The Structure and Thermodynamics of Ion Association and Solvation of Some Thiocyanates and Nitrates in 2-Methoxyethanol Studied by Conductometry and FTIR Spectroscopy

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Precise measurements on electrical conductances and Fourier transform infrared spectra (FTIR) of solutions of potassium thiocyanate (KCNS), ammonium thiocyanate (NH_4CNS), sodium nitrate ($NaNO_3$), and ammonium nitrate (NH_4NO_3) in 2-methoxyethanol (ME) at temperatures $298.15 \leq T \leq 318.15$ K have been reported. The conductance data have been analyzed by the 1978 Fuoss conductance−concentration equation. Thermodynamics of the ionic association processes have also been studied, and the Coulombic forces are found to play a major role in the association processes. The ionic contributions to the limiting equivalent conductances have been determined using the *reference electrolyte* method. Strong association was found for all of these electrolytes in this solvent medium. The cations are found to be substantially solvated in 2-methoxyethanol, whereas the anions appear to have weak interaction with the solvent molecules. The infrared spectra suggest the presence of "spectroscopically free" thiocyanate (CNS^-) and nitrate (NO_3^-) ions in solution. For all of these electrolytes, the solvent-separated ion pairs predominate over the contact species. The observed processes have been interpreted by an Eigen multistep mechanism.

1. Introduction

A knowledge of the state of association of electrolytes in solution and their interaction with the solvent molecules is essential for a proper understanding of their behavior in solution. To this end, various classical methods such as electrical conductivity and viscosity measurements have been widely employed to study the status of association of electrolytes. Such studies are complemented with structural studies of the metal ion solvates using different spectroscopic methods. Recently, we have initiated a comprehensive program to study the solvation and association behavior of 1:1 electrolytes in different nonaqueous solvents from the measurements of various transport, thermodynamic, and spectroscopic properties.[1−7] In this paper, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of potassium thiocyanate (KCNS), ammonium thiocyanate (NH_4CNS), sodium nitrate ($NaNO_3$), and ammonium nitrate (NH_4NO_3) in 2-methoxyethanol from precise conductivity and Fourier transform infrared spectral (FTIR) measurements.

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 was collected. The purified solvent had a density of 0.960 02 g cm^{-3}, a coefficient of viscosity of 1.5414 mPa s, and a specific conductance of ca. 1.01×10^{-6} S cm^{-1} at 298.15 K. These values are in good agreement with the literature data.[8] The properties of the solvent are recorded in Table 1.

The salts (all A.R., B.D.H.) were purified by recrystallization two times from conductivity water. The samples were dried in a vacuum and stored over P_2O_5 under vacuum.

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

TABLE 1: Physical Properties of 2-Methoxyethanol

T, K	ρ_0, g cm^{-3}	η_0, mPa s	ϵ
298.15	0.96002	1.5414	16.94
308.15	0.95356	1.2579	16.15
313.15	0.95040	1.1482	15.76
318.15	0.94715	1.0400	15.39
323.15	0.94381	0.9310	15.02

1.14 cm^{-1} having an accuracy of 0.1%. Measurements were made in an oil bath maintained within ±0.005 K of the desired temperature. The details of the experimental procedure have been described elsewhere.[9,10] Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald−Sprengel-type pycnometer of about 25 cm^3 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.

All FTIR spectra were recorded in the 4000−400 cm^{-1} range at a resolution of 1 cm^{-1} using a Shimadzu 8300 FTIR spectrophotometer equipped with a Ge/KBr beam splitter and a DLATGS detector with 20 scans collected for each spectrum. The interferograms were apodized with the Happ−Genzel function. Demountable cells with potassium bromide windows were used.

The dielectric constants of 2-methoxyethanol at different temperatures were taken from the literature.[11]

3. Results

3.1. Conductance. The measured molar conductances (Λ) of electrolyte solutions as a function of molar concentration (c) at 298.15, 308.15, 313.15, 318.15, and 323.15 K are given in Table 2. The conductance data have been analyzed by the 1978 Fuoss conductance−concentration equation.[12,13] For a given set of conductivity values (c_j,Λ_j; $j = 1, ..., n$), three adjustable

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TABLE 2: Molar Conductivities of Electrolytes in 2-Methoxyethanol at 298.15, 308.15, 313.15, 318.15, and 323.15 K

$T = 298.15$ K		$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K		$T = 323.15$ K	
$c \times 10^4$, mol dm^{-3}	Λ, S cm^2 mol^{-1}	$c \times 10^4$, mol dm^{-3}	Λ, S cm^2 mol^{-1}	$c \times 10^4$, mol dm^{-3}	Λ, S cm^2 mol^{-1}	$c \times 10^4$, mol dm^{-3}	Λ, S cm^2 mol^{-1}	$c \times 10^4$, mol dm^{-3}	Λ, S cm^2 mol^{-1}
				KSCN					
1.3031	46.34	2.6178	51.86	1.6629	56.01	1.1825	60.79	1.3867	61.75
2.6063	44.33	3.9267	50.23	3.3258	53.23	1.8921	59.15	2.7734	59.04
3.9094	42.79	4.5812	49.43	4.1572	52.12	2.3651	58.22	4.1601	56.96
4.5610	42.11	5.2356	48.69	4.9887	51.10	3.5476	56.24	5.5468	55.12
5.2126	41.49	6.5446	47.33	5.8201	50.18	4.7302	54.58	6.9335	53.66
6.5157	40.34	7.8535	46.11	6.6516	49.31	5.9127	53.11	8.3202	52.26
7.8189	39.31	8.5079	45.53	7.4830	48.50	7.0953	51.79	8.8749	51.74
8.4705	38.82	9.1624	44.97	8.3145	47.74	8.2778	50.57	9.7069	50.98
9.1220	38.36	9.5551	44.65	9.1459	47.01	9.4604	49.44		
				NH$_4$SCN					
1.7320	44.46	1.1313	53.02	1.3305	55.47	1.3957	61.37	2.0715	62.03
3.4641	41.88	1.8854	51.32	2.6611	52.55	2.7914	58.21	3.1072	60.02
4.3310	40.84	2.8282	49.63	3.9916	50.32	4.1871	55.78	4.1429	58.32
5.1960	39.90	3.9594	47.93	4.6569	49.37	4.8849	54.72	5.1787	56.82
6.9279	38.22	5.6563	45.80	5.3221	48.43	5.5828	53.74	6.2144	55.47
7.7940	37.47	6.5991	44.76	6.6527	46.78	6.9785	51.93	7.2501	54.23
8.6600	36.75	7.5418	43.77	7.9832	45.28	8.3742	50.31	8.2859	53.07
9.5261	36.07	9.4272	42.00	9.3137	43.89	9.0720	49.54	9.3216	51.98
						9.7696	48.81		
				NaNO$_3$					
1.6793	38.65	1.3924	45.55	3.8710	44.10	1.2400	53.70	1.1634	58.27
3.3585	36.19	2.7847	42.75	4.4652	42.99	2.4794	50.72	2.3269	55.06
5.0378	34.30	4.1771	40.81	5.0625	42.10	3.7190	48.30	3.4903	52.61
5.8774	33.47	4.8732	39.91	6.1937	40.10	4.9587	45.96	4.6537	50.53
6.7170	32.70	5.5694	39.07	6.8906	40.18	6.1984	44.45	5.8182	48.71
7.5567	31.98	6.9618	37.54	7.7421	39.42	7.4381	42.83	6.9806	47.06
8.3963	31.30	8.3541	36.16	8.5163	38.72	8.6778	41.33	8.1440	45.54
9.2359	30.65	9.7465	34.89	9.2905	37.97	9.9174	39.94	9.3074	44.13
				NH$_4$NO$_3$					
1.4293	42.94	1.6442	49.21	1.7442	52.09	1.2964	55.86	2.8006	56.34
2.8586	40.43	3.2884	45.97	3.4883	48.69	2.5927	52.78	3.5007	55.08
4.2879	38.50	4.1104	44.68	4.3603	47.32	3.8891	50.42	4.2009	53.94
5.0025	37.66	4.9326	43.50	5.2324	46.09	4.5372	49.39	4.9010	52.90
5.7171	36.88	6.5770	41.40	6.9765	43.89	5.1854	48.44	5.6012	51.92
7.1464	35.45	7.3988	40.46	7.8486	42.89	6.4818	46.68	7.0015	50.14
8.5757	34.16	8.2210	39.55	8.7206	41.95	7.7781	45.10	8.4108	48.54
9.2904	33.55	9.8651	37.90	9.5927	41.06	9.0745	43.65	9.1020	47.78
								9.8021	47.06

parameters, the limiting molar conductivity (Λ^0), the association constant (K_A), and the cosphere diameter (R), are derived from the following set of equations:

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

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

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

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

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

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

where the symbols have their usual significance. The computations were performed on a computer using the program as suggested by Fuoss.[12,18] The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation[14] of the data. Input for the program is the set ($c_j, \Lambda_j; j = 1, ..., n$), n, D, η, T, initial value of Λ^0, and an instruction to cover a preselected range of R values.

In practice, calculations are made by finding the values of Λ^0 and α that 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 the σ vs R curve. However, because a rough scan using unit increments of R values from 4 to 20 gave no significant minima in the σ (%) versus 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 by[13]

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

where M is the molecular weight of the solvent and ρ_0 is its density. The values of Λ^0, K_A, and R obtained by this procedure are reported in Table 3.

3.2. FTIR Spectra. The infrared spectra of pure 2-methoxyethanol and of the solutions of KCNS, NH$_4$CNS, NaNO$_3$, and NH$_4$NO$_3$ in 2-methoxyethanol in the range 4000−400 cm^{-1} have been presented in Figures 1−5.

4. Discussion

4.1. Limiting Molar Conductance and Association Constant. Table 3 shows that for all salts the limiting molar conductances (Λ^0) increase as the temperature increases. The Λ^0 values have been fitted to the following polynomial:

$$\Lambda^0 = a_0 + a_1(298.15 - T) + a_2(298.15 - T)^2 \quad (9)$$

and the coefficients of these fits are given in Table 4, together with the standard percentage errors (σ%).
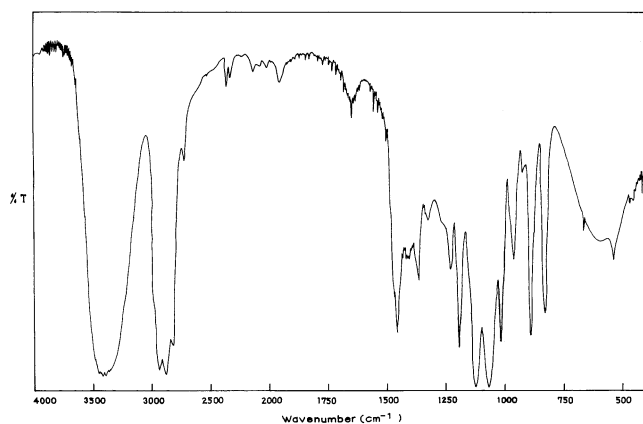
Figure 1. FTIR spectrum of 2-methoxyethanol. The vertical axis indicates the percent transmission in arbitrary units.
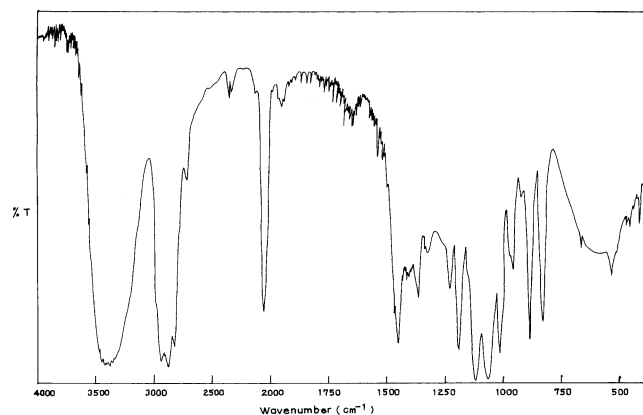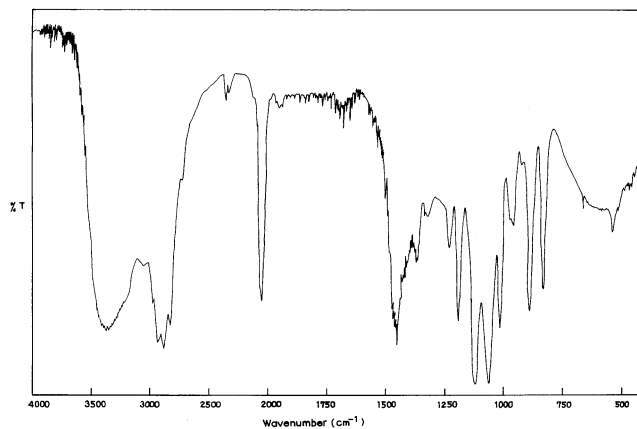

Figure 2. FTIR spectrum of KSCN in 2-methoxyethanol. The vertical axis indicates the percent transmission in arbitrary units.
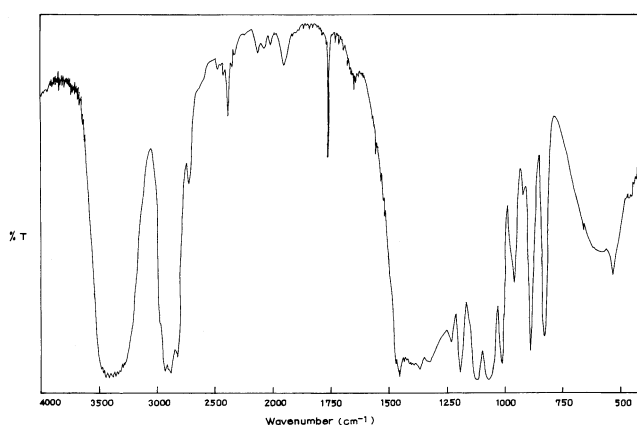

Figure 3. FTIR spectrum of NH_4SCN in 2-methoxyethanol. The vertical axis indicates the percent transmission in arbitrary units.

Figure 4. FTIR spectrum of $NaNO_3$ in 2-methoxyethanol. The vertical axis indicates the percent transmission in arbitrary units.
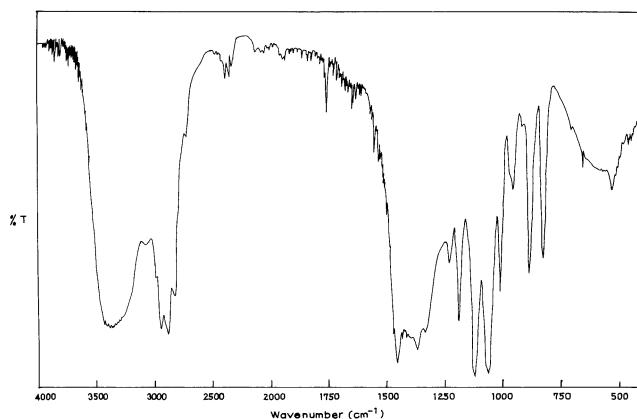
Figure 5. FTIR spectrum of NH_4NO_3 in 2-methoxyethanol. The vertical axis indicates the percent transmission in arbitrary units.

TABLE 3: Conductance Parameters of Electrolytes in 2-Methoxyethanol at 298.15, 308.15, 313.15, 318.15, and 323.15 K

T, K	Λ^0, S cm^2 mol^{-1}	K_A, dm^3 mol^{-1}	R, Å	$\sigma\%$
		KSCN		
298.15	50.65 ± 0.13	430 ± 11	8.54	0.20
308.15	59.85 ± 0.26	453 ± 18	8.55	0.24
313.15	62.84 ± 0.41	463 ± 28	8.56	0.26
318.15	66.41 ± 0.17	448 ± 12	8.56	0.24
323.15	67.96 ± 0.21	405 ± 13	8.57	0.24
		NH$_4$SCN		
298.15	49.12 ± 0.17	495 ± 15	8.69	0.22
308.15	58.18 ± 0.21	555 ± 18	8.70	0.30
313.15	61.98 ± 0.32	624 ± 26	8.71	0.35
318.15	68.61 ± 0.32	585 ± 22	8.72	0.34
323.15	70.80 ± 0.26	500 ± 17	8.73	0.22
		NaNO$_3$		
298.15	44.32 ± 0.27	709 ± 30	8.13	0.34
308.15	51.72 ± 0.37	745 ± 39	8.14	0.46
313.15	56.11 ± 0.44	807 ± 40	8.15	0.22
318.15	61.16 ± 0.52	852 ± 49	8.16	0.57
323.15	65.66 ± 0.44	788 ± 39	8.17	0.48
		NH$_4$NO$_3$		
298.15	48.61 ± 0.31	725 ± 33	8.56	0.40
308.15	56.94 ± 0.44	808 ± 42	8.57	0.44
313.15	60.23 ± 0.41	743 ± 35	8.58	0.38
318.15	62.83 ± 0.36	697 ± 32	8.59	0.39
323.15	67.58 ± 0.31	648 ± 22	8.60	0.22

TABLE 4: Coefficients of the Polynomial, Eq 9

electrolyte	a_0	a_1	a_2	$\sigma\%$
KSCN	50.65	-1.0491	-1.4044	0.172
NH$_4$SCN	48.98	-0.9566	-2.4062	0.514
NaNO$_3$	48.76	-0.7927	-2.3070	0.377
NH$_4$NO$_3$	44.26	-0.6921	6.8006	0.142

Limiting ionic equivalent conductivities at 298.15 and 308.15 K were obtained from the ionic conductances of K$^+$ ion at these two temperatures as reported earlier.[3] The single-ion conductivities ($\lambda_\pm^0$), along with the Walden products ($\lambda_\pm^0 \eta_0$) are reported in Table 5.

The Walden products for these salts in 2-methoxyethanol are substantially lower than those in aqueous solutions.[15] The

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TABLE 5: Limiting Ionic Conductances ($\lambda_\pm^0$, S cm^2 mol^{-1}), Ionic Walden Products ($\lambda_\pm^0\eta_0$, S cm^2 mol^{-1} Pa s), and Ionic Stokes Radii (r_S, Å) in 2-Methoxyethanol at 298.15 and 308.15 K

	298.15 K			308.15 K		
ion	$\lambda_\pm^0$	$\lambda_\pm^0\eta_0$	r_S	$\lambda_\pm^0$	$\lambda_\pm^0\eta_0$	r_S
Na$^+$	10.23	0.016	5.19	13.32	0.017	4.90
K$^+$	16.05	0.025	3.32	20.21	0.025	3.22
NH$_4^+$	14.52	0.022	3.66	18.54	0.023	3.52
SCN$^-$	34.60	0.053	1.54	39.64	0.050	1.60
NO$_3^-$	34.09	0.052	1.56	38.40	0.048	1.70

apparent excess of mobility in aqueous solution has been attributed to far greater solvation in the nonaqueous media.

Table 5 shows that the Stokes radii of the cations Na$^+$, K$^+$, and NH$_4$ $^+$ are significantly higher compared to their crystallographic radii.[8] This indicates that these ions are substantially solvated in 2-methoxyethanol. A slow desolvation of these ions with increasing temperature has also been observed. The Stokes radii of the anions, SCN$^-$ and NO$_3^-$, are found to be much lower than their crystallographic radii. This is physically unacceptable. They seem to indicate that the determination of solvation numbers of these ions based on Stokes law does not appear to be correct. This probably arises from the fact that the electrolyte solutions are different from the model that underlies this law and could be attributed to the unsymmetrical shape and distribution of charge on these ions. However, it may be mentioned that since 2-methoxyethanol molecules lack a well-developed center of positive charge, as indicated by spectral investigations,[16,17] the anions appear to have a weak interaction with the solvent molecules. In fact, this has been demonstrated from the present FTIR spectroscopic study on these electrolyte solutions (see section 4.3).

All of these electrolytes are found to be strongly associated (cf. K_A values from Table 3) in 2-methoxyethanol at all of the temperatures investigated. This is quite expected owing to the low relative permittivity of the medium. These electrolyte solutions, in general, show an increase in the association constant values with temperature, followed by a decrease.

4.2. Thermodynamics of Ion Pair Formation. The standard Gibbs energy changes for the ion association process, $\Delta G°$, can be calculated from the association constants using the equation

$$\Delta G° = -RT \ln K_A \tag{10}$$

To evaluate the standard enthalpy change, $\Delta H°$, and the standard entropy change, $\Delta S°$, we have fitted the $\Delta G°$ values to a polynomial of T of the type

$$\Delta G° = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \tag{11}$$

and the coefficients of the fits are compiled in Table 6, together with the $\sigma\%$ values of the fits.

The $\Delta H°$ and $\Delta S°$ values of the ion-association process can then be evaluated from the temperature dependence of $\Delta G°$ values as follows:

$$\Delta H° = -T^2\left[\frac{d(\Delta G°/T)}{dT}\right]_p \tag{12}$$

$$\Delta S° = -\left(\frac{d\Delta G°}{dT}\right)_p \tag{13}$$

The standard values of the thermodynamic parameters at 298.15

TABLE 6: Coefficients of the Polynomial, Eq 11, and Thermodynamic Standard Data of the Association

electrolyte	c_0 $\Delta G_{298.15}°$, J mol^{-1}	c_1 $\Delta S_{298.15}°$, J K^{-1} mol^{-1}	$10^2 c_2$, J K^{-2} mol^{-1}	$\sigma\%$	$c_0 + 298.15 c_1$ $\Delta H_{298.15}°$, J mol^{-1}
KSCN	−15 019.2	87.70	167.95	0.11	11 129.6
NH$_4$SCN	−15 342.2	131.31	298.16	0.28	23 807.9
NaNO$_3$	−16 239.1	89.05	75.56	0.21	10 313.1
NH$_4$NO$_3$	−16 347.4	92.60	208.56	0.15	11 262.2

TABLE 7: Coefficients of the Polynomial, Eq 20, 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}	$10^2 c_2^*$, J K^{-2} mol^{-1}	$\sigma\%$	$c_0^* + 298.15 c_1^*$ $\Delta H_{298.15}^*$, J mol^{-1}
KSCN	−4041.7	40.74	178.40	0.42	8104.9
NH$_4$SCN	−4367.9	84.35	308.66	0.94	20781.0
NaNO$_3$	−5254.6	42.10	86.00	0.66	7298.1
NH$_4$NO$_3$	−5370.5	45.64	219.05	0.46	8237.9

K can, therefore, be expressed as

$$\Delta G_{298.15}° = c_0 \tag{14}$$

$$\Delta S_{298.15}° = c_1 \tag{15}$$

$$\Delta H_{298.15}° = c_0 + 298.15 c_1 \tag{16}$$

It is observed from Table 6 that the $\Delta S°$ values of ion association for all of these electrolytes are positive. These positive $\Delta S°$ values may be attributed to the increasing number of degrees of freedom upon association mainly due to the release of solvent molecules as shown:

$$M^+ \cdot n(ME) + X^- \cdot m(ME) = $$
$$MX \cdot z(ME) + (n + m - z)ME \tag{17}$$
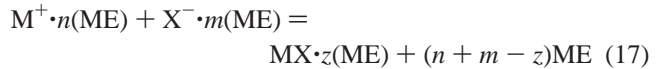
In other words, the solvation of the individual ions is weakened as soon as these ion pairs are formed.

The $\Delta S°$ values of the electrolytes are found to decrease in the following order: NH$_4$SCN > NH$_4$NO$_3$ > NaNO$_3$ > KSCN. This indicates that the degree of weakening of the ion solvation due to the formation of the ion pair also decreases in the same order.

Table 6 shows that the $\Delta H°$ values for all of the electrolytes are large and positive. It is obvious, therefore, that for these electrolytes the enthalpic term is counterbalanced by a favorable entropy change, which comes from the short- and long-range desolvation of ions. The attribution of $\Delta S°$ to desolvation is also supported by the positive enthalpies indicating lack of covalent bonds.

The non-Coulombic contribution to the Gibbs energy, ΔG^*, has been calculated from the following equation:[18]

$$\Delta G^* = N_A W_\pm^* \tag{18}$$

$$K_A = (4\pi N_A/1000)\int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_\pm^*}{kT}\right) dr \tag{19}$$

where the symbols have their usual meaning. 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 contribution to the entropy and enthalpy (ΔS^* and ΔH^*, respectively) is similar to that used for obtaining $\Delta S°$ and $\Delta H°$.

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

$$\Delta G^* = c_0^* + c_1^*(298.15 - T) + c_2^*(298.15 - T)^2 \quad (20)$$

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

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

$$\Delta G_{298.15}^* = c_0^* \quad (21)$$

$$\Delta S_{298.15}^* = c_1^* \quad (22)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (23)$$

The non-Coulobmic parts of the Gibbs energy, $\Delta G_{298.15}^*$, of all of the salts are found to be small (Table 7)—27% (KSCN), 28% (NH₄SCN), 33% (NaNO₃), 32% (NH₄NO₃) of their corresponding total Gibbs energy values 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 $\Delta S°$ and $\Delta H°$ in comparison with their non-Coulombic counterparts.

4.3. Infrared Spectral Behavior. Partial band assignments for the pure solvent, as well as for the electrolyte solutions, have been made and are discussed accordingly. The Fourier transform infrared spectrum of 2-methoxyethanol is shown in Figure 1. The solvent exhibits O—H stretching at 3396 cm⁻¹. Two C—H deformation modes appear at 1456 and 1367 cm⁻¹. The solvent also shows two C—O stretching modes, one at 1124 cm⁻¹ characteristic of an ether with —CH₂—O—CH₂— grouping and another at 1066 cm⁻¹, which is characteristic of a primary alcohol.

Figures 2−5 represent the FTIR spectra of the electrolyte solutions in 2-methoxyethanol. It can be seen that the spectra of the salt solutions show several remarkable changes compared to that of the pure solvent.

In the FTIR spectrum of 2-methoxyethanol, the signal for hydrogen bonding appears at 3396 cm⁻¹. Considerable shift of this band has been observed in the infrared spectra of all of the electrolyte solutions studied. The corresponding bands in KSCN, NH₄SCN, NaNO₃, and NH₄NO₃ solutions appear at 3386, 3368, 3375, and 3375 cm⁻¹, respectively (Figures 2−5). This indicates complexation of the cations to the 2-methoxyethanol molecules. A molecular rationale for the above observation can be found if one considers the structure of the solvent molecules. The molecular dynamics of 2-methoxyethanol have been investigated,[16] and it was found that this species exists predominantly in the gauche cyclic conformation.[17] In this arrangement, strong intramolecular hydrogen bonding takes place, providing a closed ring that resembles the simplest crown ether, and the cations are known to form stable complexes with crown ethers.[19,20] The aforementioned cyclic conformation of 2-methoxyethanol molecules facilitates complexation with the cations investigated here through specific and dipolar interactions via oxygen atoms.

The FTIR spectrum of each of KSCN and NH₄SCN solution shows a very sharp peak at 2057 cm⁻¹ due to the ν_{CN} stretching vibration of the thiocyanate anion. This peak has been assigned[21−23] to the "spectroscopically free" NCS⁻ ion, including solvent-separated ion pairs, M⁺SSCN⁻ (S is the solvent molecule) or to the solvent-separated dimer, M⁺SSCN⁻⋯M⁺SSCN⁻, which are spectroscopically indistinguishable from each other, or both. It should be pointed out

here that in nitromethane, which only poorly solvates anions,[24] the ν_{CN} stretch of SCN⁻ ion is a sharp absorption[25] at 2059 cm⁻¹. This ν_{CN} stretching vibration is found to be sensitive to electrostatic interaction in solutions. If methanol (which solvates the anion significantly) is added to this nitromethane solution, the intensity of this peak falls with concomitant broadening of the spectral envelope—this is a characteristic of the solvated thiocyanate ion. The appearance of a very sharp peak at 2057 cm⁻¹ for each of the two thiocyanate salts studied in 2-methoxyethanol solution thus clearly indicates that this anion remains unsolvated in this medium also.

A very weak shoulder at about at 2062 cm⁻¹ in the neighborhod of the 2057 cm⁻¹ peak can be seen in the spectra of KNCS and NH₄NCS solutions. This signal has been assigned to the contact ion pairs.[26,27]

The infrared spectra of the nitrate salts, NaNO₃ and NH₄-NO₃, show new sharp peaks around 1768 cm⁻¹. A similar peak has been reported earlier for nitrate ion at the same wavenumber in the solid state,[28] and this has been attributed to the ν_2 vibrational mode of this ion. Another new peak at 2396 cm⁻¹ has also been identified in the spectra of these salt solutions. The appearance of these new bands for these salt solutions has been assigned to the "spectroscopically free" nitrate ion in 2-methoxyethanol, including solvent-separated ion pairs (and possibly dimers). Moreover, on the basis of a collateral evidence for the thiocyanate salts in this medium, it can be concluded that the nitrate ions will also remain unsolvated in 2-methoxy-ethanol solutions.

A weak shoulder and a weak peak on the higher wavenumber side of the 2396 cm⁻¹ signal have been detected in the infrared spectra of NaNO₃ and NH₄NO₃ solutions, respectively (the former being weaker compared to the latter), and these have been assigned to the contact ion pairs.

The bands corresponding to the contact ion pairs for all of these electrolytes are found to be very weak. This points to the fact that the concentrations of the contact species are negligibly small and that a preponderant proportion of the ion pairs remains in the solvent-separated form.

The above observations can be interpreted in terms of the following Eigen multistep mechanism:

$$M^+ + X^- = M^+SX^- = MX \quad (24)$$

$$2M^+SX^- = M^+SX^-⋯M^+SX^- \quad (25)$$

$$2MX = (MX)_2 \quad (26)$$
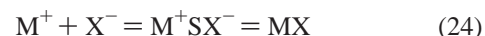
Thus, for these electrolytes, one would expect the presence of an equilibrium between the solvent-separated and contact ion pairs represented by eq 24 that is strongly shifted toward the left. The equilibrium represented by eq 25 to form solvent-separated dimer may also exist because M⁺SX⁻ and M⁺SX⁻⋯M⁺SX⁻ are indistinguishable by infrared spectroscopy. Because contact ion pairs are also found to be present, although in a very small amount, the formation of a very small amount of contact quadrupoles cannot be ruled out.

It may thus be concluded that 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 ion association process. All of the electrolytes are found to exist essentially as solvent-separated ion pairs or solvent-separated dimers or both in 2-methoxyethanol solutions, thus manifesting the signal for the "spectroscopically free" anion in the infrared spectra.

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