

# Ultrasonic Velocity and Isentropic Compressibility Studies of Monoalkylammonium Salts in Binary Mixtures of Acetonitrile and *N*,*N*-Dimethylacetamide at Variable Temperature and Atmospheric Pressure

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## Abstract

Ultrasonic velocities and densities of alkyl substituted ammonium perchlorates-RNH<sub>3</sub>ClO<sub>4</sub>, where R is methyl (Me), ethyl (Et) *n*-propyl (Pr) *n*-butyl (Bu) *n*-hexyl (Hx) and *n*-octyl (Oc), have been measured in the concentration range 0.03–0.28 mol·kg<sup>-1</sup> in binary mixtures of acetonitrile (AN) and *N*,*N*-dimethylacetamide (DMA) containing 0, 20, 40, 60, 80 and 100 mol% DMA at temperatures 298–328 K in 10 K intervals, using an Anton Paar density and sound velocity meter (DSA 5000 M). The experimental data of ultrasonic velocities and densities have been used for calculating isentropic compressibilities ( $K_{S}$ ) and apparent molal isentropic compressibilities ( $K_{S,\phi}$ ) for all the electrolytes have been evaluated from  $K_{S,\phi,\pm}$  values with solvent composition shows preferential solvation of alkylammonium (RNH<sub>3</sub><sup>+</sup>) ions by DMA in the AN rich region and by AN in the DMA rich region. The extent of solvation of the alkylammonium ions, at all studied temperatures, was found to increase with decreasing alkyl chain length; that is  $OcNH_3^+ < HxNH_3^+ < BuNH_3^+ < PrNH_3^+ < EtNH_3^+ < MeNH_3^+$ .

**Keywords** Apparent molal volume · Isentropic compressibility · Preferential solvation · Acetonitrile · N,N-dimethylacetamide · Alkylammonium ion

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## 1 Introduction

Compressibility measurements are usually used for predicting the pressure dependence of properties of electrolyte solutions. Acoustical parameters have been found to be a most powerful tool for understanding solvent structure, ion-ion association and ion-solvent interactions in pure and binary mixtures of solvents. Data of physicochemical properties of various electrolytic solutions in binary mixtures of solvents are necessary in many chemical processes, industrial applications and theoretical research [1-7]. Such data have been found to be completely lacking for electrolyte solutions of monoalkylammonium perchlorates ( $RNH_3ClO_4$ ) in acetonitrile and N.N-dimethylacetamide solvent mixtures. A literature survey indicates that no work has been done on these electrolyte solutions from the point of view of density and ultrasonic velocity measurements. Alkylammonium perchlorates have been recently used as electrolytes in developing electrical double layer capacitors [8]. Also, alkyl substituted ammonium perchlorates are used as one of the main ingredients in rocket propellants and missiles [9]. For the removal of waste explosives containing alkyl substituted ammonium perchlorate from munitions, non-aqueous solvents or binary mixtures of solvents can be used as solvating medium to recover the components ( $RNH_3ClO_4$ ) from waste composite propellants. Keeping this in view we have undertaken this research in which compressibility studies of alkyl substituted ammonium perchlorates were carried out in binary mixtures of acetonitrile and dimethylacetamide. These studies can be helpful to enhance the extraction efficiency of alkylammonium perchlorates from propellants and explosives. The compressibility studies of electrolytes in acetonitrile and dimethylacetamide, in general, is of interest because both solvents have high dipole moments, high dielectric constants ( $\mu_{AN}$  = 3.37 D,  $\mu_{DMA}$  = 3.72 D,  $D_{AN}$  = 36.0 and  $D_{DMA}$  = 37.8). Also, the Gutmann donor number of dimethylacetamide differs significantly from that of acetonitrile (14.1 for AN and 27.8 for DMA). The large difference in the values of Gutmann donor number of acetonitrile and dimethylacetamide plays an important role in solvation of ions. These solvents are extensively used as extracting solvents, because of their excellent solvating ability, which is why in relation of our work they can also be utilized for extracting alkylammonium perchlorates from propellants and explosives [10]; therefore it would be of great interest to extend electrolytic investigation in their binary mixtures. In order to investigate the compressibility behavior of monoalkylammonium perchlorates in binary mixtures of acetonitrile and dimethylacetamide, attempts have been made to measure ultrasonic velocities and densities of monoalkylammonium perchlorates (CH<sub>3</sub>NH<sub>3</sub>ClO<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>ClO<sub>4</sub>, C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>ClO<sub>4</sub>,  $C_4H_9NH_3CIO_4$ ,  $C_6H_{13}NH_3CIO_4$  and  $C_8H_{17}NH_3CIO_4$ ) over the concentration range 0.03–0.28 mol·kg<sup>-1</sup> at four different temperatures (298, 308, 318 and 328 K). Results are interpreted in terms of limiting ionic apparent molal isentropic compressibility,  $K_{S,\phi,\pm}^{o}$ . The sign and magnitude of  $\overline{K}_{S,\phi,\pm}^{o}$  will help us to understand the nature of various types of molecular interactions prevailing in these solutions. To obtain individual ion contribution to solvation behavior  $K^{o}_{S,\phi,\pm}$ , ultrasonic velocities and densities of two more salts, tetrabutylammonium perchlorate ( $C_{16}H_{36}NClO_4$ ) and tetrabutylammonium tetraphenylborate ( $C_{40}H_{56}BNa$ ) in binary mixtures of acetonitrile and dimethylacetamide have also been measured. Results show how the alkyl chain length, temperature and solvent composition affect the solvation behavior of these systems.

## 2 Experimental

## 2.1 Chemicals Used

Acetonitrile (99.8%, E.Merck), *N*,*N*-dimethylacetamide (99.8%, E.Merck) and acetone (99.8%, E.Merck) were purified further as reported earlier [11–14]. The chemicals, silver perchlorate monohydrate (AgClO<sub>4</sub>·H<sub>2</sub>O, Alfa Aesar), sodium tetraphenylborate (NaBPh<sub>4</sub>, 99.5%, CDH Chemicals) and tetrabutylammonium bromide (Bu<sub>4</sub>NBr, 99.5%, TCI Chemicals) were used without any further purification.

#### 2.1.1 Analysis of Water Content in Chemicals

The source, purity and water content of solvents used are described briefly in Table 1.

The density ( $\rho$ ) and ultrasonic velocity (u) values used for analysis of the present data for pure AN, pure DMA and their binary mixtures at temperatures 298 K, 308 K, 318 K and 328 K are reported in Table 2. AN and DMA were dried over 4 Å and 3 Å molecular sieves for 72 h before use.

#### 2.2 Preparation of Compounds

 Table 1
 Provenance and mass

 fraction purity of solvents studied

Bu<sub>4</sub>NClO<sub>4</sub> and Bu<sub>4</sub>NBPh<sub>4</sub> were prepared by methods reported earlier [20, 21]. The purity of these compounds was confirmed by determining their melting points, (Bu<sub>4</sub>NClO<sub>4</sub>, 211 °C and Bu<sub>4</sub>NBPh<sub>4</sub>, 225 °C) which agree well with the literature values [22]. Alkylammonium perchlorates (RNH<sub>3</sub>ClO<sub>4</sub>) were prepared by reacting silver perchlorate monohydrate (AgClO<sub>4</sub>·H<sub>2</sub>O) with monoalkylammonium chloride (*n*-alkylamine hydrochloride) (RNH<sub>3</sub>Cl where R = methyl, ethyl, propyl, butyl, hexyl and octyl) (TCI Chemicals) dissolved in aqueous acetone mixtures in 1:1 molar ratio. Silver chloride (AgCl) precipitated out, was filtered and the filtrate was concentrated by evaporation, again filtered and heated untill the salt separated out. The salts so obtained was collected, recrystallised twice from anhydrous acetone and dried at 60 °C under vacuum for 3 days. Characterization of the monoalkylammonium perchlorates was done by elemental analysis (C, H, N and O) using a Thermo Finnigan Flash EA 1112 Series CHNS–O Analyzer. The perchlorate content in these compounds was calculated by gravimetric analysis which relies on the insolubility of potassium perchlorate in absolute ethanol [23] (Table 3).

Chemical name	Source	Mass frac- tion purity	Water content
Acetonitrile	E.Merck	0.999ª	0.00030 <sup>b</sup>
N,N-Dimethylacetamide	E.Merck	0.999 <sup>a</sup>	$0.00009^{b}$
Acetone	E.Merck	0.999 <sup>a</sup>	0.00021 <sup>b</sup>

<sup>a</sup>Gas chromatography analysis

<sup>b</sup>Karl fischer titration method

mol of DMA	7 000			200 V			210 V			270 V		
	Z 90 N			VI ONC			V 010			V 07C		
	θ	п	$K_{S}$	θ	п	$K_S$	β	п	$K_S$	θ	п	$K_S$
0	0.777204 $0.776850^{a}$	1279.42 $1280.80^{a}$	78.60 78.73 <sup>b</sup>	0.767188 $0.765650^{\circ}$	1242.27	84.46	0.755873 0.754632°	1198.58	92.09	0.744727 $0.743466^{\circ}$	1158.77	100
20	0.828108 $0.815210^{d}$	1321.46 1324.7 <sup>d</sup>	69.15	0.818923	1283.19	74.16	0.808512	1243.51	79.99	0.797980	1203.86	86.47
40	0.868157 $0.85108^{d}$	1365.73 1367.5 <sup>d</sup>	61.75	0.854309	1322.64	66.91	0.844257	1282.96	71.96	0.834112	1243.63	77.52
60	0.894415 $0.88582^{d}$	1399.47 1403.7 <sup>d</sup>	57.09	0.889469	1366.19	60.23	0.879686	1326.59	64.59	0.869849	1287.68	69.33
80	0.919190.0.91631 <sup>d</sup>	1433.33 $1433.4^{\rm d}$	52.95	0.911718	1400.96	55.88	0.902245	1362.16	59.73	0.892707	1323.12	63.98
100	0.937067 0.936232°	1459.55 1457.40 <sup>e</sup>	50.09	0.928211 $0.926996^{\circ}$	1419.32 1417.5 <sup>e</sup>	53.48	0.919720 $0.917736^{\circ}$	1380.51 1378.20 <sup>e</sup>	57.05	0.909892 $0.908435^{\circ}$	1349.12 $1339.20^{e}$	60.27
<sup>a</sup> Ref. [15]												
<sup>b</sup> Ref. [16]												
<sup>c</sup> Ref. [17]												
<sup>d</sup> Ref. [18]												
<sup>e</sup> Ref. [19]												

Salts	MeNH <sub>3</sub> ClO <sub>4</sub>	EtNH <sub>3</sub> ClO <sub>4</sub>	PrNH <sub>3</sub> ClO <sub>4</sub>	BuNH <sub>3</sub> ClO <sub>4</sub>	HxNH <sub>3</sub> ClO <sub>4</sub>	OcNH <sub>3</sub> ClO <sub>4</sub>
С						
Found (%)	9.372%	16.022%	21.347%	26.477%	35.101%	42.006%
Theoretical (%)	9.125%	16.495%	22.570%	27.665%	35.732%	41.830%
Н						
Found (%)	4.841%	5.032%	6.610%	7.133%	7.912%	8.421%
Theoretical (%)	4.599%	5.542%	6.319%	6.971%	8.003%	8.784%
Ν						
Found (%)	11.111%	9.412%	8.449%	7.816%	6.116%	6.691%
Theoretical (%)	10.646%	9.622%	8.777%	8.069%	6.948%	6.100%
0						
Found (%)	47.606%	42.101%	39.608%	37.608%	31.009%	28.002%
Theoretical (%)	48.666%	43.984%	40.123%	36.885%	31.759%	27.885%
$ClO_4^-$						
Found (%)	75.53%	68.19%	62.09%	56.94%	50.47%	43.01%
Theoretical (%)	75.66%	68.38%	62.38%	57.34%	49.37%	43.35%

Table 3 Elemental analysis data of alkylammonium perchlorates (RNH<sub>3</sub>ClO<sub>4</sub>) and their perchlorate content

## 2.3 Measurements

A vibrating U-tube Anton Paar digital Density and Sound velocity meter (Model DSA 5000M) with inbuilt Peltier-type thermostating unit for maintaining constant temperature was used for measuring densities and ultrasonic velocities of the pure solvents and electrolyte solutions. The frequency at which ultrasonic velocities were measured was 3 MHz. The uncertainty of the density and ultrasonic velocity was  $\pm 5 \times 10^{-3}$  kg·m<sup>-3</sup> and  $\pm 0.5$  m·s<sup>-1</sup>, respectively. The experiments were carried out at 298, 308, 318 and 328 K with an accuracy of  $\pm 0.01$  K. For the calibration of the instrument, triply distilled water and dry air at atmospheric pressure (0.1 MPa) were used (as given in the apparatus manual). The reliabilities of density and sound velocity measurements were ascertained by comparing the experimental data of pure solvents, AN and DMA with literature values (Table 2). Working solutions were prepared by diluting stock solutions of appropriate concentrations. Stock solutions were prepared by mass, weighed using an ACZET-602CY balance with precision of 0.1 mg. To avoid absorption of atmospheric moisture, the solutions were kept in air tight stoppered glass bottles. The probable error in molality was found to be less than  $\pm 1 \times 10^{-4}$  mol·kg<sup>-1</sup>.

# 3 Results and Discussion

#### 3.1 Compressibility Studies

Ultrasonic velocities (*u*) and densities ( $\rho$ ) of MeNH<sub>3</sub>ClO<sub>4</sub>, EtNH<sub>3</sub>ClO<sub>4</sub>, PrNH<sub>3</sub>ClO<sub>4</sub>, BuNH<sub>3</sub>ClO<sub>4</sub>, HxNH<sub>3</sub>ClO<sub>4</sub>, OcNH<sub>3</sub>ClO<sub>4</sub>, Bu<sub>4</sub>NClO<sub>4</sub> and Bu<sub>4</sub>NBPh<sub>4</sub> were measured in the concentration range 0.03–0.28 mol·kg<sup>-1</sup> in AN + DMA solvent mixtures containing 0, 20, 40, 60, 80 and 100 mol% of DMA at 298, 308, 318 and 328 K. From plots of ultrasonic velocity (*u*) versus molal concentration (*m*) for MeNH<sub>3</sub>ClO<sub>4</sub> at different temperatures (Fig. 1), it is observed that sound velocity increases linearly with increasing concentration of electrolyte solution. This may be attributed to the greater association of the molecules due to electrostatic bonding between solute and solvent molecules or to the presence of effective solute–solvent interactions. Also, the sound velocity was found to decrease with increasing temperature (Fig. 1). A perusal of Fig. 2 shows that, at constant temperature, the density values increase with increasing concentration of salt in each of the binary systems, at the experimental temperatures. As expected, the density values decrease with increasing temperature (typical plots of variation of density with concentration are shown in Fig. 2). Possible explanation for increase in the values of density with increase in concentration would be the effect of replacing molecules of solvent containing atoms that are on



**Fig. 1** Plots of ultrasonic velocity (*u*) against molal concentration (*m*) of  $MeNH_3ClO_4$  in binary mixtures of AN + DMA containing 0, 20, 40, 60, 80 and 100 mol% of DMA at 298, 308, 318 and 328 K. Filled rhombus, 298 K; filled square, 308 K; filled triangle, 318 K; cross, 328 K



**Fig.2** Plots of density ( $\rho$ ) against molal concentration (*m*) of MeNH<sub>3</sub>ClO<sub>4</sub> in binary mixtures of AN + DMA containing 0, 20, 40, 60, 80 and 100 mol% of DMA at 298, 308, 318 and 328 K. Filled rhombus, 298 K; filled square, 308 K; filled triangle, 318 K; cross, 328 K

average lighter than the atoms in the solutes by the solute molecules. Exactly same trends of ultrasonic velocity (*u*) against molality (*m*) and density ( $\rho$ ) against molality (*m*) plots are obtained for EtNH<sub>3</sub>ClO<sub>4</sub>, PrNH<sub>3</sub>ClO<sub>4</sub>, BuNH<sub>3</sub>ClO<sub>4</sub>, HxNH<sub>3</sub>ClO<sub>4</sub> and OcNH<sub>3</sub>ClO<sub>4</sub>.

The isentropic compressibility ( $K_S$ ) of electrolytes in pure AN, pure DMA and their binary mixtures were calculated from the experimental values of ultrasonic velocities and densities ( $\rho$ ) using Eq. 1

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

The  $K_S$  values of pure AN, pure DMA and their binary mixtures at 298, 308, 318 and 328 K are reported in Table 1. The plots of  $K_S$  against molal concentration (*m*) for MeNH<sub>3</sub>ClO<sub>4</sub> in pure solvents and in all binary mixtures of solvents at different temperatures are presented in Fig. 3. From these plots, it can be seen that the  $K_S$  values decrease linearly with increasing salt concentration at all studied temperatures, indicating increasing structural effects in the solutions due to the influence of the solute on surrounding solvent



**Fig. 3** Plots of isentropic compressibility ( $K_s$ ) against molal concentration (*m*) of MeNH<sub>3</sub>ClO<sub>4</sub> in binary mixtures of AN + DMA containing 0, 20, 40, 60, 80 and 100 mol% of DMA at 298, 308, 318 and 328 K. Filled rhombus, 298 K; filled square, 308 K; filled triangle, 318 K; cross, 328 K

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molecules or, perhaps, due to the greater intrinsic  $K_S$  values of the solute compared to the solvent [24]. Also, it is observed (Fig. 3) that  $K_S$  increases with increasing temperature. Exactly the same behavior of variation of  $K_S$  with salt concentration was observed for the other alkylammonium perchlorates (EtNH<sub>3</sub>ClO<sub>4</sub>, PrNH<sub>3</sub>ClO<sub>4</sub>, BuNH<sub>3</sub>ClO<sub>4</sub>, HxNH<sub>3</sub>ClO<sub>4</sub> and OcNH<sub>3</sub>ClO<sub>4</sub>) at all studied temperatures.

Apparent molal volumes  $(V_{\phi})$  and apparent molal isentropic compressibilities  $(K_{S,\phi})$  for all the electrolytes have been calculated using Eqs. 2 and 3

$$V_{\phi} = \frac{M}{\rho} - \frac{10^3 \left(\rho - \rho_{\rm o}\right)}{m \rho \rho_{\rm o}} \tag{2}$$

$$K_{S,\phi} = V_{\phi}K_{S} + \frac{10^{3}(K_{S} - K_{S,o})}{m\rho_{o}}$$
(3)

where *m* is molality of the solution, *M* is the molecular weight of solute,  $K_S$ ,  $K_{S,o}$  are isentropic compressibilities of solution and that of pure solvent,  $\rho$  and  $\rho_o$  are the densities of solution and pure solvent, respectively.

To evaluate the limiting apparent molal isentropic compressibilities  $(K_{S,\phi}^{o})$  of various electrolytes, extrapolation of linear plots of  $K_{S,\phi}$  against  $m^{1/2}$  was made and  $K_{S,\phi}^{o}$  values were obtained by the least squares treatment using equation

$$K_{S,\phi} = K_{S,\phi}^{o} + A_{S,\phi}\sqrt{m}$$
<sup>(4)</sup>

The  $K_{S,\phi}^{o}$  values for all the salts studied at different temperatures are reported in Table 4. These values for MeNH<sub>3</sub>ClO<sub>4</sub>, EtNH<sub>3</sub>ClO<sub>4</sub>, PrNH<sub>3</sub>ClO<sub>4</sub>, BuNH<sub>3</sub>ClO<sub>4</sub>, HxNH<sub>3</sub>ClO<sub>4</sub>, OcNH<sub>3</sub>ClO<sub>4</sub> are not available in AN + DMA solvent mixtures; therefore, a comparison of these values could not be made. There are two factors which contribute to  $K_{S,\phi,\pm}^{o}$ : (a) the positive effect of larger solute molecules, which can have some intrinsic compressibility due to which intermolecular free space is created making the solution more compressible and (b) the negative effect from the insertion of solvent molecules into the intra-solute free space, which results in the interactions of solute molecules with neighboring solvent molecules [24]. Lower  $K_{S,\phi}^{o}$  values in the AN rich region of AN + DMA binary mixtures (Table 4) specially in the case of MeNH<sub>3</sub>ClO<sub>4</sub>, EtNH<sub>3</sub>ClO<sub>4</sub>, PrNH<sub>3</sub>ClO<sub>4</sub> and BuNH<sub>3</sub>ClO<sub>4</sub> may be attributed to the predominance of the negative effect over the positive effect due to which solvent surrounding solute offers greater resistance to compression than the bulk solvent.

## 3.2 Evaluation of Limiting Ionic Apparent Molal Isentropic Compressibilities $(K_{s,d}^{o})_{\pm}$

To gain better insight of the tendency of each ion to produce solvation or structural effects, the  $K_{S,\phi,\pm}^{o}$  values of various salts, including the reference electrolytes Bu<sub>4</sub>NClO<sub>4</sub> and Bu<sub>4</sub>NBPh<sub>4</sub>, have been split into individual ion contribution,  $K_{S,\phi,\pm}^{o}$ . As reported earlier [22]  $K_{S,\phi}^{o}$  values are additive, so they can be directly split into the contribution of individual ions to obtain structural effects. Milero had used Bu<sub>4</sub>AsBPh<sub>4</sub> as the reference electrolyte [25] for splitting the partial molar volume of electrolytes into individual ion contribution. A similar model in which the use of Bu<sub>4</sub>NBPh<sub>4</sub> as reference electrolytes to evaluate limiting ionic apparent molal isentropic compressibility was suggested by Gill and coworkers [26].

Table 4 Limiting	g apparent molal ise	entropic compressib	ility $10^4 \times K_{S,\phi}^0/\text{cm}^3 \cdot \text{m}$	ol <sup>-1</sup> ·bar <sup>-1</sup> of some s	alts in solvent mixtu	ires of AN+DMA at	different temperature	S
mol % DMA	$Bu_4NCIO_4$	${\rm Bu}_4{\rm NBPh}_4$	MeNH <sub>3</sub> ClO <sub>4</sub>	EtNH <sub>3</sub> CIO <sub>4</sub>	PrNH <sub>3</sub> CIO <sub>4</sub>	$BuNH_3CIO_4$	HxNH <sub>3</sub> CIO <sub>4</sub>	OcNH <sub>3</sub> CIO <sub>4</sub>
298 K								
0	22.4 22.4	106.5	14.4	27	47	56	100.8	104.4
20	36.4	(141 ± 24)	ر د	16	18	22	30	35.2
40	45.9	161	-55.5	-44.5	- 28	-23	24.9	28.2
60	57.6	184	6.6	37.6	38.1	60.2	64	73.5
80	75.7	222	11	47	54	99	71	89.5
100	90.2 91.1 <sup>b</sup>	245.3 245.3 <sup>b</sup>	20	59.2	64.9	79.6	109	112.2
308 K								
0	33.1	127.6	16.9	30.5	52	72	113	144.9
20	55.2	181.6	8	21	25	27	33	38.6
40	65.8	203.3	-32	-20.5	- 19	- 11	30.1	34
60	77.3	225.3	28.5	39	48.5	73.7	95.1	115.4
80	95.8	263.2	48	59	68.5	76	108.9	124
100	113.9	297.3	57	63	72.6	82	129.9	151.9
318 K								
0	44	147.8	21.3	34	57	86	126	177
20	73.3	220.6	11	25	30	32	36	48
40	84.9	244.9	- 18	-10.5	-8	-3	32	39
60	95.6	264.3	37.6	45.8	58	78	66	120.6
80	114.2	303.4	57	64	71.6	85	115.5	147.3
100	132.8	338	64	71	75.4	06	133.3	185
328 K								
0	54.3	169.2	23.8	36	73	91.4	152	212
20	93.2	262.3	16	27	35	38	41	53.5
40	103.9	285.3	-8	-3.7	- 1	4	37	41

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Table 4 (continue	ed)							
mol % DMA	$Bu_4NCIO_4$	$\mathrm{Bu}_4\mathrm{NBPh}_4$	MeNH <sub>3</sub> ClO <sub>4</sub>	EtNH <sub>3</sub> CIO <sub>4</sub>	PrNH <sub>3</sub> ClO <sub>4</sub>	BuNH <sub>3</sub> ClO <sub>4</sub>	HxNH <sub>3</sub> CIO <sub>4</sub>	OcNH <sub>3</sub> CIO <sub>4</sub>
60	113.3	303.2	46.2	50.8	63	89.7	110.9	131.4
80	134	346.3	65	69	79.5	93	135.2	177.3
100	153.4	383	73	75	84.5	97.6	161	218
Maximum uncert	ainity in these value	es is $\pm 2.4 \times 10^{-4}$ cm	<sup>3</sup> .mol <sup>-1</sup> .bar <sup>-1</sup>					
<sup>a</sup> Ref. [15]								
<sup>s</sup> Ref. [18]								

This model has been used in the present work, which uses following equations to split  $K_{S,\phi}^{o}$  values into its ionic contributions.

$$\frac{K_{S,\phi}^{o}(\mathrm{Bu}_{4}\mathrm{N}^{+})}{K_{S,\phi}^{o}(\mathrm{Ph}_{4}\mathrm{B}^{-})} = \frac{r_{c}^{3}(\mathrm{Bu}_{4}\mathrm{N}^{+})}{r_{c}^{3}(\mathrm{Ph}_{4}\mathrm{B}^{-})} = \frac{5.00^{3}}{5.35^{3}}$$
(5)

$$K^{\mathrm{o}}_{S,\phi}(\mathrm{Bu}_{4}\mathrm{NBPh}_{4}) = K^{\mathrm{o}}_{S,\phi}(\mathrm{Bu}_{4}\mathrm{N}^{+}) + K^{\mathrm{o}}_{S,\phi}(\mathrm{Ph}_{4}\mathrm{B}^{-})$$
(6)

where  $r_c$  represents the crystallographic radius of the ion. Using Eqs. 4 and 5, firstly,  $K_{S,\phi}^{o}$  values of Bu<sub>4</sub>NBPh<sub>4</sub> were split into the ionic contribution for Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> ions and then  $K_{S,\phi,\pm}^{o}$  values of Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> were further used to calculate  $K_{S,\phi,\pm}^{o}$  values for RNH<sup>+</sup><sub>3</sub> ions (Table 5) on the basis of the additive principle. A perusal of Table 5 shows that  $Bu_4N^+$  and  $Ph_4B^-$  have positive values of  $K^o_{S, \psi, \pm}$  throughout the whole composition range. This may be attributed to some special type of ion-solvent interactions, which may be due to solvophobic, dispersive or solvent-solvent interactions. Also, these special interactions of  $Bu_4N^+$  and  $Ph_4B^-$  with AN and DMA were reported by Gill and Rana [18] and for Ph<sub>4</sub>B<sup>-</sup> with AN were reported by Bose and Kundu from conductance measurements [27].  $ClO_4^-$  has negative  $K_{S,\phi,\pm}^{o}$  values throughout the whole composition range indicating that the  $ClO_4^-$  ion shows better solvation in AN + DMA mixtures. It can be seen from Table 5 that, there is an increase in  $K_{S,\phi,\pm}^{o}$  values for RNH<sup>+</sup><sub>3</sub> ions with increase in temperature and with increases in the alkyl chain length. Negative or lower  $K_{S,\phi,\pm}^{o}$  values may be attributed to the smaller size of the ion or due to the predominance of the penetration of solvent molecules into the intra ionic free space of the solute, over the effect of their solvent intrinsic compressibility or due to electrostriction as a result of which, the solvent molecules are directed by the electrostatic field of the solute molecules in the primary solvation shell and solvent molecules become more compressed leading to decrease in  $K_{S,\phi,\pm}^{\circ}$  values. Also, at temperatures 308, 318 and 328 K, the  $K_{S,\phi,\pm}^{\circ}$  values for all the RNH<sup>3</sup> ions are large and positive throughout the whole composition range except at 40 mol% DMA in AN + DMA binary mixtures, showing weak solvation of these ions at higher temperatures (308, 318 and 328 K).

The variation of  $K_{S,\phi,\pm}^{o}$  for RNH<sup>+</sup><sub>3</sub> ions with change in solvent composition shows interesting behavior. A perusal of Table 5 shows that for RNH<sup>+</sup><sub>3</sub> ions the  $K_{S,\phi,\pm}^{o}$  values decrease with increasing DMA composition up to 40 mol% DMA and beyond this solvent composition,  $K_{S,\phi,\pm}^{o}$  values start increasing again, passing through a minimum (Fig. 4) showing preferential solvation of  $RNH_3^+$  ions by DMA in the AN rich region and by AN in the DMA rich region of AN + DMA solvent mixtures. The non-linear behavior of  $K^{o}_{S,\phi,\pm}$  with solvent composition has been attributed to the existence of solute-solvent and solvent-solvent interactions, which are maximized at about 40 mol% of DMA in AN + DMA mixtures. This can be hypothesized to be due to the fact that for 20 mol% of DMA in AN + DMA binary mixtures, the first solvation shell of RNH<sup>+</sup><sub>3</sub> ions, which is formed when AN molecules in pure AN are partially replaced by larger DMA molecules with higher donicities (definite solvent coordination occurs with solvents having large donicities); with increasing mol% composition of DMA the first solvation shell is significantly enriched with DMA and up to 40 mol% DMA, the first solvation shell is formed exclusively by DMA molecules and at this composition maximum interactions between AN and DMA solvent molecules take place. Above this composition the solvation shell further incorporates AN molecules leading to a decrease in ion-solvent and solvent-solvent interactions and increasing the values of

10 014	DI D-	D )1+	C10-		<b>F</b> 3 474	D+	5	** >***	0 ) W
mol % DMA	Ph <sub>4</sub> B	Bu <sub>4</sub> N'	CIO <sub>4</sub>	$MeNH_3^+$	EtNH <sub>3</sub>	PrNH <sub>3</sub> <sup>+</sup>	BuNH <sub>3</sub> <sup>+</sup>	$HxNH_3^+$	OcNH <sub>3</sub>
298 K									
0	58.6 59.1ª	47.8 48.3 <sup>a</sup>	-25.4 $-25.5^{a}$	39.8	52.4	72.4	81.4	126.2	129.8
20	77.6	63.4 63.7ª	-27	32	43	38.6	42.6	50.6	55.8
40	88.7	72.3 73.4 <sup>a</sup>	-26.4	-29.1	- 18.1	- 1.6	3.4	35.7	39
60	101.3	82.7	-25.1	31.7	62.7	63.2	85.3	89.1	98.6
80	122.2	99.8	-24.1	35.1	71.1	78.1	90.1	95.1	113.6
100	135 135.1 <sup>a</sup>	110.3 110.2 <sup>a</sup>	-20.1	40.1	80.3	85	99.7	129.1	132.3
308 K									
0	70.3	57.3	-24.2	41.1	4.7	76.2	96.2	137.2	169.1
20	100	81.6	-26.4	34.4	47.4	51.4	53.4	59.4	65
40	111.9	91.4	-25.6	-6.4	5.1	6.6	14.6	55.7	59.6
60	124	101.3	-24	52.5	63.2	72.5	97.7	119.1	139.4
80	144.9	118.3	-22.5	70.5	81.5	91	98.5	131.4	146.5
100	163.7	133.6	- 19.7	76.7	82.7	92.3	101.7	149.6	171.6
318 K									
0	81.4	66.4	-22.4	43.7	56.4	79.4	108.4	148.4	199.4
20	121.5	99.1	-25.8	36.8	50.8	55.8	57.8	61.8	73.8
40	134.9	110	-25.1	7.1	14.6	17.1	22.1	57.1	64.1
60	145.5	118.8	-23.2	60.8	69	81.2	101.2	122.2	143.8
80	167.1	136.3	-22.1	79.1	86.1	93.7	107.1	137.6	169.4
100	186.1	151.9	- 19.1	83.1	90.1	94.5	109.1	152.4	204.1
328 K									
0	93.2	76	-21.7	45.5	57.7	94.7	113.1	173.7	233.7
20	144.4	117.9	-24.7	40.7	51.7	59.7	62.7	65.7	78.2
40	157.1	128.2	-24.3	16.3	20.6	23.3	28.3	61.3	65.3
60	166.9	136.3	-23	69.2	73.8	86	112.7	133.9	154.4
80	190.7	155.6	-21.6	86.6	90.6	101.1	114.6	156.8	198.9
100	210.9	172.1	-18.7	91.7	93.7	103.2	116.3	179.7	236.7

**Table 5** Limiting ionic apparent molal isentropic compressibility  $10^4 \times K^{o}_{S,\phi,\pm}/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$  of some ions in AN + DMA solvent mixtures at different temperatures

Maximum uncertainity in these values is  $\pm 2.7 \times 10^{-4} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$ 

<sup>a</sup>Ref. [27]

 $K_{S,\phi,\pm}^{o}$ . These results are similar to those found by Gill and coworkers in AN + DMA mixtures using conductance measurements [28] and by Gill and Cheema in AN + DMF mixtures using conductance and viscosity measurements [29]. So in accordance with our  $K_{S,\phi,\pm}^{o}$  data collected for RNH<sup>+</sup><sub>3</sub> ions, notable changes in RNH<sup>+</sup><sub>3</sub> solvation have been produced at 40 mol% DMA in AN and DMA solvent mixtures.



**Fig. 4** Limiting ionic apparent molal isentropic compressibility  $K^{\circ}_{S,\phi,\pm}$  versus mol% of DMA for alkylammonium ions (RNH<sup>4</sup><sub>3</sub>) in AN + DMA mixtures at 298, 308, 318 and 328 K. Filled rhombus, 298 K; filled square, 308 K; filled triangle, 318 K; cross, 328 K

## 4 Conclusion

Monoalkylammonium ions (RNH<sub>3</sub><sup>+</sup>) do not appear to interact strongly with pure DMA and AN. Negative  $K_{S,\phi,\pm}^{o}$  values at 298 K for MeNH<sub>3</sub><sup>+</sup>, EtNH<sub>3</sub><sup>+</sup>, PrNH<sub>3</sub><sup>+</sup> ions and at 308 K for the MeNH<sub>3</sub><sup>+</sup> ion at 40 mol% DMA in AN + DMA binary mixtures indicate structural effects arising due to solute–solvent and solvent–solvent interactions. The extent of ion–solvent interactions for RNH<sub>3</sub><sup>+</sup> ions at all studied temperatures decreases in the order;

MeNH<sub>3</sub><sup>+</sup>>EtNH<sub>3</sub><sup>+</sup>>PrNH<sub>3</sub><sup>+</sup>>BuNH<sub>3</sub><sup>+</sup>>HxNH<sub>3</sub><sup>+</sup>>OcNH<sub>3</sub><sup>+</sup>. The non-linear variation of  $K_{S,\phi,\pm}^{o}$  values of RNH<sub>3</sub><sup>+</sup> ions with solvent composition shows preferential solvation of these ions by DMA in the AN rich region and by AN in the DMA rich region. Positive  $K_{S,\phi,\pm}^{o}$  values of Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> show some special type of solvophobic interactions in DMA and AN + DMA binary mixtures. Large positive values of HxNH<sub>3</sub><sup>+</sup> and OcNH<sub>3</sub><sup>+</sup> throughout the whole composition range except at 40 mol% DMA shows very weak solvation of these ions in AN + DMA mixtures, which may be due to their large size and small charge density. The ClO<sub>4</sub><sup>-</sup> ion, however, shows better solvation throughout the whole composition range and the extent of solvation is greater in the AN rich region of the AN + DMA mixtures. Also, the increase in  $K_{S,\phi,\pm}^{o}$  values of RNH<sub>3</sub><sup>+</sup> ions with increasing temperature indicates that the extent of solvation of these ions decreases with increasing temperature.

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