Ionic Association of Potassium and Tetrabutylammonium Thiocyanate Salts in Binary Mixtures of γ-Butyrolactone and *N,N*-Dimethylacetamide at 298.15 K and 308.15 K

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Solvation consequences of potassium thiocyanate (KSCN) and tetrabutylammonium thiocyanate (Bu₄NSCN) in γ-butyrolactone (GBL), *N,N*-dimethylacetamide (DMA) and their binary mixtures in concentration range (0.01-0.001) mol Kg⁻¹ of 0, 25, 50, 60, 80 and 100 mol% DMA at T = 298.15 K and 308.15 K have been studied using conductometric study and some samples of KSCN in GBL + DMA binary mixtures of different electrolytic concentrations at ambient conditions studied by FTIR spectroscopic methods. The Shedlovsky equation has been used to elucidate the data in terms of the limiting molar conductances (Λ_o), ion-pair association constants (K_A). The Walden products ($\Lambda_o \eta_o$), solvated radii (r_r) and standard free energies of association (ΔG_A^o) were further evaluated in terms of solvation of ions. The reference electrolyte tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) was used to determine the limiting molar ionic conductances. In pure solvents and their binary mixtures, electrolytes showed a strong association. The K⁺ ions have greater solvation in GBL than in DMA observed on basis of solvated radii in GBL + DMA binary solvent mixtures at both experimental temperatures. The study demonstrates that the ion-solvent interactions decrease on enhancing the temperature. The FTIR analysis was applied to obtain information about molecular as well as ionic association of KSCN in GBL + DMA binary mixtures at the ambient conditions, which has provided the information on structuring infrared modes of vibrational stretching frequencies according to the nature of the solvents or the cations. Shifting of vibrational frequencies of several functional groups of DMA and GBL in binary mixed solvents has been observed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Keywords: Solvation, Molar conductance, Potassium thiocyanate, Tetrabutylammonium thiocyanate, Bathochromic shift, Binary mixtures.

INTRODUCTION

Studies of the physico-chemical properties of electrolytic solutions in different solvents have a great applicability to identify the ion-solvation behaviour. In a wide variety of industrial and chemical processes, knowledge of the conductance and IR spectra of electrolytic solutions in both aqueous and non-aqueous media is extremely useful [1-3]. It also provides useful information on the structure of the solution as well as about many interactions taking place within it [4-6]. For chemical researchers, the conductance measurements of electrolytes in various solvent systems are of great importance. By incorporating electrolytes into binary solvent mixtures, high energy density batteries have also improved [7,8]. Different interactions of electrolytes in protic and aprotic solvents as well as in their binary mixtures have been the focus of conductometric study [9-11].

Ions are preferentially solvated by electrolytic solutions and binary solvent mixtures. The conductometric method is an important approach that is used to analyze the ionic association, solvation behaviour and physico-chemical properties of electrolytes in pure as well as in binary mixed solvents. Even in the current scenario, these findings are still interesting [7,12]. Several comprehensive investigations [4,13-15] have evaluated the thermodynamic and transport properties of *N,N*-dimethylacetamide (DMA) solvent. γ-Butyrolactone (GBL) and *N,N*-dimethylacetamide (DMA) are the polar aprotic solvent in nature and its binary mixture with water and organic solvents are found to be very useful in the field of high energy density batteries, electrical double layer capacitors pharmaceutical industries, hydrometallurgy *etc.* [16-18]. There have been several numbers of studies regarding the conductivities of non-aqueous electrolytes containing the solvent at high concentrations [19,

20]. These studies revealed several forms of interactions, such as hydrogen bonding, electrostatic and hydrophobic, which enable organic macromolecule conformations.

The IR spectroscopy has a broad application to determine the structure and dynamics of salt solutions [1,21,22]. Dipolar aprotic solvents have broad applications, as a basis for non-electrolytes in chemical sources of current and supercapacitors because of their ability to solvate metal cations. Potassium salts like KPF_6, $KClO_4$, KBr, KBF_4 and $KN(SO_2F)_2$ are solvated in carbonate ester solvents [23,24]. It is believed that choosing the proper electrolyte solution is more significant to enhance the long life stability for K^+ ion batteries [8]. Study on potassium salt solutions in aprotic solvents is still a promising area of research. High-energy-density batteries, which may make use of these electrolyte solutions, are a current topic now [20]. As a result of the emerging markets for grid-scale battery applications, the demand for high energy density technologies, light weight and cost-effectiveness is rapidly increasing.

In the present work, the conductance study of KSCN and Bu_4NSCN has been carried out in pure solvents and their binary mixtures in the concentration range $(10-100) \times 10^{-3}$ mol kg^{-1} at 298.15 K and 308.15 K. FTIR spectral studies investigate were also applied to the solvation of KSCN using different concentrations (0.1-1.0 M) of molal ratio 4:4:4 with GBL + DMA binary solvent mixtures at room temperature (298.15 K) and ambient pressure [25].

EXPERIMENTAL

γ-Butyrolactone (GBL) (99.5% GC grade, TCI, Japan) was purified by the procedure suggested by Wang *et al.* [26] and *N,N*-dimethylacetamide (DMA) (99.5%, GC grade, TCI, Japan) was purified by the procedure suggested by Das *et al.* [27]. Potassium thiocyanate (KSCN) (Alfa Aesar, ACS grade 99%) was saturated twice in water and then dried at 150 ºC under vacuum [28]. Tetrabutylammonium thiocyanate (Bu_4NSCN) (TCI Japan, assay > 99%) was dried under vacuum over P_2O_5 at 45 ºC for 24 h. Reference electrolyte tetrabutyl-ammonium tetraphenylborate (Bu_4NBPh_4) was prepared by standard method [12].

Binary solvent mixtures were prepared by combining a based on requirements of GBL and DMA using experimental density conversions at 298.15 K and 308.15 K. Using the stock solution prepared each electrolytic concentration were prepared with dilution. The calculation of density (ρ) and viscosity (η) data of the samples have been already reported in previous works [29-31].

The densities (ρ) and viscosities (η) of the GBL and DMA were determined and are presented in Table-1 agreed well with the literature [20,32-35] at 298.15 and 308.15 K, respectively.

Rohdewald and Moldner's approach [36] was used to calculate the relative permittivities (ϵ_o) of binary solvent mixtures (GBL + DMA). The physical properties of the binary mixtures of different mol% DMA at experimental temperatures are reported in Table-1. Molar conductance measurements of potassium thiocyanate and tetrabutylammonium thiocyanate in DMA, GBL and GBL + DMA binary solvent mixtures were performed at 1000 Hz and 298.15 K ± 0.001 K by digital

TABLE-1
PHYSICAL PROPERTIES OF GBL, DMA (RELATIVE PERMITTIVITY (ε), DENSITY (ρ) (g cm^{-3}) AND VISCOSITY (η) (cP) VALUES) OF GBL + DMA BINARY MIXED SOLVENT SYSTEMS

Solvent (mol%)	Property	298.15 K	308.15 K
0	ε	41.68	40.48
	ρ	1.12458 [20,32,33]	1.12035 [20,32,33]
	η	1.72452 [20,32,33]	1.62892 [20,32,33]
25	ε	40.95	39.61
	ρ	1.09500	1.09490
	η	1.40254	1.18600
50	ε	40.21	38.74
	ρ	1.00148	1.00141
	η	1.18119	1.02210
60	ε	39.72	38.39
	ρ	0.99337	0.99330
	η	1.02934	0.96623
80	ε	39.34	37.74
	ρ	0.97080	0.97067
	η	0.94432	0.83174
100	ε	38.75	37.00
	ρ	0.93604 [34,35]	0.92643 [34,35]
	η	0.92790 [34,35]	0.80939 [34,35]

conductivity meter (Model NDC-736, Naina Electronics, New Delhi, India), having cell constant precision of 0.2%. The conductance cell was calibrated using KCl solution and conductivity water by the method suggested by Linde *et al.* [37].

Using the ABB Horizon (MB 3000) spectrometer with signal to noise ratio of 50,000:1, all the FTIR spectra were collected in the 4000-400 cm^{-1} region with a resolution of 4 cm^{-1}. FTIR spectra of samples with KSCN concentrations from 0.1-1.0 m in GBL + DMA (1:1), KSCN:DMA (1:1) and KSCN:GBL:DMA (4:4:4) solvent solutions were recorded. The sample collection point was cleaned with acetone before measuring the samples.

RESULTS AND DISCUSSION

The physical properties of γ-butyrolactone (GBL) and *N,N*-dimethylacetamide (DMA) and their binary mixtures at 298.15 K and 308.15 K are listed in Table-1. The specific conductance of the studied electrolytic solutions of KSCN, Bu_4NSCN and Bu_4NBPh_4 in DMA, GBL and their binary mixtures at 298.15 K and 308.15 K in the concentration range of $(10-100) \times 10^{-3}$ mol kg^{-1} in 0, 25, 50, 60, 80 and 100 mol% DMA were measured as in the procedure already reported earlier [29]. The molar conductances for KSCN, Bu_4NSCN and Bu_4NBPh_4 electrolytic solution systems were calculated by using eqn. 1:

$$\Lambda = \frac{1000K}{C} \qquad (1)$$

where, C is concentration (mol/L) and K is specific conductance of the solutions.

To obtain limiting molar conductances (Λ_o), plot (Λ *vs.* ($\sqrt{C}$) at extrapolation of ($\sqrt{C}$) for the electrolytes [38] from eqn. 2. The conductance data were analyzed by Shedlovsky equation and are tabulated in Table-2 at 298.15 and 308.15 K.

		0 Mol%		25 Mol%		50 Mol%		60 Mol%		80 Mol%		100 Mol%	
Salt	Temp. (K)	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A
Bu₄NBPh₄	298.15	41.09	26.4	54.34	44.8	56.53	13	60.95	14	68.32	60.2	71.83	20.13
	308.15	50.00	21.3	59.93	27.69	63.83	14	68.94	108	75.45	38.8	84.96	27.28
KSCN	298.15	54.38	34.4	61.61	73.68	69.08	67	71.51	130	73.58	89.99	85.14	127.73
	308.15	59.13	41.3	68.59	31.60	73.92	37	79.06	51.8	84.71	87.40	96.43	144.35
Bu₄NSCN	298.15	48.99	25.5	54.96	28.76	59.51	32.30	66.65	57.9	69.12	86.70	70.77	82.22
	308.15	57.75	28.9	61.12	37.67	67.35	45.11	68.08	73	71.73	88.70	78.53	67.85

TABLE-2
LIMITING MOLAR CONDUCTANCES (Λ_o) (S cm² mol⁻¹) FOR SOME IONS IN
γ-BL + DMA BINARY MIXED SOLVENT MIXTURES AT 298.15 AND 308.15 K

$$\Lambda = \Lambda_o - S\sqrt{C} \qquad (2)$$

where Λ_o is intercept and S is the slope of straight line which was obtained by the plot between Λ and $(\sqrt{C})$.

Table-2 lists the limiting molar conductances (Λ_o) and ion-pair association constants (K_A). These values were estimated using least squares with Shedlovsky equation [39]. The Shedlovsky equation is as follows:

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_o} + \frac{C\Lambda S f_{\pm}^2 K_A}{\Lambda_o^2} \qquad (3)$$

$$S = \left[\frac{\beta(C\Lambda)^{1/2}}{2\Lambda_o^{3/2}} + \left(1 + \frac{\beta^2 C}{4\Lambda_o^3}\right)^{1/3} \right]^2 \qquad (4)$$

$$\beta = \frac{8.204 \times 10^5 \Lambda_o}{(\varepsilon T)^{3/2}} + \frac{82.5}{\eta(\varepsilon T)^{1/2}} \qquad (5)$$

$$\log f_{\pm} = \frac{1.8246 \times 10^6 (C\alpha)^{1/2} / (\varepsilon T)^{3/2}}{1 + 50.29 \times 10^8 R(C\alpha)^{1/2} / (\varepsilon T)^{1/2}} \qquad (6)$$

$$\alpha = \frac{S\Lambda}{\Lambda_o} \qquad (7)$$

where Λ is molar conductance at concentration C, (Λ_o) is molar conductance at infinite dilution, S is Shedlovsky's function, α is degree of dissociation for electrolytes, K_A is association constant, $f_{\pm}$ is mean ionic activity coefficient of the electrolyte, β is Onsager slope. At this R is ion-size parameter (cm), which is identical as the Bjerrum critical q distance [40] suggested by Justice [41] and is given by relation:

$$R = q = \frac{e^2}{2\varepsilon kT} \qquad (8)$$

where, ε is the dielectric constant of the solvent.

The study reveals that the molar conductance of the electrolytes is lower when DMA is present in a smaller proportion to the GBL + DMA binary mixtures. A decrease in conductance with increasing solvent system concentration can most likely be interpreted as an expansion of the solvated ion due to the activation of solvent molecules forming sheath. From the overview, Table-3 shows that the limiting molar conductances for the KSCN was found to be greater those of Bu₄NSCN and reference electrolyte Bu₄NBPh₄ in all the binary mixtures studied here at 298.15 K and 308.15 K. This agrees with the result obtained in other solvents [1,42].

Table-3 reveals that KSCN in GBL, DMA and their binary mixtures has a higher limiting molar conductance (Λ_o) than the Bu₄NSCN and Bu₄NBPh₄. The Λ_o values increase with the increase in DMA composition in GBL + DMA binary mixtures. The investigation from Λ_o reveals that K⁺ ions are more solvated than bulkier alkyl size group (Bu₄N⁺) rendering to high value of conductance, which enhances with the decrease in relative permittivity and viscosity of the GBL + DMA binary mixtures. The result obtained from the conductivity data of K⁺ ions and Bu₄N⁺ with common anion is following the work of Bijan *et al*. [1,42-44]. This can also be understood in terms of how ions tend to solvate first. The limiting molar conductances (Λ_o) of KSCN, Bu₄NSCN and Bu₄NBPh₄ in same mixtures were observed at 308.15 K and observed that the Λ_o values increase with enhancing the temperature from 298.15 to 308.15 K. The study shows that at 308.15 K, potassium salt (KSCN) is less solvated than those of terabutylammonium salts, which indicate weaker ionic interactions and ion-solvent interactions, affected by increase in temperature for both the ions. The structure of DMA and GBL also favours the observation [45]. Due to the presence of polar nature of carbonyl group (C=O) in both molecules, K⁺ ions are preferentially solvated by GBL than DMA, on the basis of result obtained from limiting molar conductance (Λ_o) values. As the Λ_o values of the electrolytic solutions increases with the increase in temperature, this is due to the decrease in viscosity of the solvent media and increase in ion mobility and an decrease in solvation with increasing DMA content in binary mixtures of GBL and DMA.

The association constant for ion pairs (K_A) are listed in Table-3 for studied electrolytes containing 0, 25, 50, 60, 80 and 100 mol% DMA at the studied temperatures. At 298.15 K and 308.15 K, the association constants for ion-pairs of the investigated salts in all binary solvent mixture compositions remains dissociated as the fraction of DMA increase in GBL + DMA binary mixtures. The K_A value of KSCN, Bu₄NSCN and Bu₄NBPh₄ indicates that these salts are slightly associated in both solvents and in their binary mixtures at 298.15 K and 308.15 K temperatures. This means that a significant amount of the utilized electrolytes remain dissociated in the GBL + DMA binary mixtures. This could possibly be owing to the low relative permittivities of the binary solvent systems employed. The K_A value for KSCN is found to be greater than those of Bu₄NSCN and Bu₄NBPh₄ in GBL DMA as well as in their binary mixtures shows the higher conductance of KSCN than those of Bu₄NSCN and Bu₄NBPh₄.

TABLE-3
FORMATION CONSTANT FOR LIMITING MOLAR CONDUCTANCE (Λ_o) (S cm² mol⁻¹)...

Mol% DMA	Temp. (K)	Λ_o (S cm² mol⁻¹)	K_A (dm³mol⁻¹)	$\Delta G°_A$ (Kj mol⁻¹)	$\Lambda_o\eta_o$ (Scm² mol⁻¹)	R_H (Å)
			KSCN			
0	298.15	54.38	34.4	-8.7702	93.77831	0.008744
	308.15	59.13	41.3	-9.5327	96.31686	0.008514
25	298.15	61.61	73.68	-10.6583	86.41049	0.009490
	308.15	68.59	31.6	-8.84685	81.34774	0.010080
50	298.15	69.08	67	-10.4227	81.59661	0.010049
	308.15	73.92	37	-9.25102	75.55363	0.010853
60	298.15	71.51	130	-12.0657	73.6081	0.011140
	308.15	79.06	51.8	-10.1131	76.39014	0.010734
80	298.15	73.58	89.99	-11.1539	69.48307	0.011801
	308.15	84.71	87.4	-11.4532	70.4567	0.011638
100	298.15	85.14	127.73	-12.0221	79.00141	0.01038
	308.15	96.43	144.35	-12.7387	78.04948	0.010506
			Bu₄NSCN			
0	298.15	48.99	7.8	-8.0281	84.48326	0.009706
	308.15	57.75	28.9	-8.61802	94.06898	0.008717
25	298.15	54.96	28.76	-8.32632	77.0836	0.010638
	308.15	61.12	37.67	-9.297	72.48832	0.011312
50	298.15	59.51	32.3	-8.61406	70.29262	0.011666
	308.15	67.35	45.11	-9.75877	68.83844	0.011912
60	298.15	66.65	57.9	-10.0608	68.60551	0.011952
	308.15	68.08	73	-10.992	65.78094	0.012466
80	298.15	69.12	86.7	-11.0616	65.2714	0.012563
	308.15	71.73	88.7	-11.4911	59.66071	0.013744
100	298.15	70.77	82.22	-10.9301	65.66748	0.012487
	308.15	78.53	67.85	-10.8045	63.5614	0.012901
			Bu₄NBPh₄			
0	298.15	41.09	26.4	-8.1140772	70.85971	0.011572
	308.15	50.00	21.3	-7.8362824	81.445	0.010068
25	298.15	54.34	44.8	-9.4249862	76.21402	0.010759
	308.15	59.93	27.69	-8.5084489	71.07698	0.011537
50	298.15	56.53	13	-6.3580455	66.77267	0.012280
	308.15	63.83	14	-6.7611569	65.24064	0.012569
60	298.15	60.95	14	-6.5417457	62.73827	0.013070
	308.15	68.94	108	-11.995429	66.6119	0.012310
80	298.15	68.32	60.2	-10.157388	64.51594	0.012710
	308.15	75.45	38.8	-9.372723	62.75478	0.013067
100	298.15	71.83	20.13	-7.4419386	66.65106	0.012303
	308.15	84.96	27.28	-8.4702309	68.76577	0.011925

(Table header note, continued: ION-PAIRS (K_A) AND ASSOCIATION, FREE ENERGY ($\Delta G°_A$), WALDEN PRODUCT ($\Lambda_o\eta_o$), HYDRODYNAMIC RADII FOR USED SALTS IN GBL + DMA BINARY MIXTURES AT 298.15 AND 308.15 K)

With the decreasing dielectric constant of binary solvent mixtures at different temperatures, the association constants K_A for ion-pairs of studied salts show that the effect of ion-solvent and molecular interactions is important for ion-pair formation process and which also affects the ionic mobility of the solvated ion [46]. It provides the information about ionic association and ion-solvent interactions. This behaviour shows that the decrease in relative permittivity is proportional to binary solvent mixture compositions [47,48].

At 298.15 K and 308.15 K, the standard free energy of association ($\Delta G°_A$) values for KSCN, Bu₄NSCN and Bu₄NBPh₄ salts in utilized solvent system compositions were determined. K_A values derived from conductance data are largely dependent on the solutions' dielectric constant. Eqn. 9 was used to compute the change in the standard free energy ($\Delta G°_A$) values.

$$\Delta G°_A = RT \ln K_A \qquad (9)$$

where, R is universal gas constant and taken the value as 8.314 J⁻¹ K⁻¹ mol⁻¹.

For each solvent system, the calculated values are listed in Table-3. All the results are negative and in the range of 3-13 kJ mol⁻¹ entirely all over the solutions. The negative standard free energy of association ($\Delta G°_A$) values indicate that the association process in all used electrolytic solutions is spontaneous in nature. This result reveals the extent to which all ions in binary mixtures are preferentially solvated. In binary mixture of GBL and DMA, the tendency for ion pair formation increases significantly with increasing DMA concentrations at both temperatures. It also indicates about the strong ion-pair formation of all used salts solutions in binary mixtures at both temperatures are accordance with the results investigated by Barthel *et al.* [49] and Hazra *et al.* [2,27]. The association constants for ion-pairs (K_A) do not represent all types of interactions.

Table-2 also reveals that Bu$_4$NBPh$_4$ has the lowest GBL association, followed by KSCN, Bu$_4$NSCN and DMA. In pure GBL, Bu$_4$NSCN has a higher ion-solvent inter-action those of Bu$_4$NBPh$_4$ and DMA, with KSCN having the highest GBL/DMA association. However, the study of solvated radii indicates that the solvation of K+ ion is greater in GBL than in DMA and their binary mixtures for KSCN confirms the observation because decreasing viscosity should enhance limiting molar conductance (Λ_o) of the electrolytes in the non-aqueous binary mixtures [50].

Walden product ($\Lambda_o\eta_o$) of the ions are usually employed to explain the ion solvent interactions. From the overview of Table-3 and Fig. 1, the variation in Walden product ($\Lambda_o\eta_o$) of the cations (in the order: K$^+$ than Bu$_4$N$^+$) and electrolytes are decreasing with the increasing in DMA composition in used binary solvent mixtures at 298.15 K and 308.15 K, indicating change of solvation [51]. This product ($\Lambda_o\eta_o$) is found to be constant at a particular condition and are decreasing with the increase in temperature. The plot of Walden product ($\Lambda_o\eta_o$) vs. DMA mol% at 298.15 K and their binary mixtures shows that the Walden product ($\Lambda_o\eta_o$) arbitrarily decreases with the solvent composition of DMA in GBL + DMA binary mixtures. Because the Walden product ($\Lambda_o\eta_o$) is dependent upon the viscosity and limiting molar conductance of the electrolytes, these are inversely proportional to each other. Since, the molar conductances of electrolytic solutions are only dependent on the ion mobility, their product with respect to medium viscosity should not be affected by the solvent type [52,53].
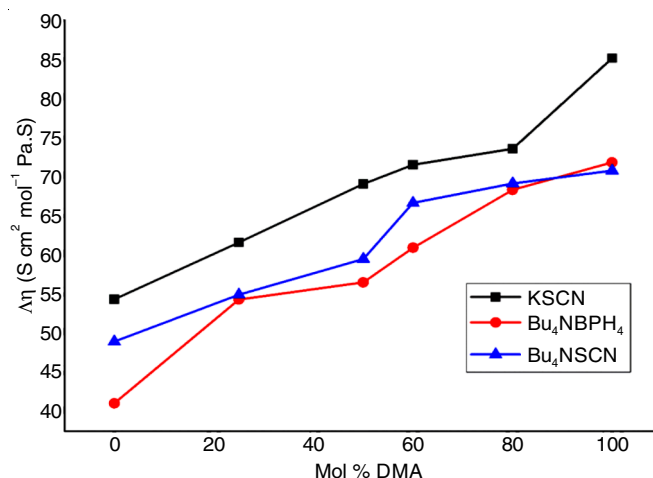

Fig. 1. Plot of limiting molar conductance *versus* Walden product $\Lambda_o\eta_o$ of DMA mol% at 298.15 K

The Walden product values were calculated for KSCN, Bu$_4$NSCN and Bu$_4$NBPh$_4$ electrolytes and ions in GBL + DMA binary mixtures using eqn. 10 and are reported in Table-3.

$$\lambda_o\eta_o = 0.82\left(\frac{1}{r_s^+} + \frac{1}{r_s^-}\right) \qquad (10)$$

From an examination of Walden products, it was determined that the Walden products decrease as the temperature is raised. At extremely low DMA compositions, these ions (K$^+$) are found to be more solvated by DMA rather than GBL. The decrease in Walden product ($\Lambda_o\eta_o$) reveals the preferential solvation of ions (K$^+$, Bu$_4$N$^+$, Ph$_4$B$^-$ and SCN$^-$) when the composition of DMA in binary GBL + DMA mixtures increases. However, diminishing of the Walden product may be a result of the Zwanzig solvent relaxation effect [54]. The inclination is noticed with the change in temperature, Walden product values change based on the solvent composition and electrolyte characteristic [55].

The limiting ionic conductance ($\Lambda_{\pm}^{\circ}$) of the standard electrolytes was proposed by Gill [56] using (Bu$_4$NBPh$_4$) as reference electrolyte from eqns. 11 and 12 for this purpose.

$$\frac{\lambda_{\pm}^{\circ}(Bu_4N^+)}{\lambda_{\pm}^{\circ}(Ph_4B^-)} = \frac{5.35 - (0.0103\varepsilon + r_y)}{5.00 - (0.0103\varepsilon + r_y)} \qquad (11)$$

$$\lambda_{\pm}^{\circ}(Bu_4N^+) + \lambda_{\pm}^{\circ}(Ph_4B^-) = \Lambda^{\circ}(Bu_4NBPh_4) \qquad (12)$$

Kohlrausch's law was used to obtain the values of the limiting ionic conductances of Bu$_4$N$^+$ and Ph$_4$B$^-$ in DMA and GBL-DMA binary solvent compositions, which were then used to calculate the Λ° values of Bu$_4$NBPh$_4$. Using eqns. 11 and 12, the limiting ionic conductivity ($\lambda_{\pm}^{\circ}$) in pure DMA and GBL + DMA binary solvent mixtures was also calculated and is shown in Table-4.

As a result of the eqn. 13, Gill [56] devised a method for estimating the solvated radii of the ions K$^+$, Bu$_4$N$^+$, Ph$_4$B$^-$ and SCN$^-$ in non-aqueous solvents using the limiting ionic conductance ($\Lambda_{\pm}^{\circ}$) values of the electrolytes.

$$r_i = \frac{|Z|F^2}{6\pi\eta N\lambda_i} + (0.0103\varepsilon + r_y) \qquad (13)$$

In Table-5, the r_i values and crystallographic radii for various ions are shown (r_c for K$^+$ = 0.133; Ph$_4$B$^-$ = 0.53, Bu$_4$N$^+$ = 0.50; SCN$^-$ = 0.25 and ClO$_4^-$ = 0.292 nm) [56,57]. The Z and r_i are the ion's effective charge and radius in solution, respectively. *N,N*-Dimethylacetamide and its binary mixture of GBL + DMA

TABLE-4
LIMITING ION CONDUCTANCE ($\Lambda_{\pm}^{\circ}$) (S cm^2 mol^{-1}) FOR SOME IONS IN GBL + DMA AT 298.15 AND 308.15 K

Ions	Temp. (K)	mol% DMA					
		0	25	50	60	80	100
Bu$_4$N$^+$	298.15	21.37	28.19	29.32	31.61	35.44	37.2
	308.15	25.94	31.09	33.11	35.76	39.13	44.06
K$^+$	298.15	26.76	31.83	38.89	44.02	39.90	51.57
	308.15	27.42	41.36	39.68	45.74	52.11	61.96
Ph$_4$B$^-$	298.15	19.82	26.15	27.21	29.34	32.88	34.53
	308.15	24.06	28.84	30.72	33.18	36.32	40.90
SCN$^-$	298.15	27.62	26.77	30.19	35.04	33.68	33.57
	308.15	31.71	23.87	33.24	32.32	32.60	34.47

TABLE-5
SOLVATED RADII (r_i) OF SOME IONS IN GBL + DMA MIXTURES AT 298.15 AND 308.15 K

Ions		T (K)	r_i (nm)					
			0	25	50	60	80	100
Bu_4N^+	(r_c = 0.50)	298.15	0.537	0.528	0.523	0.519	0.515	0.508
		308.15	0.521	0.515	0.508	0.504	0.499	0.489
Ph_4B^-	(r_c = 0.53)	298.15	0.538	0.529	0.525	0.521	0.517	0.510
		308.15	0.523	0.517	0.510	0.506	0.501	0.491
K^+	(r_c = 0.133)	298.15	0.532	0.525	0.517	0.512	0.512	0501
		308.15	0.520	0.510	0.504	0.499	0.493	0.482
SCN^-	(r_c = 0.25)	298.15	0.532	0.529	0.522	0.517	0.516	0.510
		308.15	0.518	0.522	0.508	0.507	0.504	0.495

r_c represents the crystallographic radii of the solvated ion

have r_y values of 0.085 nm for non-associated solvents and 0.113 nm for associated solvents [56]. The adverse change of Robinson-Stokes' law proposed by Gill [56]. Eqn. 13 from which actual solvated radii of the several ions in aprotic solvents can be evaluated and this was serves as the foundation for most ionic conductance evaluations in aprotic solvents. This law states that the limiting Walden product (the limiting ionic conductance solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and as a result, is constant under normal conditions. The solvated radii (r_i) that we determined for K^+, Bu_4N^+, Ph_4B^- and SCN^- ions in GBL + DMA binary solvent mixtures are listed in Table-5.

For K^+ ions, the solvated radii were found to be greater than their crystallographic radii, which suggests that K^+ ions were significantly more solvated than those of SCN^-, Bu_4N^+ and BPh_4^- ions in GBL, DMA and its binary mixtures containing 25-80 mol% DMA. The solvated radii of SCN^- ions were found to be very close to each other but greater than their crystallographic radii, which indicates that SCN^- ions were less solvated than K^+ in the used solvent system at both experimental temperatures. The solvated radii of Bu_4N^+ and BPh_4^- ions were found to be very close to that of crystallographic radii due to the bigger size of the alkyl groups. These observations indicate that Bu_4N^+ and Ph_4B^- ions are poorly solvated than small size K^+ ions in GBL + DMA binary solvent mixtures.

Solvated radii values decrease with increase in temperature, which indicates that the solvation of ions decreases. The K^+ and SCN^- ions shows greater solvation than Bu_4N^+, Ph_4B^- in GBL + DMA binary solvent mixtures because of electrostatic interactions at higher temperatures (298.15-308.15 K). The electrostatic interactions between the solvated ions and solvent molecules surrounding the ions fall in magnitude suggesting decrease in solvation with temperature.

In GBL + DMA binary solvent mixture system, the molar conductances of the electrolytes under investigation increases as the size of the alkyl group increases, in concomitant to the conductance behaviour of the alkali metal cations, as tetrabutylammonium salts are characterized by their low surface charge density

In GBL + DMA binary solvent mixture system, the (Λ_o) values of the KSCN and Bu_4NSCN increases as the size of the alkyl group increases, in accordance with the conductance behaviour of the alkali metal cations, since tetrabutylammonium salts possess low surface charge density [58]. The limiting

ionic conductivity ($\lambda_{\pm}^o$) for the K^+, SCN^-, Bu_4N^+ and BPh_4^- ions in pure GBL, pure DMA and its binary mixtures of 25-80 mol% DMA were calculated using reference electrolytes following the method suggested by Das *et al.* [27].

The alkali metal ions electrolyte transport features, such as ionic conductivity and transference number, have a significant impact on battery rate performance. This means that K^+ and SCN^- ions have large solvation in DMA + GBL binary mixtures. It may be concluded that these KSCN electrolytes are highly associated in both solvents, in their binary mixtures and that solvation of the SCN^- ions get weaker the movement of ion-pair formation.

FTIR studies: Ion-solvent interactions in pure solvents as well as their binary mixtures can be studied qualitatively and quantitatively by using FTIR spectroscopy. It shifts the carbonyl group, cyclic oxygen (C-O), C-C, N-CH_3 deformation band, O=C-N stretching vibrational frequencies and SCN^- interactions with solvents in binary/tertiary mixtures of KSCN salt of varying electrolytic concentrations of GBL + DMA (1:1), KSCN:DMA (1:1) and KSCN:GBL:DMA (4:4:4) ranges from 0.1-1.0 molal solution were observed by FTIR spectroscopy [57,58].

Liquid binary mixture was examined by McDermott [59] for its IR and Raman spectroscopic properties. These studies were used to assign the bands in this article. Since binary liquid is a poor anion solvent, the shifts in the GBL spectra were considered to be the result of a K^+-BL interaction [26]. To explore the dipole-dipole and ion-dipole interaction in salt solutions in binary mixtures due to solvent-solvent and ion-solvent interactions reveal the structural changes in the binary mixtures of DMA and GBL, the FTIR absorption spectroscopic studies have been performed in the ambient condition.

The influence that monoatomic cations have on the DMA spectrum can be comprehended without much effort. Because lithium ion is less massive than Na^+ ion, the polarizing impact that it exerts on the electron density of the bond where it interacts is far more pronounced. In this particular instance, the location of the site for cation solvation is quite obviously at the electronegative oxygen atom of the -C=O dipole, which is already reported [31]. It is more difficult to interpret the data for the monoatomic anions. Two methyl groups bound to nitrogen have magnitude of charges, when the hydrogen charges are added to the carbon charges in a methyl group. As a result, these methyl groups are great choice for anion solvation. The methyl group imparts a small amount of negative charge to

the carboxylic carbon. The electronegative oxygen in the C=O and C-O group is expected to be the site for cation solvation, as is commonly assumed. In addition, it is not obvious if the electropositive carbon in the same group is available for anion solvation [22,60]. The size of the cation obviously influences this. Therefore, FTIR spectrum of each studied electrolytic concentrations of KSCN + GBL + DMA binary mixtures of molal ratio 1:1:1, reported in Fig. 2.
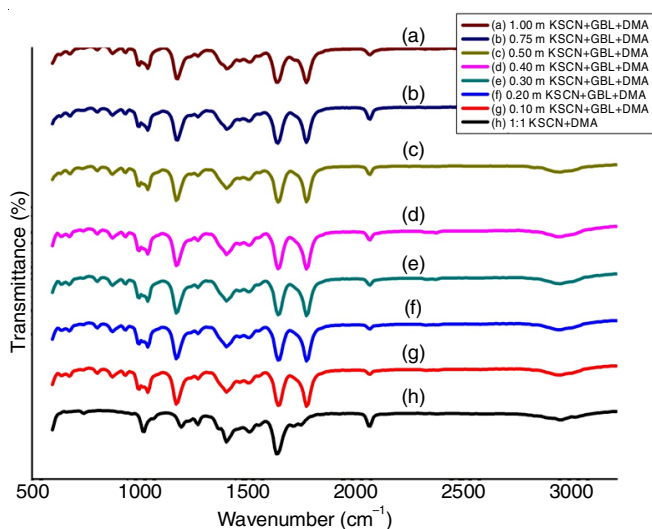

Fig. 2.   FTIR spectra of potassium thiocyanate in binary solvent mixtures of GBL + DMA (KSCN + GBL + DMA)

Interactions of KSCN with GBL + DMA: The FTIR spectra of KSCN have been studied in GBL + DMA binary mixed solvents. In the FTIR spectra of GBL + DMA, the band at 2932 cm⁻¹ shifted to 2939 cm⁻¹ is assigned for C-H stretching frequency of *cis*-methyl group indicates strong ion-solvent interactions with K⁺ ions. The band corresponds to 1396 cm⁻¹ shifted to 1404, 1265 shifted to 1273 and 1034 cm⁻¹ are assigned to several stretchings such as ν(C-N), ν(N-CH₃) and ν(NC-CH₃) deformation, respectively [61] (Fig. 2). The ν(O=CNC) torsion is attributed to the band at 671 cm⁻¹, while ν(C=O) stretching was observed at 1643 cm⁻¹. Putting KSCN to GBL + DMA binary solvent solutions might change the FTIR spectra due to K⁺−DMA interaction. The band at 2939, 1265 cm⁻¹ shifts when KSCN was added to DMA + GBL binary mixtures. The IR peaks at 1636, 1396 and 679 cm⁻¹ exhibited a frequency shift. The ν(C=O) of pure DMA [61] shifts to 1643 cm⁻¹ in GBL + DMA binary mixtures and 1636-1628 cm⁻¹ for 0.1 m KSCN to 1.0 m KSCN (4:4:4). This shift in frequency may be attributed for the interaction or solvation of K⁺ ion by C=O group of DMA. Such frequency shift may be due to K⁺ ion solvation by C=O group of DMA.

From the peaks at 2939 cm⁻¹ and 2816 cm⁻¹ correspond to the (C-C) ring stretching and the peak at 1759 cm⁻¹ corresponds to νₛₜ(C=O) in the FTIR spectrum of GBL + DMA, KSCN interactions with GBL were observed. The addition of KSCN to binary solvent mixture of GBL and DMA did not result in a significant frequency shift in the C-C ring stretching.

The bands at 2939 and 1265 cm⁻¹ exhibit a considerable frequency shift when KSCN was added to DMA + GBL binary

mixture. Only at the carbonyl (C=O) stretching area, which was changed from 1759 to 1767 cm⁻¹, there a bathochromic (red) frequency shift. Increased electrolytic KSCN concentrations in GBL + DMA binary solvent mixture affect the frequency shift, indicating a moderate interaction with GBL. According to Sarkar *et al.* [62], KSCN may exhibit some degree of ion-pair creation.

Conclusion

The conductometric analyses of the physico-chemical properties of Bu₄NSCN, KSCN and reference electrolytes in GBL + DMA binary mixture proved the preferential solvation of ions by the result obtained from the analysis of standard free energy of association, Walden product and solvated radii at different temperatures. The results indicated that K⁺ and SCN⁻ ions were solvated by solvents at 298.15 K and 308.15 K. However, the conductometric study also revealed that K⁺ ions are preferentially more solvated than Bu₄N⁺ in GBL + DMA binary mixtures. However, these values were influenced by temperature; as the temperature rose, the solvated radii (rᵢ) values decreased which indicates about the weak ionic and molecular interactions of K⁺, SCN⁻ ions in GBL + DMA binary mixtures and hence, solvation decreases. This investigation shows that the ion-solvent interaction decreases when the temperature rises from 298.15 K to 308.18 K. The formation of the ion pairs, aggregations and the K⁺-DMA solvent complex was confirmed in GBL + DMA mixed binary solvent by FTIR studies. The different stretching frequencies *viz.* (C=O) stretching, O=C-N deformation bands, (N-CH₃) stretching shows hypsochromic (blue shift) and bathochromic shift (red shift) as well as SCN⁻ ions shows the ionic association and ion-aggregation with the increase in electrolytic concentrations of KSCN in GBL + DMA binary mixtures. However, the FTIR studies under different electrolytic concentrations of KSCN in GBL + DMA binary mixtures suggests about the ion-solvent and molecular interactions such as ion-dipole, dipole-dipole interactions. Both studies reveal that K⁺ has higher solvation than Bu₄N⁺ in GBL + DMA mixed binary solvent at all concentrations.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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