

Thermodynamics of Ion Association and Solvation in 2-Methoxyethanol: Behavior of Tetraphenylarsonium, Picrate, and Tetraphenylborate Ions from Conductivity and Ultrasonic Data

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Precise measurements on electrical conductances and ultrasonic velocities of solutions of potassium picrate (KPic), potassium tetraphenylborate (KBPh₄), tetrabutylammonium tetraphenylborate (Bu₄NBPh₄), and tetraphenylarsonium picrate (Ph₄AsPic) in 2-methoxyethanol (ME) at temperatures 288.15 ≤ *T*/K ≤ 308.15 have been reported. The conductance data have been analyzed by the 1978 Fuoss conductance–concentration equation. Thermodynamics of the association processes have also been studied and the Coulombic forces are found to play a major role in the association processes. The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity values of the “reference electrolyte” Bu₄NBPh₄. Strong association was found for all these salts in this solvent medium. The results strongly suggest the electrostriction of the solvent molecules around the potassium and picrate ions, while for the larger tetrabutylammonium and tetraphenylarsonium ions they are accommodated inside the space between the alkyl or aryl chains attached to the nitrogen or arsenic atom; for tetraphenylborate ion, however, neither electrostriction nor penetration of the solvent molecules is found to be important.

1. Introduction

2-Methoxyethanol (ME) is an amphoteric dipolar solvent of low dielectric constant (*D* = 16.94 at 298.15 K)¹ with large dipole moment (*μ* = 2.36 D).² But, unfortunately, it is hygroscopic, fairly toxic, a weak narcotic, and a systemic poison, and for these reasons, careful handling of this solvent is essential.³ ME could be considered as a moderate Lewis acid (*pK*_{autoprot} = 20.5 at 298.15 K),⁴ and is a probable solvent for anions through its hydrogen-bonding network and dipole-induced interactions. It has unique solvating properties associated with its “quasiaprotic” character and is widely used for electrochemical investigations and various industrial processes.^{5–7}

Even though ME has drawn much attention in recent years as a solvent for electroanalytical investigations,^{8,9} very few reliable studies on the electrolytic behavior in this nonaqueous medium have so far been made. Therefore, as a part of a series of investigations on the chemical nature of structure of ions on their mutual and specific interactions with solvent molecules,^{10–18} we have performed conductivity and ultrasonic velocity measurements on 2-methoxyethanol solutions of potassium picrate (KPic), potassium tetraphenylborate (KBPh₄), tetrabutylammonium tetraphenylborate (Bu₄NBPh₄), and tetraphenylarsonium picrate (Ph₄AsPic) as functions of temperature (288.15 ≤ *T*/K ≤ 308.15). The results have been interpreted in terms of specific constitutional and structural factors of the solvent molecules and of the solutes.

2. Experimental Section

2.1 Materials. 2-Methoxyethanol (ME, G. R.E Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction collected. The purified solvent had a density of 0.96002 g cm^{−3}, a coefficient of viscosity of 1.5414 mPa s, and a specific

TABLE 1: Physical Properties of 2-Methoxyethanol

<i>T</i> /K	<i>ρ</i> ₀ /g cm ^{−3}	<i>η</i> ₀ /mPa s	<i>D</i>
288.15	0.96960	1.9377	17.77
293.15	0.96490	1.7287	17.35
298.15	0.96002	1.5414	16.94
308.15	0.95356	1.2579	16.15

conductance of ca. 1.01 × 10^{−6} S cm^{−1} at 298.15 K. These values are in good agreement with the literature data.¹⁹ The solvent properties are recorded in Table 1.

Potassium picrate (KPic) was prepared²⁰ by neutralizing picric acid (A.R., BDH) with an equal molar amount of potassium hydroxide (A.R., BDH) in ethanol. The resulting potassium picrate, which precipitated, was recrystallized from water and dried in vacuo for 3–4 weeks.

Potassium tetraphenylborate (KBPh₄) was precipitated by mixing equimolar aqueous solutions of potassium nitrate (KNO₃) and sodium tetraphenylborate (NaBPh₄). The product was recrystallized from 30 mass % aqueous acetone and dried in vacuo for several weeks.

Tetraphenylarsonium picrate (Ph₄AsPic) was prepared by the metathesis between potassium picrate obtained as above and tetraphenylarsonium chloride (Ph₄AsCl) both dissolved in 50 mass % aqueous ethanol. The precipitate was washed with water, repeatedly crystallized from ethanol, and dried in vacuo for several weeks.

Tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) was prepared by mixing equimolar quantities of sodium tetraphenylborate and tetrabutylammonium bromide (Bu₄NBr) in water. The salt was dried in vacuo at 353.15 K for 48 h.

2.2. Apparatus and Procedures. Conductance measurements were carried out on a pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{−1} and having an accuracy of 0.1%. Measurements were made in an oil bath maintained within ± 0.005 K of the desired

TABLE 2: Molar Conductivities of Electrolytes in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

<i>T</i> = 288.15 K		<i>T</i> = 293.15 K		<i>T</i> = 298.15 K		<i>T</i> = 308.15 K	
<i>c</i> × 10 ⁴ mol dm ⁻³	Λ S cm ² mol ⁻¹	<i>c</i> × 10 ⁴ mol dm ⁻³	Λ S cm ² mol ⁻¹	<i>c</i> × 10 ⁴ mol dm ⁻³	Λ S cm ² mol ⁻¹	<i>c</i> × 10 ⁴ mol dm ⁻³	Λ S cm ² mol ⁻¹
KPic							
3.5164	27.41	4.0216	30.07	3.0172	33.67	3.0065	39.39
4.5456	26.80	5.5090	29.17	4.0230	32.93	4.0287	38.46
5.5748	26.26	6.2802	28.75	5.0287	32.22	5.0509	37.65
6.5182	25.82	6.9964	28.38	6.0344	31.59	6.0130	36.97
7.5474	25.37	7.7126	28.04	7.0402	31.02	7.0352	36.31
8.5766	24.96	8.5389	27.67	8.0459	30.47	7.9973	35.74
9.5200	24.62	9.0347	27.46	9.0516	29.98	9.0195	35.19
10.5492	24.26	10.0263	27.06	10.0574	29.51	10.0417	34.67
11.5784	23.93	11.0180	26.68	11.0631	29.04	11.0037	34.21
		12.0096	26.33	12.0689	28.67	11.9057	33.81
KBPh ₄							
3.0274	22.05	2.9546	23.94	3.4658	25.65	3.0584	31.80
4.0365	21.55	3.9774	23.42	5.0412	24.91	4.1704	31.12
5.0456	21.11	5.0002	22.97	6.0495	24.51	5.0111	30.66
6.0547	20.73	6.0231	22.56	7.0971	24.13	6.0443	30.16
7.0639	20.37	7.0459	22.19	8.0030	23.82	7.0258	29.73
8.0057	20.07	8.0119	21.88	9.0112	23.51	8.0070	29.33
9.0148	19.77	9.0347	21.56	10.0195	23.21	9.0620	28.93
10.0240	19.49	10.0007	21.29	11.0277	22.94	10.0221	28.59
11.0331	19.23	11.0234	21.01	12.0186	22.76	11.0392	28.25
12.0422	18.99	12.0458	20.78			11.5804	27.98
Bu ₄ NBPh ₄							
3.2400	18.99	3.3104	21.11	5.6183	22.42	4.1616	27.70
4.0621	18.58	4.0460	20.75	6.6039	22.02	5.0176	27.33
5.0242	18.16	5.5174	20.07	7.5896	21.65	6.0516	26.78
5.9863	17.79	7.0623	19.47	8.5753	21.32	7.0421	26.31
7.0018	17.43	8.0187	19.14	9.5609	21.00	8.0571	25.87
8.0173	17.10	9.1957	18.76	10.5466	20.71	8.9453	25.51
8.9794	16.82	10.0785	18.50	11.5323	20.44	10.0238	25.11
9.9950	16.54	11.0348	18.24	12.5179	20.18	11.0389	24.76
11.0639	16.30	11.8441	18.03	13.5036	19.94	12.0540	24.42
Ph ₄ AsPic							
2.9869	23.59	2.9801	26.30	2.9909	29.29	4.0011	32.54
4.0025	23.00	4.0286	25.58	3.4992	28.94	4.9425	31.87
5.0181	22.48	5.0220	24.99	4.7198	28.09	5.8839	31.24
5.9739	22.04	6.0153	24.46	5.9818	27.33	6.8842	30.65
6.9894	21.62	7.0087	23.99	7.0150	26.79	7.8256	30.13
8.0050	21.24	8.0021	23.55	7.9938	26.31	8.8259	29.63
8.9906	20.90	8.9954	23.16	9.0271	25.86	9.8262	29.16
9.9764	20.58	10.0440	22.77	10.0059	25.45	10.7676	28.75
10.9913	20.27	10.9821	22.54	11.0391	25.05	11.5325	28.43
11.5296	20.20						

temperature. The details of the experimental procedure have been described earlier.^{10,21} Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald–Sprenkel type pycnometer of about 25 mL capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent at all temperatures.

Sound velocities were measured using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 4 MHz, which was calibrated with water, methanol, and benzene at each temperature. The temperature stability was maintained within ±0.01 K by circulating thermostated water around the cell by a circulating pump.

The dielectric constants of 2-methoxyethanol at different temperatures were taken from the literature.¹

3. Results

3.1. Conductance. The measured molar conductances (Λ) of electrolyte solutions as a function of molar concentration (*c*) at 288.15, 293.15, 298.15, and 308.15 K are given in Table 2.

The conductance data have been analyzed by the 1978 Fuoss conductance–concentration equation.^{22,23} For a given set of conductivity values (*c_j*, Λ_{*j*}; *j* = 1, ..., *n*), three adjustable parameters, the limiting molar conductivity (Λ°), association constant (*K_A*), and the cosphere diameter (*R*), are derived from the following set of equations:

$$\Lambda = p[\Lambda^0(1 + R_X) + E_L] \quad (1)$$

$$p = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta k/2(1 + kR) \quad (4)$$

$$\beta = e^2/Dk_B T \quad (5)$$

$$K_A = K_R/(1 - \alpha) = K_R(1 + K_S) \quad (6)$$

where *R_X* is the relaxation field effect, *E_L* is the electrophoretic countercurrent, *k*⁻¹ is the radius of the ion atmosphere, *D* is the dielectric constant of the solvent, *e* is the electron charge, *k_B* is the Boltzmann constant, *γ* is the fraction of solute present

TABLE 3: Conductance Parameters of Electrolytes in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

electrolyte	<i>T</i> /K	$\Lambda^\circ/S \text{ cm}^2 \text{ mol}^{-1}$	$K_A/\text{dm}^3 \text{ mol}^{-1}$	$R/\text{\AA}$	$\sigma\%$
KPic	288.15	31.80 ± 0.04	347 ± 5	10.00	0.07
	293.15	35.54 ± 0.05	373 ± 5	10.01	0.07
	298.15	38.94 ± 0.12	381 ± 11	10.02	0.18
	308.15	45.29 ± 0.07	347 ± 5	10.03	0.09
KBPh ₄	288.15	25.20 ± 0.03	308 ± 4	10.60	0.07
	293.15	27.23 ± 0.03	275 ± 5	10.60	0.08
	298.15	29.37 ± 0.04	237 ± 4	10.61	0.07
	308.15	36.17 ± 0.08	240 ± 7	10.62	0.15
Bu ₄ NBPh ₄	288.15	22.32 ± 0.02	430 ± 4	14.20	0.05
	293.15	24.82 ± 0.04	410 ± 6	14.21	0.10
	298.15	27.57 ± 0.03	371 ± 3	14.22	0.04
	308.15	33.03 ± 0.11	354 ± 11	14.23	0.15
Ph ₄ AsPic	288.15	27.24 ± 0.04	395 ± 5	12.87	0.09
	293.15	30.51 ± 0.04	426 ± 5	12.88	0.08
	298.15	34.05 ± 0.06	426 ± 7	12.89	0.11
	308.15	38.93 ± 0.06	421 ± 6	12.89	0.07

as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ° values for the iteration procedure were obtained from Shedlovsky extrapolation²⁴ of the data. Input for the program is the set (c_j , Λ_j ; $j = 1, \dots, n$), n , D , η , T , initial value of Λ° , and an instruction to cover a preselected range of R values.

In practice, calculations are made by finding the values of Λ° and α which minimize the standard deviation, σ ,

$$\sigma^2 = \sum [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2 / (n - 2) \quad (7)$$

for a sequence of R values and then plotting σ against R ; the best-fit R corresponds to the minimum in σ vs R curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the σ (%) vs R curves, the R value was assumed to be $R = a + d$, where a is the sum of the ionic crystallographic radii and d is given by²³

$$d = 1.183(M/\rho_0)^{1/3} \quad (8)$$

where M is the molecular weight of the solvent and ρ_0 is its density.

The values of Λ° , K_A , and R obtained by this procedure are reported in Table 3.

3.2. Compressibility. Adiabatic compressibility coefficients (β) were derived from the relation

$$\beta = 1/u^2 \rho \quad (9)$$

where ρ is the solution density and u is the sound velocity in the solution.

The apparent molar adiabatic compressibility (ϕ_K) of liquid solutions was calculated from the relation

$$\phi_K = \frac{1000}{m\rho\rho_0}(\beta\rho_0 - \beta_0\rho) + \beta\frac{M}{\rho_0} \quad (10)$$

where m is the molality of the solution and the other symbols have their usual significance.

The molar concentration (c), density (ρ), and the adiabatic compressibility coefficient (β) of the solutions of KPic, KBPh₄, and Ph₄AsPic at 298.15 K are given in Table 4.

The limiting apparent molar adiabatic compressibilities (ϕ_K°) were obtained²⁵ by extrapolating the plots of ϕ_K versus

TABLE 4: Ultrasonic Velocities and Adiabatic Compressibilities of Electrolytes in 2-Methoxyethanol at 298.15 K

c mol dm ⁻³	u cm s ⁻¹	$\beta \times 10^{12}$ cm ² dyn ⁻¹	c mol dm ⁻³	u cm s ⁻¹	$\beta \times 10^{12}$ cm ² dyn ⁻¹
KPic					
0.03536	135385	56.437	0.09862	135827	55.556
0.04732	135478	56.261	0.12601	135988	55.206
0.05928	135567	56.089	0.15340	136135	54.870
0.07124	135650	55.923			
KBPh ₄					
0.01010	135002	56.905	0.03510	135405	56.361
0.02516	135257	56.567	0.04503	135537	56.166
0.03013	135333	56.463	0.04967	135612	56.072
Ph ₄ AsPic					
0.00501	135431	56.658	0.02045	136354	55.702
0.00835	135651	56.432	0.02588	136626	55.415
0.01169	135859	56.217	0.03131	136884	55.143
0.01503	136052	56.015			

TABLE 5: Coefficients of the Polynomial, Eq 12

electrolyte	a_0	a_1	a_2	$\sigma\%$
KPic	38.97	-0.6735	0.04209	0.054
KBPh ₄	29.49	-0.5459	0.01196	0.217
Bu ₄ NBPh ₄	27.53	-0.5369	0.00141	0.075
Ph ₄ AsPic	33.89	-0.5900	0.00828	0.287

the square root of molal concentration of the solute to zero concentration:

$$\phi_K = \phi_K^\circ + S_K m^{1/2} \quad (11)$$

where S_K is the experimental slope.

4. Discussion

4.1. Limiting Molar Conductance and Association Constant. Table 3 shows that for all salts the limiting molar conductances (Λ°) increase as the temperature increases. The Λ° values were fitted to the following polynomial:

$$\Lambda^\circ = a_0 + a_1(298.15 - T) + a_2(298.15 - T)^2 \quad (12)$$

and the coefficients of these fits are given in Table 5 together with the standard percentage errors ($\sigma\%$).

The single ion conductivities at different temperatures have been evaluated from the division of the Λ° value of Bu₄NBPh₄ using the following relationship:

$$\frac{\lambda^\circ(\text{Bu}_4\text{N}^+)}{\lambda^\circ(\text{Ph}_4\text{B}^-)} = \frac{r_{\text{Ph}_4\text{B}^-}}{r_{\text{Bu}_4\text{N}^+}} = 1.07 \quad (13)$$

The ionic radii of Bu₄N⁺ and Ph₄B⁻ ions were taken from the work of Gill and Sekhri.^{25,26}

The single-ion conductivities (λ°_{\pm}) along with the Walden products ($\lambda^\circ_{\pm} \eta_0$) of all the ions are reported in Table 6.

The single-ion conductivities have also been fitted to the following polynomial equation:

$$\lambda^\circ_{\pm} = b_0 + b_1(298.15 - T) + b_2(298.15 - T)^2 \quad (14)$$

and the coefficients of the fits along with the $\sigma\%$ values are recorded in Table 7.

The Walden products for these salts in 2-methoxyethanol are substantially lower than those in aqueous solutions.²⁷ The apparent excess of mobility in aqueous solution has been attributed to far greater solvation in the nonaqueous media.

TABLE 6: Limiting Ionic Conductances ($\lambda_{\pm}^0/S \text{ cm}^2 \text{ mol}^{-1}$) and Ionic Walden Products ($\lambda_{\pm}^0 \eta_0/S \text{ cm}^2 \text{ mol}^{-1} \text{ Pa s}$) in 2-Methoxyethanol at 288.15, 293.15, 298.15, and 308.15 K

ion	288.15 K		293.15 K		298.15 K		308.15 K	
	λ_{\pm}^0	$\lambda_{\pm}^0 \eta_0$	λ_{\pm}^0	$\lambda_{\pm}^0 \eta_0$	λ_{\pm}^0	$\lambda_{\pm}^0 \eta_0$	λ_{\pm}^0	$\lambda_{\pm}^0 \eta_0$
K ⁺	14.39	0.279	15.24	0.263	16.05	0.247	20.21	0.254
Bu ₄ N ⁺	11.54	0.224	12.43	0.215	14.25	0.220	17.07	0.215
Ph ₄ As ⁺	9.83	0.190	10.21	0.176	11.16	0.172	13.85	0.174
Pic ⁻	17.41	0.337	20.30	0.351	22.89	0.353	25.08	0.315
Ph ₄ B ⁻	10.78	0.209	11.99	0.207	13.32	0.205	15.96	0.201

TABLE 7: Coefficients of the Polynomial, Eq 14

ion	b_0	b_1	b_2	$\sigma\%$
K ⁺	16.19	-0.2862	0.01129	0.254
Bu ₄ N ⁺	14.05	-0.2831	0.00219	0.344
Ph ₄ As ⁺	11.11	-0.2026	0.00722	0.088
Pic ⁻	22.78	-0.3873	-0.01550	0.199
Ph ₄ B ⁻	13.30	-0.2579	0.00067	0.036

TABLE 8: Coefficients of the Polynomial, Eq 18, and Thermodynamic Standard Data of the Association

electrolyte	c_0 $\Delta G_{298.15}^0$ J mol ⁻¹	c_1 $\Delta S_{298.15}^0$ J K ⁻¹ mol ⁻¹	$10^2 c_2$ J K ⁻² mol ⁻¹	$\sigma\%$	$c_0 + 298.15c_1$ $\Delta H_{298.15}^0$ J mol ⁻¹
KPic	-14734.6	48.59	234.85	0.028	-248.3
KBPh ₄	-13614.1	14.00	-274.93	0.073	-9442.9
Bu ₄ NBPh ₄	-14709.1	24.13	-77.81	0.162	-7513.2
Ph ₄ AsPic	-15034.3	56.72	126.88	0.106	1877.5

We find (cf. K_A values from Table 3) that all these salts are moderately associated in 2-methoxyethanol at all the temperature investigated. This is quite expected owing to the low dielectric constant ($D = 16.94$ at 298.15 K)¹ of the solvent.

4.2. Thermodynamics of Ion Pair Formation. The standard Gibbs energy changes for the ion association process, ΔG° , can be calculated from the equation

$$\Delta G^\circ = -RT \ln K_A \quad (15)$$

The values of the standard enthalpy change, ΔH° , and the standard entropy change, ΔS° , can be evaluated from the temperature dependence of ΔG° values as follows:

$$\Delta H^\circ = -T^2 \left[\frac{d(\Delta G^\circ/T)}{dT} \right]_p \quad (16)$$

$$\Delta S^\circ = - \left(\frac{d\Delta G^\circ}{dT} \right)_p \quad (17)$$

The ΔG° values can be fitted with the help of a polynomial of the type

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (18)$$

and the coefficients of the fits are compiled in Table 8, together with the $\sigma\%$ values of the fits.

The standard values at 298.15 K are then

$$\Delta G_{298.15}^\circ = c_0 \quad (19)$$

$$\Delta S_{298.15}^\circ = c_1 \quad (20)$$

$$\Delta H_{298.15}^\circ = c_0 + 298.15c_1 \quad (21)$$

It is observed from Table 8 that the ΔS° values of ion association for all these electrolytes are positive. These positive ΔS° values may be attributed to the increasing number of degrees of freedom upon association mainly due to the release

of solvent molecules

$$M^+ \cdot n(\text{ME}) + X^- \cdot m(\text{ME}) = \text{MX} \cdot z(\text{ME}) + (n + m - z)\text{ME} \quad (22)$$

In other words, the solvation of ions is weakened as soon as the ion pair is formed.

The ΔS° values of the electrolytes are found to decrease in the following order:



which indicates that the degree of weakening of the ion solvation due to the formation of ion pair also decreases in the same order.

The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors is discussed in section 4.3.

The variation of ΔH° from one salt to another is quite interesting. For Ph₄AsPic, the ΔH° value is sufficiently positive. It is obvious, therefore, that, for this salt, the enthalpic term is counterbalanced by a favorable entropy change which comes from the short- and long-range desolvation of both ions. The attribution of ΔS° to desolvation is also supported by the positive enthalpies indicating lack of covalent bonds.

The ΔH° value of KPic is very small. The enthalpic term for the ion association process here is so small that it plays a negligible role in the association equilibrium, which is mainly determined by the positive entropic term which comes from the desolvation of the cations.

It is especially noteworthy that the ΔH° values for KBPh₄ and Bu₄NBPh₄ are negative. The electrostatic theories of ionic association,²⁹ however, never give negative values for ΔH° , since the theoretical equation for ΔH° contains the $[1 + (d \ln D/d \ln T)_p]$ term; thus, the experimental value of $(d \ln D/d \ln T)_p$ makes the theoretical ΔH° value positive, contrary to the expectation.

The negative values of ΔH° can be explained by considering the participation of specific covalent interaction in the ion association process. Here, in this case, the covalent interaction somewhat works between the ions, and hence, the binding enthalpy between the ions is sufficiently negative to compensate for the positive contribution from the weakening of ion solvation. In this case, ΔG° of the ion association should have a large negative value (a large K_A value) and should depend on the kind of ions, and this is found to be true here.

The non-Coulombic part of the Gibbs energy, ΔG^* , has also been calculated using the following equation³⁰:

$$\Delta G^* = N_A W_{\pm}^* \quad (23)$$

$$K_A = (4\pi N_A/1000) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}^*}{kT}\right) dr \quad (24)$$

where the symbols have their usual significance. The quantity $2q/r$ is the Coulombic part of the interionic mean force potential and W_{\pm}^* is its non-Coulombic part.

The procedure for the evaluation of the non-Coulombic part of the entropy and enthalpy (and ΔS^* and ΔH^* , respectively) is the same as that used for obtaining ΔS° and ΔH° .

TABLE 9: Coefficients of the Polynomial, Eq 25, for the Non-Coulombic Contribution to the Association Process

electrolyte	c_0^* $\Delta G_{298.15}^*$ J mol ⁻¹	c_1^* $\Delta S_{298.15}^*$ J K ⁻¹ mol ⁻¹	c_2^* J K ⁻² mol ⁻¹	σ %	$c_0^* + 298.15c_1^*$ $\Delta H_{298.15}^*$ J mol ⁻¹
KPic	-3805.9	1.03	242.50	0.023	-3497.2
KBPh ₄	-2712.7	-33.60	-267.27	0.487	-12729.8
Bu ₄ NBPh ₄	-4170.9	-23.97	-77.81	0.162	-7513.2
Ph ₄ AsPic	-15034.3	8.92	134.96	0.390	-1655.5

The ΔG^* values at different temperatures were fitted to the polynomial

$$\Delta G^* = c_0^* + c_1^*(298.15 - T) + c_2^*(298.15 - T)^2 \quad (25)$$

and the coefficients of the fits along with the σ % values are given in Table 9.

The values of ΔG^* , ΔS^* , and ΔH^* at 298.15 K are then easily obtained from the following equations:

$$\Delta G_{298.15}^* = c_0^* \quad (26)$$

$$\Delta S_{298.15}^* = c_1^* \quad (27)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (28)$$

The non-Coulombic parts of the Gibbs energy, $\Delta G_{298.15}^*$, of all the salts are found to be small (Table 9), 20% (KBPh₄), 26% (KPic), 29% (Ph₄AsPic), and 28% (Bu₄NPh₄) in 2-methoxyethanol. This indicates that the Coulombic forces play a major role in the association processes. This is further supported by the fairly higher values of the Coulombic parts of ΔS° and ΔH° compared to their non-Coulombic counterparts.

4.3. Compressibility Behavior. The limiting apparent molar adiabatic compressibilities (ϕ_K°) of KPic, KBPh₄, and Ph₄AsPic are found to be negative (ϕ_K° values at 298.15 K for KPic, KBPh₄, and Ph₄AsPic are -104.22×10^{-10} , -139.41×10^{-10} , and -617×10^{-10} cm⁵ mol⁻¹ dyn⁻¹, respectively). These negative ϕ_K° values of the electrolytes can be interpreted in terms of loss of compressibility of the solvent 2-methoxyethanol due to the presence of these solutes in solution.

A comparison of the ϕ_K° values of these three salts can unravel some interesting and intricate aspects of electrostriction of the solvent molecules around the small sized ions and penetration of those molecules into the larger ions and their influence on the compressibility of the medium.

For small ions with higher surface charge density on them, there will be loss of compressibility in solution arising out of the electrostriction of the solvent molecules around those ions. Electrostriction will, however, be negligible in the vicinity of larger ions with low charge density on their surface. But, in these cases also the loss of compressibility might be effected by other factors; one effect that can play an important role for the large tetraphenylborate and tetraphenylarsonium ions is the penetration of the solvent molecules (ME) into the space between the phenyl chains attached to the boron atom of the former or arsenic atom of the later ion. This obviously will cause constriction of the solution volumes resulting in a more compact and hence less compressible medium. The possibility of penetration of the 2-methoxyethanol molecules into the tetraphenylborate ions is rather less due mainly to (i) the repulsive effect of the negatively charged boron atom upon the 2-methoxyethanol molecules (arsenic is positively charged, in contrast) and (ii) the less available space between the phenyl groups

attached to the smaller boron atom compared to the bigger arsenic atom.

Among KPic and KBPh₄ solutions, the former solution is more compressible than the later (Table 4) indicating that the loss of compressibility of the medium is less in the presence of KPic. In these two salts, K⁺ ion being common, the anions are evidently making the difference. In case of picrate ion, electrostriction will be predominant, whereas in the case of tetraphenylborate ion, neither electrostriction nor penetration is expected to affect compressibility of the medium. From the observed trend in the compressibility (and also in the apparent molar adiabatic compressibility), it appears that electrostrictive effect plays a major role here. In case of picrate ion, more solvent was associated with the ion compared to the tetraphenylborate ion; hence on association, a greater number of solvent molecules are released into the bulk, thereby making the medium more compressible. This observation also gets support from the ΔS° value of the association process. Greater desolvation for KPic solution helps make the system more compressible.

Among KPic and Ph₄AsPic solutions, once again the former solution has higher compressibility. The plausible reason for this observation is similar to that described for the pair KPic and KBPh₄ except that some amount of penetration is possible for tetraphenylarsonium ion. But, the most striking observation is that though KPic is more compressible, Ph₄AsPic has a higher ΔS° value of the ion association. A possible explanation for this might be that the solvent molecules which are released from the tetraphenylarsonium ion upon association will remain trapped inside the tetraphenyl chains around the arsenic atom. These trapped solvent molecules are, thus, free to move within the territory of the phenyl chains to increase the entropic term; but, since these remain inside the chains, these are not sufficiently compressible under applied pressure.

It may thus be concluded that all these electrolytes remain strongly associated in 2-methoxyethanol to form ion pairs and the solvation of the ions is weakened as soon as the ion pair is formed. The results indicate that the Coulombic forces play a major role in the association process. Electrostriction is found to be important for potassium and picrate ions while penetration of the solvent molecules occurs inside the space between the alkyl or aryl chains attached to the nitrogen or arsenic atom of the tetrabutylammonium or tetraphenylarsonium ion. For tetraphenylborate ion, on the other hand, neither electrostriction nor penetration is found to be operative.

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