Indian Journal of Chemistry
Vol. 61, March 2022, pp. 245-253

Ion association and solvation characteristics of Li^+, Na^+ and K^+ ions in binary mixtures of 2-Aminoethanol + N,N-Dimethylacetamide probed by conductometry study at 298.15 K and 308.15 K

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Received 01 September 2021; revised and accepted 10 February 2022

Molar conductances (Λ) of $LiClO_4$, $NaClO_4$, KSCN, Bu_4NSCN, Bu_4NClO_4 and Bu_4NBPh_4 in binary solvent mixtures of 2-aminoethanol (AE) and N,N-dimethylacetamide (DMA) containing 25, 50, 60, 80 and 100 mol% DMA have been measured at 298.15 K and 308.15 K in the concentration range of (30-500) × 10^{-3} mol kg^{-1}. The conductance data of the electrolytes in the binary mixtures of AE+DMA are analyzed using Shedlovsky's equation to evaluate limiting molar conductances (Λ_o), association constants (K_A), Walden products ($\Lambda_o\eta_o$), hydrodynamic radii (R_H) and the standard free energies of association (ΔG_A^0). The individual limiting ionic molar conductances ($\lambda^o_\pm$) are obtained using the reference electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) and tetrabutylammonium tetraphenylborate (Bu_4NBPh_4). A modified form of Stokes' law helped to determine the solvated ionic radii (r_i) in solutions and are assessed in the facet of ion-ion, ion-solvent interactions and show structural changes in the binary mixtures. The results has revealed that the solvated radii (r_i) values of Li^+, Na^+ and K^+ ions show preferential solvation of these ions by DMA in AE+DMA binary mixtures and these interactions get weaker with the increase in temperature. Also, the preferential solvation and ion-solvent interactions of these ions in binary mixtures are proved by the analysis of Walden products ($\Lambda_o\eta_o$) and the standard free energies of association (ΔG_A^0) with the effect of temperature.

Keywords: Molar conductance, Solvation, Binary Mixtures, 2-aminoethanol, N,N-dimethylacetamide

Studies of various types of interactions of electrolytes in aqueous and organic protic and aprotic solvents and their binary mixtures have been widely accepted for their greater relevancy in various fields such as industries, organic synthesis and pharmaceuticals and also in the field of technology[1-5]. Several conductometric methods are associated with dissimilar electrolytes in exclusive of organic binary mixtures are being used in high-density power batteries, hydrometallurgy, mechanism of reactions, the ionic association of salts and electrolytes in solution is dependent on the nature of solvent or their binary mixtures.

The binary solvent mixtures and their electrolytic solutions give a conception about solvent-solvent and ion-solvent interactions with preferential solvation of ions. Examinations such types of interactions (in mixed solutions, aqueous and non-aqueous) have been studied as conductometric methods[6-10]. The relative permitivity and viscosity data are largely related to the molar and electrical conductance of an electrolyte and the evaluation of conductance equations was convenient for many electrolytes. Relative permitivity and viscosity assist indecisive the types of interactions and their associations. One of the mathematical equations is the Shedlovsky equation[11-12] which makes it possible to assess the molar conductance at infinite dilution and association constant for ion pairs. Several research groups adopted the Fuoss-Shedlovsky conductivity method for the analysis of a large number of electrolytes in solutions that have ion association phenomenon[13-18]. The study of solvation of different electrolytes in binary mixed solvents of -aminoethanol (AE) and N,N-dimethylacetamide (DMA) is of interest due to the applications of such studies in high energy batteries, hydrometallurgy, supercapacitors, pharmaceutical industries, etc. AE is a very fascinating solvent having its shared use in the pharmaceutical industry and medicines act as a sclerosing agent in addition to its antihistamatic property. Several systematic studies show when DMA, a polar aprotic is mixed with water and organic solvents, it assesses the thermodynamic and transport properties of electrolytic solutions[19-25]. These studies revealed many types of interactions, e.g. hydrogen bonding, electrostatic and hydrophobic interactions. The use of polar solvents and their minute interactions between alcohols and amides were based on relative permitivity and it has broad application in the drug industry[13].

The study is observing the impact of solvation on the physicochemical behaviour of $LiClO_4$, $NaClO_4$, KSCN, Bu_4NClO_4, Bu_4NSCN and Bu_4NBPh_4 in binary mixed solvents of AE + DMA with mol% of 25, 50, 60, 80 and 100 AE in DMA at 298.15 K and 308.15 K, which were measured in range (30-500) $\times 10^{-3}$ mol kg^{-1} by applying Shedlovsky conductivity equation.

Experimental Details

2-Aminoethanol (99.5% (GC grade), TCI Japan) and N, N-dimethylacetamide (99.5%, (GC grade), TCI Japan) were used without further purification. The densities of AE were found to be 1.019 g cm^{-3} at 298.15 K[13,26-27], and 1.00443 gcm^{-3} at 308.15 K[13,26-27]. The densities of DMA were found to be 0.9360 g cm^{-3} at 298.15 K and 0.9264 g cm^{-3} at 308.15 K[28-29]. The viscosities of AE were found to be 18.96 cP at 298.15 K and 12.267 cP at 308.15 K. The viscosities of DMA were found to be 0.9279 cP at 298.15 K and 0.8182 cP at 308.15 K as reported by literature[28-29]. $LiClO_4$ (Hi-Media, AR grade) was twice purified by recrystallization in acetonitrile as reported[30]. $NaClO_4$ (98.5%, Rankem) was purified by recrystallization in acetone whereas KSCN (Alfa Aesar, (ACS Grade 99%) and Bu_4NSCN (> 98%, (AR Grade, TCI Japan) were used without further purification because they already had high purity. The procedure for preparation of reference electrolytes i.e., tetrabutylammonium perchlorate (Bu_4NClO_4) and tetrabutylammoniumtetra phenylborate (Bu_4NBPh_4) was followed as per the method already reported[31].

Molar conductances of the electrolytes were measured in pure DMA and AE-DMA binary solvent mixtures at the frequency of 1000 Hz at 298.15 K ± 0.001 K and 308.15 K ± 0.001 K employing a digital conductivity meter (Model NDC-736, Naina Electronics, New Delhi). The method of the experiment was similar as reported[7,32]. But there is a drawback related to the solubility of both reference electrolytes and salts in pure AE[27]. The general accuracy of the conductance values was found to be correct to ± 0.2%. Cell constant values of the conductivity cell were determined with several concentrations of KCl solutions with conductivity water which was suggested by Füoss and coworkers[6].

A series of concentrations of above-used salts in DMA and AE + DMA mixtures were set by diluting reserve solutions of proper concentrations. The samples were prepared by mass and were reserved in a glass conical flask sealed by a Teflon cap to prevent the absorption of atmospheric moisture. Solutions were prepared by mass, with the help of an electronic balance of company (A&D limited, Japan, Model GR-202) with the accuracy of ± 0.01 mg. The conversion of molality into molarity was using density values. The probable error in the molarity was expected to be less than $\pm 1 \times 10^{-4}$. To get reproducible results, the measurements were repeated twice.

Density measurements of the solvents AE, DMA and their binary solvent mixtures and their salt solutions have been measured with a Borosil glass made pycnometer of capacity 10 cm^3 with a stem of 0.05 cm^3 divisions and was calibrated by double distilled water and some reference solvents such as acetone, DMA, hexane, etc. at T=298.15 and 308.15 K. The weight of the empty pycnometer with a Teflon cap was first taken at desired experimental temperatures (298.15 K and 308.15 K) by using an A & D company limited electronic balance (Japan, Model GR-202) with a precision of ± 0.01 mg. The sample was introduced in the pycnometer through a hypodermic syringe with a precaution that no air bubble was produced. Then the mouth of the filled pycnometer was closed with a Teflon cap and weighed. The pycnometer was immersed in a thermostat maintained at an experimental temperature and the level of the solution was observed in the pycnometer, which was utilized in the calculation of density data. Measurements were performed thrice for every solution at different temperatures. The reproducible results were obtained with the standard minimum error of $\pm 2\times10^{-5}$ $g\cdot cm^{-3}$. The approximate values of densities of pure solvents were found very close to the literature values with uncertainty in the value as $\pm 0.0001 g\cdot cm^{-3}$.

The viscosities of the solution samples were measured using Ubbelohde suspended level viscometer with a fine capillary tube suspended vertically in a glass-walled thermostat maintained to ±0.01 °C. After attainment of thermal equilibrium, the time flow of solutions and solvents were recorded from the stopwatch at experimental temperatures. The cleaning of the used apparatus for both the measurements to obtained viscosities and densities data was done by first using distilled water, then ethanol and finally with acetone to get quick dryness for accurate results.

The experimental molar conductances (Λ) were calculated for all salts in mixed binary solvents at 298.15 K and 308.15 K by applying the following equation.

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

where *C* is ordinary concentration (molarity) and *K* is the specific conductance of the solutions.

The limiting molar conductances (Λ_0) of used salt solutions under examination were determined from Eqn. (2) as Onsager equation[5] by extrapolation the linear Onsagar plot by using the relation Eq. (2) at both experimental temperatures.

$$\Lambda = \Lambda_0 - SC^{1/2} \quad \ldots (2)$$

where Λ_0 is the intercept i.e., molar conductance at infinite dilution and *S* is the slope of straight line obtained from Λ versus ($C^{1/2}$) plot. Few plots were reported in Figs 1 and 2.

Results and Discussion

The physicochemical properties i.e., densities (ρ), viscosities (η) and relative permitivitys(ε) of 2-aminoethanol (AE) and N,N-dimethylacetamide (DMA) with mol % of 25, 50, 60, 80, and 100 mol% DMA at 298.15 K and 308.15 K are reported in Table 1. The molar conductances of $LiClO_4$, $NaClO_4$, KSCN, Bu_4NSCN, Bu_4NClO_4 and Bu_4NBPh_4 were measured in the concentration range of $(30\text{-}500)\times10^{-3}$ mol·kg^{-1} in binary solvent mixtures of DMA and AE containing 25, 50, 60, 80 and 100 mol% DMA at 298.15 K and 308.15 K. Limiting molar conductances (Λ_o) and association constant values for the ion-pairs (K_A) are reported in Table 2. These values were evaluated by making use of the least-squares method via a computer program of the Shedlovsky equation[12]. This process involves linear extrapolation using the following equation by Bag *et al*.

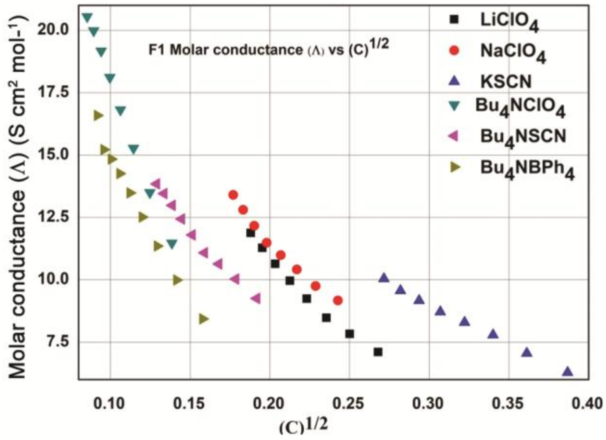

Fig. 1 — Plot of F1 molar conductance (Λ) versus ($C^{1/2}$) for all used salts in 25 Mol % AE+DMA binary mixtures at 298.15 K

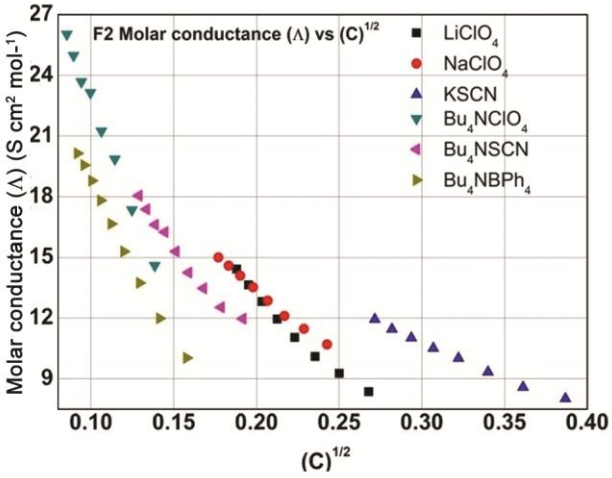

Fig. 2 — Plot of F2 molar conductance(Λ) versus ($C^{1/2}$) for all used salts

The Shedlovsky equation is given as

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda S f_{\pm}^2 K_A}{\Lambda_0^2} \quad \ldots (3)$$

Where $f_\pm$ = mean ion activity coefficient of the electrolyte and, *S* = Onsager slope.

$$S(Z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \ldots \text{.... etc.} \quad \ldots (4)$$

$$Z = \frac{s\left((\Lambda_m C)^{\frac{1}{2}}\right)}{\Lambda^{3/2}} \quad \ldots (5)$$

$$S = a\Lambda_0 + b \quad \ldots (6)$$

$$\alpha = \frac{S(Z)\Lambda_m}{\Lambda_0} \quad \ldots (7)$$

$$\beta = \frac{8.20X10^5\Lambda_m^0}{(\varepsilon T)^{\frac{3}{2}}} + \frac{82.5}{\eta(\varepsilon T)^{\frac{1}{2}}} \quad \ldots (8)$$

Table 1 — Relative permittivities (ε), densities (ρ) (g.cm^{-3}) and viscosities (η) (cP) in AE+DMA binary solvent mixtures

Mol% DMA	Physical quantity	298.15 K	308.15 K
0	ε	34.20	33.05
	ρ	1.01172	1.00443
	η	18.96	12.267
25	ε	36.89	35.3
	ρ	0.96476	0.95985
	η	7.735	4.105
50	ε	38.52	37.29
	ρ	0.93955	0.93913
	η	2.021	1.584
60	ε	39.68	37.45
	ρ	0.93106	0.93067
	η	1.752	1.465
80	ε	40.81	39.47
	ρ	0.91393	0.91336
	η	1.152	0.9553
100	ε	43.00	42.5
	ρ	0.93604	0.92643
	η	0.9279	0.8182

Table 2 — The Association constant for ion-pairs ($K_{A,}$) and the thermodynamic parameters of associations of free energy ($\Delta G^{0}_{A,}$), Walden products and hydrodynamic radii for used salts in AE+DMA binary mixtures at 298.15 K and 308.15 K

Mol% DMA	T(K)	K_A (dm^{3}mol^{-1})	ΔG_A^0 (kJ mol^{-1})	□$_0\eta_0$ (S cm^2 mol^{-1})	R_H (Å)
$LiClO_4$					
25	298.15 K	36.31219	-8.90433	177.3636	0.004623
	308.15 K	37.02276	-9.25261	116.6231	0.007031
50	298.15 K	31.11806	-8.52166	56.32527	0.014558
	308.15 K	12.25903	-6.42094	55.86768	0.014678
60	298.15 K	25.90258	-8.06693	55.27561	0.014835
	308.15 K	15.05288	-6.94693	54.82030	0.014958
80	298.15 K	30.70148	-8.48825	45.75744	0.017921
	308.15 K	21.31215	-7.83774	44.2686	0.018523
100	298.15 K	30.35261	-8.45992	56.59056	0.014492
	308.15 K	32.99039	-8.95716	57.42946	0.014278
$NaClO_4$					
25	298.15 K	28.42795	-8.29753	188.8887	0.004341
	308.15 K	26.24098	-8.37075	110.014	0.007454
50	298.15 K	12.85874	-6.33096	69.56282	0.011788
	308.15 K	4.700641	-3.96514	67.35168	0.012175
60	298.15 K	47.77458	-9.58434	65.50728	0.012518
	308.15 K	51.61805	-10.1042	68.45945	0.011978
80	298.15 K	176.99481	-12.8307	62.8992	0.013037
	308.15 K	111.04891	-12.0668	57.16515	0.014344
100	298.15 K	125.79960	-11.9843	111.1968	0.007374
	308.15 K	128.48252	-12.4403	110.7843	0.007402
KSCN					
25	298.15 K	12.16474	-6.19343	146.0368	0.005615
	308.15 K	10.26866	-5.96705	88.0933	0.009308
50	298.15 K	10.37485	-5.79891	52.04075	0.015757
	308.15 K	8.732691	-5.55195	44.93808	0.018247
60	298.15 K	12.86175	-6.33154	53.75136	0.015255
	308.15 K	7.055901	-5.00572	50.1616	0.016347
80	298.15 K	16.63263	-6.96886	39.20256	0.020917
	308.15 K	15.62381	-7.04230	35.38431	0.023174
100	298.15 K	9.143165	-5.48564	57.85416	0.014174
	308.15 K	10.16941	-5.94217	60.75135	0.013498
Bu_4NSCN					
25	298.15 K	52.71661	-9.82835	179.4522	0.004569
	308.15 K	55.21261	-10.2765	125.8593	0.006515
50	298.15 K	37.28211	-8.96964	79.20299	0.010353
	308.15 K	34.53634	-9.07449	73.38672	0.011174
60	298.15 K	50.06547	-9.70044	76.80768	0.010676
	308.15 K	51.75129	-10.1106	78.4947	0.010447
80	298.15 K	38.07552	-9.02184	65.7216	0.012477
	308.15 K	38.03367	-9.32162	58.87514	0.013928
100	298.15 K	51.42669	-9.76694	87.92784	0.009326
	308.15 K	65.99615	-10.7336	93.19298	0.008799
Bu_4NBPh_4					
25	298.15 K	6.819341	-4.75874	202.1929	0.004946
	308.15 K	7.495787	-5.16066	141.2531	0.007079
50	298.15 K	86.61465	-11.0592	70.59353	0.014166
	308.15 K	83.65079	-11.3409	74.7648	0.013375
60	298.15 K	130.5933	-12.0771	82.67688	0.012095
	308.15 K	127.5308	-12.4213	85.98085	0.01163
80	298.15 K	173.9052	-12.7871	75.93984	0.013168
	308.15 K	140.6595	-12.6723	70.45338	0.014194
100	298.15 K	109.8534	-11.6483	64.94904	0.015397
	308.15 K	96.12602	-11.6973	63.97506	0.015631

(*Contd*.)

Table 2 — The Association constant for ion-pairs (K_A) and the thermodynamic parameters of associations of free energy (ΔG^0_A), Walden products and hydrodynamic radii for used salts in AE+DMA binary mixtures at 298.15 K and 308.15 K — (*Contd.*)

Mol% DMA	T(K)	K_A (dm^3mol^{-1})	ΔG^0_A (kJ mol^{-1})	$\square_0\eta_0$ (S cm^2 mol^{-1})	R_H (Å)
Bu_4NClO_4					
25	298.15 K	144.29412	-12.3243	273.3549	0.003001
	308.15 K	138.45212	-12.6318	181.8515	0.004509
50	298.15 K	80.20615	-10.8686	86.41796	0.009489
	308.15 K	77.82382	-11.1559	83.42928	0.009829
60	298.15 K	81.09972	-10.8961	94.08240	0.008716
	308.15 K	74.34608	-11.0388	85.92225	0.009544
80	298.15 K	83.48220	-10.9679	69.14304	0.011859
	308.15 K	84.17501	-11.3569	64.79822	0.012992
100	298.15 K	34.53481	-8.77990	63.11448	0.012992
	308.15 K	36.62851	-9.22517	61.99501	0.013227

$$\alpha = \frac{8.20\text{X}10^5\Lambda^0_m}{(\varepsilon\text{T})^{\frac{3}{2}}} \quad \dots (9)$$

$$b = \frac{82.5}{\eta((\varepsilon\text{T})^{1/2}} \quad \dots (10)$$

$$logf_{\pm} = -\frac{1.8246\text{X}10^6(c\alpha)^{\frac{1}{2}}/(\varepsilon\text{T})^{3/2}}{1+50.24\text{X}10^8R(c\alpha)^{\frac{1}{2}}/(\varepsilon\text{T})^{1/2}} \quad \dots (11)$$

$$A = 1.8246 \times 10^6/(\varepsilon\text{T})^{\frac{3}{2}} \quad \dots (12)$$

$$B = 50.24 \times 10^8/(\varepsilon\text{T})^{\frac{1}{2}} \quad \dots (13)$$

where R be the ion-size parameter, and same as the Bjerrum critical distance q is given by the relation

$$R = q = \frac{e^2}{2\varepsilon\text{kT}} \quad \dots (14)$$

where, c is the concentration of electrolytic solutions and ε is the relative permitivity of the solvent. The relative permittivity (ε), density (ρ), and viscosity (η) of all binary mixed solvent systems at experimental temperatures are in Table 1.

Association constant for ion-pairs

The evaluated values of the association constant for ion-pairs (K_A) of $LiClO_4$, $NaClO_4$, KSCN and Bu_4NSCN in AE+DMA binary mixed solutions for all studied systems are presented in Table 2. Association constant values (K_A) were determined from the Shedlovsky equation for all compositions of the binary mixed solvent systems as well as in pure DMA at 298.15 K and 308.15 K. From an examination of K_A values it was observed that the values of association constants for ion-pairs of the studied salts in all binary solvent mixture compositions, decreases with an increase in the proportion of DMA at the same temperature except at 100 mol% of DMA at 308.15 K and show the irregular trends in association constant (K_A) with change in the proportion composition of DMA in all binary solvent mixture compositions as well as with the increase in temperature. From the inspection of studied salts, the association constant for ion-pairs values (K_A) for all studied solvent compositions show that the effect of hydrogen bonding is extremely responsible for the association of ion-pair process and also affects the ionic mobility of the solvated ion with the increasing value of the relative permitivity of binary solvent mixtures at different temperatures[13]. It suggests about the ion-association process and the ion-solvent interactions. This behaviour can reveal that the increase in the relative permitivity of the used solvent system is proportional to the binary solvent mixture compositions[32].

Thermodynamics of association

The standard free energy association values (ΔG^0_A) were evaluated for $LiClO_4$, $NaClO_4$, KSCN, Bu_4NSCN, Bu_4NClO_4 and Bu_4NBPh_4 salts in used solvent system compositions at 298.15 K and 308.15 K. K_A values determined from the conductance data are strongly depend upon the relative permitivity of the solutions[33]. The change in standard free energy values (ΔG^0_A) were calculated by using K_A values according to Eqn 15.

$$\Delta G^0_A = -RTlnK_A \quad \dots (15)$$

where R =Universal gas constant (8.314 J/mol/K)

The calculated values in each solvent system are tabulated in Table 2. The values are all negative and have the domain of 3-12 kJ mol^{-1}. This result indicates the extent of preferential solvation of all ions in all binary solvent mixtures of AE+DMA.

From the overview of Table 2, the values of Gibb's free energy of association (ΔG^0_A) are decreasing with the increase in the concentration of DMA in the binary mixtures of AE+ DMA, which indicates the ion-pair formations increase significantly with an increase in the association process for the used salts in AE+ DMA binary mixtures. These values were decreasing with the increase of temperature from 298.15 K to 308.15 K. The study showed that the ion-ion and ion-solvent association process of all the studied compositions of the solvent system is spontaneous due to negative values of (ΔG_A^0). It also indicates the strong ion–pair formation of all used salts solutions in binary mixtures with the increase in temperature following the results investigated by Barthel *et al*.[34] and Hazra *et al*.[35-36].

From inspection of Table 2, the temperature has no impact on the values of the standard free energy values (ΔG_A^0) of ion-pair association process when the temperature is raised from 298.15 to 308.15 K. This study suggests that the association process for ion-pairs are opposed to an increase in values of relative permitivity for all solutions. Association constants for ion-pairs (K_A) however, do not carry out any significant notice about all types of interactions.

Walden product

Ion-solvent interactions can be explained because of the Walden product. The molar conductances (Λ) of the electrolytic solutions depend only on the mobility of ions and hence, their product with the viscosity of the medium should not depend upon the nature of the solvent[37-39]. Therefore, the Walden products ($\Lambda_o\eta_o$) are found to vary for $LiClO_4$, $NaClO_4$, KSCN and Bu_4NSCN in the binary mixed solvents used which shows that all types of interactions are uniform in nature. The Walden product values are calculated from his rule in the form of Eqn. (16) for the all studied salts and ions and are presented in Table 2.

$$\lambda_O\eta_O = 0.82\left[\frac{1}{r_s^+} + \frac{1}{r_s^-}\right] \qquad \ldots (16)$$

From the overview of Walden products, it was found that the Walden products are decreasing with the increase in temperature. The slight changes in the values of Walden product for all studied salts in binary mixtures of AE+DMA with the increase in mol% DMA are reported in Table 2. The results indicate that the values of limiting molar conductances are compensated by the decrease in viscosity of the binary solvent mixture with the Walden product. The impact on Walden products is related to the limiting molar conductances and viscosities of all studied compositions. This scrutiny of studied salt solutions in binary mixtures of AE+DMA shows that the role of viscosity values is the most influential characteristic on the contrary behavior of Walden products among temperature.

At a very low concentration of DMA, these ions (Li^+, Na^+ and K^+) are found to be preferentially solvated by AE rather than by DMA (25 mol% DMA). The viscosity of the solvent in the vicinity of these ions is lower than that of bulk solvent. Since the bulk viscosity value is used in the calculation of ($\Lambda_o\eta_o$), the calculated values go as high as the point corresponding to the viscosity maximum of the solvent mixtures and then the values decrease gradually, causing a maximum in the Walden product. The decrease in the Walden product indicates the preferential solvation of all the ions i.e., Li^+, Na^+ and K^+ with the increase in the concentration of DMA in the binary mixtures of AE+DMA. However, the decrease in the Walden product is may be due to the Zwanzig solvent relaxation effect[40].

The Walden product values are found to decrease with an increase in the proportion in DMA and hence, decrease in the order 25> 50> 60> 80 >100 mol% DMA. The limiting molar conductances values are also reported in Table 2. This suggests that the impact of the increase in limiting molar conductances is greater as compared to the impact of fall in the viscosity values in that medium. The inclination is noticed with the temperature change, Walden product values also change with the solvent composition and nature of electrolyte[32,41].

Limiting ion conductance

Gill and coworkers[42] utilized the following equations for the evaluation of limiting ion conductance of reference electrolyte (Bu_4NBPh_4).

$$\frac{\lambda_\pm^O(Bu_4N^+)}{\lambda_\pm^O(Ph_4B^-)} = \frac{5.35-(0.0103\varepsilon+r_y)}{5.00-(0.0103\varepsilon+r_y)} \qquad \ldots (17)$$

$$\lambda_\pm^o(Bu_4N^+) + \lambda_\pm^o(Ph_4B^-) = \Lambda^O(Bu_4NBPh_4) \ldots (18)$$

From Eqns (17) and (18), the values of limiting ion conductances ($\lambda_\pm^o$) of Bu_4N^+ and Ph_4B^- in DMA and AE + DMA binary solvent compositions were evaluated from the Λ° values of Bu_4NBPh_4 by applying the principle of Kohlrausch's law of independent migrations of ions.

The values of Limiting molar conductances (Λ_o) in pure DMA and AE + DMA mixtures were also evaluated by applying Eqns (1) and (2), which are presented in Table 3.

Solvated radii and preferential solvation

Gill[42] developed a method for the calculation of solvated radii for Li^+, Na^+, K^+, Bu_4N^+, Ph_4B^- and ClO_4^- ions, from the help of limiting ionic conductance ($\lambda^o_\pm$) values of the electrolytes in pure and mixed non-aqueous solvents evaluated by using the equation :

$$r_i = \frac{|Z|F^2}{6\pi\eta N\lambda_i} + (0.0103\varepsilon + r_y) \qquad \ldots (19)$$

where r_i values for different ions. Limiting ion conductances ($\Lambda^o_\pm$) for some ions in mol% DMA in AE+DMA binary mixtures at 298.15 and 308.15 K are listed in Table 4. r_i values along with their crystallographic radii (r_c for Li^+ = 0.60; Ph_4B^-=0.53, Bu_4N^+ = 0.50 and ClO_4^- = 0.36 nm)[41-42] where Z and r_i are the charge and actual radius of an ion in solution (Table 5). Where r_y is an adjustable parameter have values of 0.085 nm for AE (associated solvent) and for 0.113 nm (non-associated solvents) for DMA and their binary mixtures[43].

The relationship between solvated radii r_i values and crystallographic radii (r_c) of the ions recommends the superior solvation in the order of Li^+> Na^+> K^+. Li^+ ions are found to be much higher preferential solvated than Na^+ and K^+ up to a greater extent by DMA as compared to AE+DMA binary mixtures in the entire solvent composition range. The $r_i$values for ClO_4^- and SCN^- ions are found to be very close to their crystallographic radii but the values indicate some solvation in all compositions of binary mixed solvents as compared to bulkier Ph_4B^- and Bu_4N^+ ions. The solvated radii $r_i$values (Bu_4N^+ = 0.50 *nm* and BPh_4^- = 0.53 *nm*) are approximately very close to crystallographic radii (Bu_4N^+= 0.50 nm and BPh_4^-=0.535 nm). This shows that Bu_4N^+ and BPh_4^-

Table 3 — Limiting molar conductance (Λ_o) (S cm^2 mol^{-1}) for used salts in mol% DMA in AE+DMA mixtures at 298.15 K and 308.15 K

Mol% DMA	25			50		60		80		100	
Salt	T(K)	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A	Λ_o	K_A
Bu_4NBPh_4	298.15	26.14	6.8	34.93	-	47.19	-	65.9	-	69.39	-
	308.15	34.55	7.5	47.2	-	58.69	-	73.75	-	86.86	-
Bu_4NClO_4	298.15	35.3	-	42.77	-	53.7	-	60.02	-	67.4	-
	308.15	44.3	-	52.68	-	58.65	-	67.83	-	75.7	-
$LiClO_4$	298.15	22.93	13.18	27.87	31.11	31.55	25.89	39.72	-	60.46	-
	308.15	28.41	10.2	35.27	12.25	37.42	15.04	46.34	-	70.19	-
$NaClO_4$	298.15	24.42	28.42	28.78	-	37.39	-	54.6	-	118.8	-
	308.15	26.80	26.24	40.22	-	46.73	-	59.84	-	135.4	-
KSCN	298.15	18.88	12.19	25.75	10.37	30.68	12.85	34.03	16.63	61.8	9.14
	308.15	21.46	10.32	28.37	8.73	40.81	7.05	41.87	15.62	74.25	10.17
Bu_4NSCN	298.15	23.2	-	39.9	-	48.8	-	57.05	-	93.9	-
	308.15	30.66	-	46.33	-	53.6	-	61.63	-	113.19	-

Table 4 — Limiting ion conductances ($\Lambda^o_\pm$) (S cm^2 mol^{-1}) for some ions in mol% DMA in AE+DMA binary mixtures at 298.15 and 308.15 K

	Mol% DMA					
Ions	T (K)	25	50	60	80	100
	298.15 308.15	$\Lambda^o_\pm$	$\Lambda^o_\pm$	$\Lambda^o_\pm$	$\Lambda^o_\pm$	$\Lambda^o_\pm$
Bu_4N^+	298.15	13.63	18.22	24.61	34.37	36.35
	308.15	18.02	24.62	30.61	38.46	41.56
Li^+	298.15	1.27	1.5	2.46	14.07	26.1
	308.15	2.13	2.64	9.42	16.97	39.05
Na^+	298.15	2.75	4.23	8.3	28.95	5.94
	308.15	9.91	12.16	18.73	30.47	16.66
K^+	298.15	9.31	4.07	6.49	11.35	4.55
	308.15	8.82	6.66	11.19	18.70	2.62
Ph_4B^-	298.15	12.51	16.71	22.58	31.53	33.34
	308.15	16.53	22.58	28.08	35.29	45.3
ClO_4^-	298.15	21.67	24.55	29.09	25.65	34.06
	308.15	26.28	28.06	28.00	29.37	34.14
SCN^-	298.15	9.57	21.68	24.19	22.68	57.25
	308.15	12.64	21.71	25.6	23.17	71.63

Table 5 — Solvated radii (r_i) of some ions in mol% DMA in AE+DMA binary mixtures at 298.15 K and 308.15 K

r_i(nm) Ions		T (K)	25 mol%	50 mol%	60 mol%	80 mol%	100 mol%
Bu_4N^+	(r_c =0.50)	298.15	0.47	0.50	0.51	053	0.55
		308.15	0.46	0.49	0.49	0.51	0.54
Ph_4B^-	(r_c=*0.53)*	298.15	0.47	0.49	0.51	0.53	0.55
		308.15	0.46	0.50	0.49	0.51	0.54
ClO_4^-	(r_c =0.292)	298.15	0.47	0.48	0.51	0.54	0.55
		308.15	0.46	0.50	0.49	0.52	0.55
Li^+	(r_c=0.060)	298.15	0.55	0.74	0.69	0.57	0.56
		308.15	0.54	0.68	0.53	0.54	0.55
Na^+	(r_c=0.095)	298.15	0.50	0.56	0.55	0.54	0.68
		308.15	0.47	0.52	0.50	0.52	0.58
K^+	(r_c=0.133)	298.15	0.48	0.57	0.57	0.58	072
		308.15	0.47	0.56	0.52	0.54	0.88
SCN^-	(r_c=0.25)	298.15	0.48	0.49	0.51	0.54	0.54
		308.15	0.47	0.51	0.49	0.52	0.54

r_c represent the crystallographic radii of the solvated ions

ions were not solvated in AE + DMA binary mixtures which are owed to their big size and low charge density. Several past studies about the solvation of ions in non-aqueous organic media[15-16,18]. The studies inform about the electrostatic interaction between an ion and dipole[27].

The values increase with the rise in DMA mol%, indicating the inclination of the degree of solvation and the limiting ionic conductances for Bu_4N^+ and BPh_4^- decrease with an increase in DMA composition in all mixed binary solvent systems. The solvated radii (r_i) values of K^+, Na^+, Li^+ and Bu_4N^+ decrease with an increase in temperature from 298.15 K to 308.15 K. However, the study reveals that the ion-solvent interactions decrease with an increase in temperature.

These observations indicate that the anions SCN^- and ClO_4^- show some solvation but the bulkier size ions Bu_4N^+ and BPh_4^- remain unsolvated in AE + DMA mixed binary solvent system than in pure DMA investigated here. It shows that the smaller the size of ions with greater surface charge density may well unite a large number of solvent molecules to shape a bigger solvodynamic unit of lesser mobility.

Conclusions

The r_i values of Li^+ are higher than that of Na^+ and K^+ ions which specifies the preferential solvation of all studied ions in all binary system compositions. SCN^-, ClO^{4-}anions are moderately solvated but $Bu4N^+$ and $Ph4B^-$ remain unsolvated in all AE+DMA mixed binary solvent compositions. However, from the study, the Li^+ has higher solvation than Na^+ and K^+ in AE+DMA mixed binary solvent at all compositions and increases with an increase in DMA compositions. This shows thereby that DMA replaces the AE region. But these values are affected by temperature, as the increase in temperature, the r_i values decreased. This study showed that the ion-solvent interaction decrease with rising temperature from 298.15 K to 308.15 K. Solvated radii values of Li^+ and Na^+ are maximum in the 50 mol% DMA region as breaking of hydrogen bonding and formation of new solvation sphere, it can be said that these ions are solvated in the 50 mol% of DMA and also in 100% DMA. The solvated radii of K^+ are larger than crystallographic radii in 100% DMA, seem to be preferentially solvated in that composition. Walden products of Li^+, Na^+, K^+, Ph_4B^-, Bu_4N^+, ClO_4^- and SCN^- ions are studied with the effect of temperature which shows the nature of ions in the solvent systems.

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