pr_4N^+ only in AN the $(K^o_{s,\phi})_\pm$ values are negative, indicating the solvation of these two ions in these systems. The extent of ion-solvent interactions, however, decreases with the increase of the *n*-BTN concentration in the mixture.

The $(K^o_{s,\phi})_\pm$ values for Cu^+ in some mixed solvents were recently reported in [4]. These results have been incorporated for comparing their ion-solvent interactions with the present system. Plots of $(K^o_{s,\phi})_\pm$ for Cu^+ in some solvents mixtures as a function of the mol% AN and TEP are presented in Figs. 1 and 2, respectively. The results show that $(K^o_{s,\phi})_\pm$ for Cu^+ becomes most negative between 20 – 60 mol% AN in AN + DMF mixtures, passes through a minimum negative value at about 80 mol% AN in AN + DMSO mixture and changes linearly in AN + *n*-BTN, AN + TEP, BN + TEP and PY + TEP mixtures with the value becoming more negative and larger with the increase of TEP, NM and *n*-BTN composition. The ion-solvent behaviour of Cu^+ in AN + *n*-BTN mixtures is similar to that in AN + NM, AN + TEP, BN + TEP and PY + TEP mixtures, but different from that observed in AN + DMF and AN + DMSO mixtures.

4. Conclusions

Cu^+, Na^+, R_4N^+ and Ph_4B^- ions show strong ion-solvent interactions in AN + *n*-BTN mixtures. In the cases of Na^+ and Cu^+ this interaction seems to be mainly due to electrostatic ion-dipole interaction. The interaction between R_4N^+ and Ph_4B^- ions with the solvent molecules appears to be mainly due to hydrophobic or dispersion forces. All anions interact weakly with the solvent molecules in AN + *n*-BTN mixtures.

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