



Thermodynamic Parameters and Solvation Behavior of 1-Ethyle-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Tetrafluoroborate in N,N-Dimethylformamide and Acetonitrile at Different Temperature



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THE present paper investigations made on the ion-solvation interaction of new class of salts ionic liquids (IL) such as 1-Ethyle-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Tetrafluoroborate in N,N-Dimethylformamide and Acetonitrile at temperature range of 283.15 to 318.15K with the aid of using electrical conductivity precept. The electrical conductance data were analyzed with the aid of Fuoss – Justice equation of conductivity. The molar conductance (Λ), the limiting molar conductance (Λ_0), the association constants (K_A), the Walden product ($\Lambda_0 \eta_0$), The Eyring activation energy of charge transport ($\Delta H^\ddagger_\lambda$) and the standard thermodynamic parameters of association (ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger) were calculated and mentioned. The results show that, the molar conductance and the limiting molar conductance values have been diminished as the relative permittivity of the solvent lowered at the same time, the association constant increased. Additionally, the outcome exhibit that the values of the molar conductance, and the limiting molar conductance were increased as the temperature increased at the same time, the association constant increased indicating that the association process is an endothermic one as indicated from ΔH^\ddagger value. The effect of the alkyl chain length of IL is clear on the thermodynamic parameters and association properties.

Keywords: Molar Conductance; Solvation; Ion Association; Ionic Liquids

Introduction

We are in our past [1-3]; we investigate thermodynamic parameters of different ions in aqueous and partial aqueous solvents. The new class of electrolytes called ionic liquids has the attention of researchers in the last few years due to their applications in many branches of science such as catalysis [4- 6], various separation techniques, solar cell and batteries [7-9] but the ability of ionic liquids to dissolve many insoluble materials in traditional solvents stays the major use of these compounds. Therefore, these liquid salts with low vapor pressure at room temperature can be used instead of usual used solvents during chemical reactions. Ionic liquids contain anions and

cations with distorted crystal in which physical and chemical properties are essentially depend on the present anion and cation. One of these properties is the miscibility with water which depends essentially on the type of the anion [10, 11]. Generally, the ionic liquids show miscibility behavior with solvents has high dielectric constant like water and immiscibility behavior with solvents have low dielectric constant [11]. Now we present the effect of these anions and cations on the association constant of ionic liquids in mixed solvents due to the lack of literature that deal with thermodynamic parameters of ionic liquids. However, there are some limited previous works [12-17] introduce the conductance study

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of ionic liquids with a discussion of ion-ion and ion-solvent interaction inside ionic liquids solutions. The most applicable ionic liquids which are conductometrically studied are these with 1,3-dialkylimidazolium, tetraalkylammonium, or N-alkylpyridinium cations and anions containing halide ions, tetrachloroaluminate tetrafluoroborate, trifluoromethylsulfonate, or hexafluorophosphate. Due to the limitation of previous works to study the thermodynamic behavior of ionic liquids in organic solvents, we decide to study the behavior of [emim]BF₄ and [bmim]BF₄ over wide variety of temperatures from 283.15K-313.15K within DMF and acetonitrile solvent. The conductance measurements of the mentioned systems are utilized to determine the molar conductance (Λ), limiting molar conductance (Λ_0) at different temperatures. Λ_0 and Λ are determined using the technique of Fuoss-Justice so as to calculate the constant of association for ILs. Also, the Gibbs free energy (ΔG^\ddagger) of association, enthalpy (ΔH^\ddagger) of association, entropy (ΔS^\ddagger) of association and the Eyring activation enthalpy of charge transport (ΔH^\ddagger_c) have been calculated. From our results, there is an agreement with literature that the length of alkyl chain of cation, the anion type beside the properties of used solvent like dielectric constant and viscosity play an important role in determining the association constant inside the IL.

Experimental

Materials and solutions preparations

[emim]BF₄ (99.8%) and [bmim]BF₄ (99.0%), were supplied from Fluka Co. and used directly without further purification. DMF solvent was supplied from Sigma-Aldrich Co. and used without further purification. Acetonitrile was supplied from Merck Co. and used without further purifications. Karl Fischer coulometric titration technique is used to determine the water mass fraction of used materials [emim]BF₄, [bmim]BF₄, DMF and acetonitrile which found to be 0.0002, 0.0005, 0.00005 and 0.00004 respectively. Usually ten solutions of the IL under investigation were prepared by mass using a digital balance (Sartorius RC 210D) with an error ± 0.0001 .

Apparatus

The IL prepared solutions are used for the determination of conductance by the mean of LF 191 conductivity meter (Germany) which has uncertainty equal to $\pm 0.1 \mu\text{S cm}^{-1}$. The temperature is kept constant with uncertainty equal to $\pm 0.05^\circ\text{C}$ via MLW 3230 thermostat which connected to the mentioned conductivity meter.

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Densities measurements were carried out at atmosphere pressure using a vibrating tube densimeter (Anton Paar DMA4500M, Austria), and the temperature was spontaneously kept up inside ± 0.01 K amid the estimation through two incorporated Pt100 platinum thermometers with implicit peltier components. The density of each sample was measured three times and the average value is considered. Deionized water was used to calibrate the apparatus, and the vibrating tube was cleaned automatically after each measurement by using the distilled H₂O and anhydrous ethyl alcohol. The atmospheric pressure was recorded once an hour from a Fortin barometer.

The viscosity of used solution was measured by means of an iVisc capillary viscometer (LAUDA, Germany), and Shanghai Glass Instruments Factory of China is used to provide the Ubbelohde capillary (1835A) with a diameter equal to 0.54 mm. The clean and dry Ubbelohde capillary was placed vertically in a thermostat (Lauda Eco Sliver) with uncertainty equal to ± 0.01 K. The infrared is used to measure the sample flow time automatically that has an uncertainty equal to ± 0.01 s, and a deviation equal to 0.2 s was taken at the specified temperature and atmospheric pressure for at least four sets of flow time. The kinetic energy and the end corrections were found to be negligible due to all flow time was greater than 100 s.

Results and Discussion

Table 1 contains the different properties dielectric constant (ϵ), viscosity (η) and density (ρ_0) of DMF and Acetonitrile solvents at temperatures of (283.15, 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15K). The values of dielectric constant are taken from literature [18, 19]. The specific conductance (κ_s , $\mu\text{S}\cdot\text{cm}^{-1}$) of solutions of the salt under investigation in the (DMF) and (AN) at different temperatures was measured experimentally. The molar conductance (Λ) for all studied systems was calculated by applying Eq. (1). The values of the molar conductance for the studied IL in used solvents at different temperatures were recorded in Tables 2 and Table 3.

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

Where C is the normal concentration and κ_s is the measured specific conductance of the studied solution from which the specific conductance of the used solvent was subtracted. The molar conductance (Λ) for all systems under study decreases with increase in concentration.

TABLE 1. The relative permittivity (ϵ), density (ρ , $\text{g}\cdot\text{cm}^{-3}$) and viscosity (η , $\text{mPa}\cdot\text{s}$) of DMF and AN at working different temperatures and pressure 0.1MPa

| T/K | DMF | | | AN | | |
|---------------|--|--------------------------------------|--------------------------|--|--------------------------------------|--------------------------|
| | ρ_0 ($\text{g}\cdot\text{cm}^{-3}$) | η ($\text{mPa}\cdot\text{s}$) | ϵ ¹⁸ | ρ_0 ($\text{g}\cdot\text{cm}^{-3}$) | η ($\text{mPa}\cdot\text{s}$) | ϵ ¹⁹ |
| 283.15 | 0.958102 | 1.0161 | 39.62 | 0.792899 | 0.3979 | 38.40 |
| 288.15 | 0.953359 | 0.9549 | 38.69 | 0.787518 | 0.3775 | 37.57 |
| 293.15 | 0.948597 | 0.8989 | 37.76 | 0.782109 | 0.3589 | 36.77 |
| 298.15 | 0.943829 | 0.8459 | 36.82 | 0.776673 | 0.3415 | 35.97 |
| 303.15 | 0.939055 | 0.7996 | 35.89 | 0.771213 | 0.3258 | 35.20 |
| 308.15 | 0.934269 | 0.7558 | 34.96 | 0.765722 | 0.3109 | 34.44 |
| 313.15 | 0.929469 | 0.7175 | 34.02 | 0.760205 | 0.2969 | 33.97 |
| 318.15 | 0.924661 | 0.6829 | 33.08 | 0.754702 | 0.2820 | 33.20 |

¹⁸Combined uncertainties, $U_c(\eta) = 0.0040$ $\text{mPa}\cdot\text{s}$ for viscosity, are $U_c(\rho_0) = 3\cdot 10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$ for density (confidence level=0.95)

Standard uncertainties, $u(T) = 0.01$ K for temperature, $u(p) = 0.04$ p

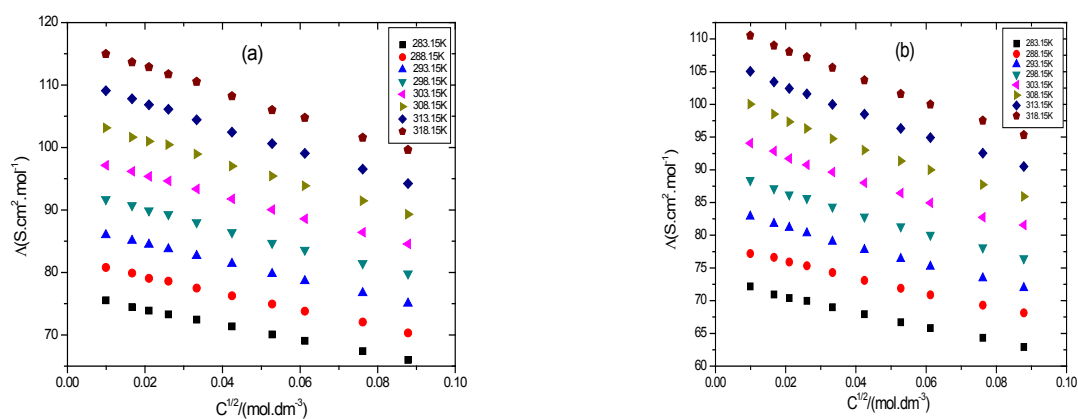
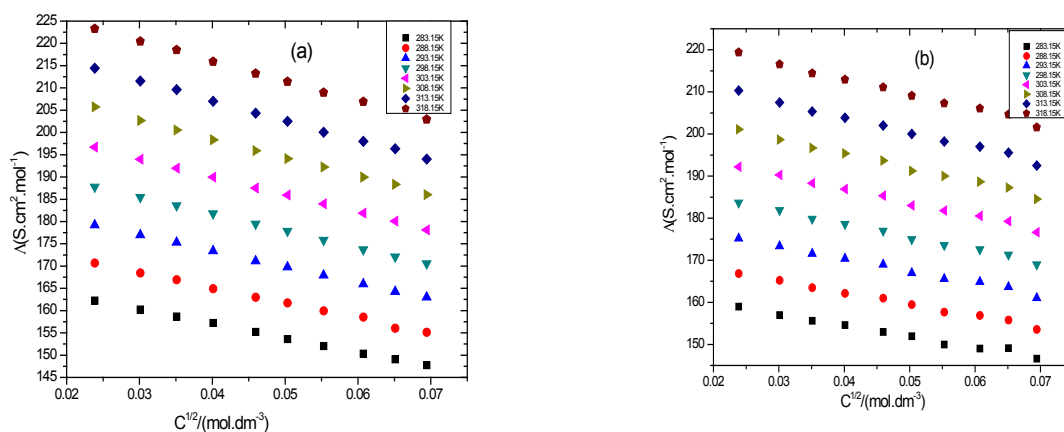
**Fig. 1.** The relation between molar conductance (Λ) and \sqrt{c} for (a) [emim]BF₄, (b) [bmim]BF₄ in DMF solvent at working temperatures.**Fig.2.** The relation between molar conductance (Λ) and \sqrt{c} for (a) [emim]BF₄, (b) [bmim]BF₄ in AN solvent at working temperatures.

TABLE 2. The molar conductance of [emim]BF₄ and [bmim]BF₄ at different temperatures in Dimethyl formamide solvent

| C·10 ⁴ (mol.dm ⁻³) | Λ (S.cm ² .mol ⁻¹) | C·10 ⁴ (mol.dm ⁻³) | Λ (S.cm ² .mol ⁻¹) | C·10 ⁴ (mol.dm ⁻³) | Λ (S.cm ² .mol ⁻¹) | C·10 ⁴ (mol.dm ⁻³) | Λ (S.cm ² .mol ⁻¹) |
|---|---|---|---|---|---|---|---|
| 283.15K | | [emim]BF₄ 288.15K | | 293.15K | | 298.15K | |
| 0.9786 | 75.53 | 0.87316 | 80.79 | 1.1620 | 86.00 | 1.0688 | 91.69 |
| 2.7729 | 74.47 | 2.5695 | 79.89 | 2.7802 | 85.11 | 2.5526 | 90.73 |
| 4.4236 | 73.88 | 4.8601 | 79.06 | 4.6544 | 84.45 | 4.4641 | 89.89 |
| 6.7745 | 73.3 | 6.6088 | 78.6 | 6.8824 | 83.75 | 6.3419 | 89.30 |
| 11.0927 | 72.45 | 11.1340 | 77.50 | 11.1676 | 82.66 | 10.8651 | 88.00 |
| 17.9809 | 71.38 | 18.2618 | 76.26 | 17.9514 | 81.40 | 18.2398 | 86.42 |
| 27.8458 | 70.08 | 27.5237 | 74.95 | 27.6169 | 79.79 | 27.4668 | 84.71 |
| 37.4752 | 69.05 | 37.5118 | 73.81 | 37.3084 | 78.63 | 36.6526 | 83.58 |
| 57.9548 | 67.39 | 56.4045 | 72.05 | 56.7391 | 76.71 | 56.2474 | 81.47 |
| 77.1033 | 66.00 | 76.0734 | 70.31 | 75.7271 | 75.03 | 74.7158 | 79.81 |
| 303.15K | | 308.15K | | 313.15K | | 318.15K | |
| 1.3455 | 97.15 | 0.9581 | 103.15 | 0.8847 | 109.11 | 0.9265 | 114.99 |
| 2.7948 | 96.18 | 3.4019 | 101.66 | 2.5790 | 107.79 | 2.5170 | 113.65 |
| 4.7606 | 95.36 | 4.6862 | 100.99 | 4.3871 | 106.85 | 3.3702 | 112.88 |
| 6.7010 | 94.65 | 6.2257 | 100.44 | 6.3539 | 106.11 | 6.3366 | 111.74 |
| 11.0092 | 93.35 | 10.7149 | 98.95 | 10.7723 | 104.44 | 10.8470 | 110.54 |
| 17.7840 | 91.75 | 18.1933 | 97.02 | 18.1074 | 102.46 | 17.5633 | 108.23 |
| 27.3580 | 90.04 | 27.0466 | 95.44 | 27.0472 | 100.63 | 27.2534 | 106.00 |
| 36.8760 | 88.59 | 36.2861 | 93.87 | 36.5779 | 99.05 | 36.1520 | 104.77 |
| 55.2281 | 86.41 | 54.5784 | 91.45 | 55.3775 | 96.55 | 54.9580 | 101.60 |
| 74.7547 | 84.55 | 74.6967 | 89.31 | 74.0643 | 94.22 | 73.4178 | 99.64 |
| 283.15.K | | [bmim]BF₄ 288.15K | | 293.15K | | 298.15K | |
| 0.5309 | 72.18 | 1.2290 | 77.21 | 1.0532 | 82.87 | 1.1761 | 88.41 |
| 2.7928 | 70.95 | 2.5050 | 76.63 | 2.7918 | 81.77 | 3.0196 | 87.15 |
| 4.6898 | 70.41 | 4.0713 | 75.9 | 4.2527 | 81.15 | 4.9736 | 86.21 |
| 6.6510 | 69.99 | 5.7863 | 75.33 | 6.5832 | 80.33 | 6.5217 | 85.67 |
| 11.0514 | 69.00 | 9.7418 | 74.31 | 11.5498 | 79.05 | 11.0868 | 84.33 |
| 18.5690 | 67.95 | 16.1826 | 73.11 | 18.9330 | 77.77 | 18.1818 | 82.81 |
| 28.0510 | 66.71 | 24.2737 | 71.91 | 27.8465 | 76.41 | 27.6539 | 81.33 |
| 37.2561 | 65.81 | 32.9368 | 70.91 | 37.3531 | 75.22 | 37.3433 | 80.05 |
| 56.5764 | 64.33 | 49.3891 | 69.33 | 56.1409 | 73.44 | 56.2099 | 78.11 |
| 76.7259 | 62.92 | 67.1717 | 68.15 | 75.2880 | 71.97 | 75.9540 | 76.47 |
| 303.15K | | 308.15K | | 313.15K | | 318.15K | |
| 0.9728 | 94.05 | 0.5384 | 100.02 | 0.8423 | 105.05 | 0.8692 | 110.53 |
| 2.6425 | 92.87 | 2.2865 | 98.51 | 2.7440 | 103.44 | 2.5805 | 109.00 |
| 4.6392 | 91.72 | 4.1996 | 97.32 | 4.5244 | 102.45 | 4.1846 | 108.05 |
| 6.9561 | 90.77 | 6.3733 | 96.31 | 6.5203 | 101.61 | 5.9810 | 107.21 |
| 11.1989 | 89.66 | 11.0568 | 94.75 | 10.9435 | 100.00 | 10.579 | 105.62 |
| 17.7143 | 88 | 18.0634 | 93.01 | 18.1355 | 98.51 | 17.5389 | 103.71 |
| 27.3556 | 86.43 | 27.2035 | 91.34 | 27.3881 | 96.33 | 26.8226 | 101.61 |
| 36.7482 | 84.95 | 36.6234 | 89.99 | 36.3129 | 94.91 | 35.9987 | 99.99 |
| 57.3733 | 82.75 | 55.3952 | 87.74 | 54.9739 | 92.53 | 54.7409 | 97.52 |
| 74.9209 | 81.55 | 74.8542 | 85.93 | 73.7022 | 90.5 | 73.8361 | 95.33 |

****Combined uncertainties, $U_c(\eta) = 0.0040$ mPa·s for viscosity, are $U_c(\rho_0) = 3 \cdot 10^{-3}$ g·cm⁻³ for density, $U_c(\Lambda) = 0.01 - 0.09$ S·cm²·mol⁻¹ (confidence level=0.95). Standard uncertainties, $u(T) = 0.01$ K for temperature, $u(p) = 0.04$ p, $u(c) = 10^{-6}$ mol.dm⁻³.

TABLE 3. The molar conductance of [emim]BF₄ and [bmim]BF₄ at different temperatures in AN solvent

| $C \cdot 10^4$ (mol.dm ⁻³) | A (S.cm ² .mol ⁻¹) | $C \cdot 10^4$ (mol.dm ⁻³) | A (S.cm ² .mol ⁻¹) | $C \cdot 10^4$ (mol.dm ⁻³) | A (S.cm ² .mol ⁻¹) | $C \cdot 10^4$ (mol.dm ⁻³) | A (S.cm ² .mol ⁻¹) |
|---|---|--|---|--|---|--|---|
| 283.15K | | [emim]BF ₄ 288.15K | | 293.15K | | 298.15K | |
| 5.6924 | 162.269 | 5.6924 | 170.675 | 5.6924 | 179.211 | 5.6924 | 187.776 |
| 9.0698 | 160.251 | 9.0698 | 168.461 | 9.0698 | 176.992 | 9.0698 | 185.467 |
| 12.3169 | 158.677 | 12.3169 | 166.941 | 12.3169 | 175.321 | 12.3169 | 183.582 |
| 16.0956 | 157.222 | 16.0956 | 164.944 | 16.0956 | 173.397 | 16.0956 | 181.776 |
| 21.1065 | 155.221 | 21.1065 | 162.985 | 21.1065 | 171.145 | 21.1065 | 179.465 |
| 25.3114 | 153.616 | 25.3114 | 161.731 | 25.3114 | 169.765 | 25.3114 | 177.854 |
| 30.5646 | 152.052 | 30.5646 | 159.961 | 30.5646 | 167.942 | 30.5646 | 175.833 |
| 36.8889 | 150.331 | 36.8889 | 158.551 | 36.8889 | 165.977 | 36.8889 | 173.723 |
| 42.3792 | 149.051 | 42.3792 | 156.075 | 42.3792 | 164.275 | 42.3792 | 172.091 |
| 48.2054 | 147.741 | 48.2054 | 155.155 | 48.2054 | 163.001 | 48.2054 | 170.572 |
| 303.15K | | 308.15K | | 313.15K | | 318.15K | |
| 5.6924 | 196.672 | 5.6924 | 205.722 | 5.6924 | 214.412 | 5.6924 | 223.312 |
| 9.0698 | 193.991 | 9.0698 | 202.667 | 9.0698 | 211.559 | 9.0698 | 220.459 |
| 12.3169 | 191.966 | 12.3169 | 200.523 | 12.3169 | 209.629 | 12.3169 | 218.529 |
| 16.0956 | 189.976 | 16.0956 | 198.334 | 16.0956 | 206.999 | 16.0956 | 215.899 |
| 21.1065 | 187.512 | 21.1065 | 195.897 | 21.1065 | 204.349 | 21.1065 | 213.249 |
| 25.3114 | 185.942 | 25.3114 | 194.123 | 25.3114 | 202.519 | 25.3114 | 211.419 |
| 30.5646 | 183.989 | 30.5646 | 192.231 | 30.5646 | 200.067 | 30.5646 | 208.967 |
| 36.8889 | 181.865 | 36.8889 | 189.945 | 36.8889 | 198.01 | 36.8889 | 206.91 |
| 42.3792 | 180.101 | 42.3792 | 188.321 | 42.3792 | 196.331 | 42.3792 | 205.231 |
| 48.2054 | 178.121 | 48.2054 | 186.019 | 48.2054 | 194.041 | 48.2054 | 202.941 |
| 283.15.K | | [bmim]BF ₄ 288.15K | | 293.15K | | 298.15K | |
| 2.3328 | 158.997 | 2.3328 | 166.856 | 2.3328 | 175.198 | 2.3328 | 183.669 |
| 4.0547 | 156.976 | 4.0547 | 165.234 | 4.0547 | 173.342 | 4.0547 | 181.884 |
| 6.2978 | 155.634 | 6.2978 | 163.478 | 6.2978 | 171.567 | 6.2978 | 179.832 |
| 8.4484 | 154.632 | 8.4484 | 162.124 | 8.4484 | 170.399 | 8.4484 | 178.579 |
| 11.1406 | 152.965 | 11.1406 | 160.987 | 11.1406 | 168.967 | 11.1406 | 176.999 |
| 14.1873 | 151.967 | 14.1873 | 159.453 | 14.1873 | 166.956 | 14.1873 | 174.981 |
| 17.5668 | 149.997 | 17.5668 | 157.654 | 17.5668 | 165.569 | 17.5668 | 173.573 |
| 20.7299 | 149.009 | 20.7299 | 156.875 | 20.7299 | 164.876 | 20.7299 | 172.567 |
| 24.2212 | 149.09 | 24.2212 | 155.779 | 24.2212 | 163.666 | 24.2212 | 171.321 |
| 31.1600 | 146.597 | 31.1600 | 153.554 | 31.1600 | 161.034 | 31.1600 | 168.976 |
| 303.15K | | 308.15K | | 313.15K | | 318.15K | |
| 2.3328 | 192.191 | 2.3328 | 201.106 | 2.3328 | 210.334 | 2.3328 | 219.414 |
| 4.0547 | 190.245 | 4.0547 | 198.654 | 4.0547 | 207.501 | 4.0547 | 216.581 |
| 6.2978 | 188.287 | 6.2978 | 196.678 | 6.2978 | 205.332 | 6.2978 | 214.412 |
| 8.4484 | 186.889 | 8.4484 | 195.387 | 8.4484 | 203.867 | 8.4484 | 212.947 |
| 11.1406 | 185.347 | 11.1406 | 193.654 | 11.1406 | 202.011 | 11.1406 | 211.091 |
| 14.1873 | 183.00 | 14.1873 | 191.231 | 14.1873 | 200.00 | 14.1873 | 209.08 |
| 17.5668 | 181.776 | 17.5668 | 189.987 | 17.5668 | 198.231 | 17.5668 | 207.311 |
| 20.7299 | 180.543 | 20.7299 | 188.654 | 20.7299 | 197.00 | 20.7299 | 206.08 |
| 24.2212 | 179.245 | 24.2212 | 187.234 | 24.2212 | 195.567 | 24.2212 | 204.647 |
| 31.1600 | 176.654 | 31.1600 | 184.542 | 31.1600 | 192.503 | 31.1600 | 201.583 |

****Combined uncertainties, $U_c(\eta) = \dots \pm \dots$ mPa·s for viscosity, are $U_c(\rho_0) = 3 \cdot 10^{-5}$ g·cm⁻³ for density, $U_c(\Lambda) = 0.01 - 0.09$ S·cm²·mol⁻¹ (confidence level=0.95). Standard uncertainties, $u(T) = 0.01$ K for temperature, $u(p) = 0.04p$, $u(c) = 10^{-6}$ mol.dm⁻³.

Limiting molar conductance

To start the calculations, the limiting molar conductance (Λ_0) at infinite dilutions were estimated for salt solution in DMF and AN organic solvents at different temperatures by extrapolating the linear Onsager plot (Eq. 2) between Λ_M and $C^{1/2}$ to zero concentration.

$$\Lambda = \Lambda_0 - S\sqrt{C} \quad (2)$$

where a plot of Λ versus \sqrt{C} gives a straight line of an intercept equal (Λ_0) and a slope equal to the Onsager constant. The limiting molar conductance (Λ_0) of each salt under investigation is directly proportional to the temperature and has the sequence as follows: AN > DMF as indicated in Table 4 which indicate the effect of dielectric constant and viscosity of the solvent. Meaning that this behavior may be due to the higher viscosity value of DMF than that of AN so reduce the ions mobility and decrease the Λ_0 values. Also it is obvious that Λ_0 values increase with temperature increase, as a result of increase in the kinetic energy and ions mobility. The relation between Λ and \sqrt{C} are shown in Fig.1 and Fig.2.

Ion pair association constant

The experimental conductivities were analyzed by means of the Fuoss-Justice conductivity equations [20, 21]. In our solutions, the following equilibria are considered: $M^+ + A^- \rightleftharpoons MA$ so that the conductometric data were treated by Fuoss-Justice method to evaluate the ion-pair association constants of the studied salts and to re-evaluate the limiting molar conductance (Λ_0), where they proposed the following equation:

$$\Lambda = \alpha[\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J(\alpha c) + J_{1/2}(\alpha c)^{1/2}] \quad (3)$$

$$K_A = (1 - \alpha) / (\alpha^2 c y_{\pm}^2) \quad (4)$$

$$\ln y_{\pm} = -(A\alpha^{1/2} c^{1/2}) / (1 + BR\alpha^{1/2} c^{1/2}) \quad (5)$$

According to the literature each parameter has its significant mean while the Debye-Hückel coefficients are represented by A and B, y_{\pm} is the molar scale activity coefficient of ions, R is the ions distance parameter. Λ_0 , α and K_A parameters have its usual meanings that is limiting molar conductance, electrolyte dissociation degree and ion pair constant sequentially. The literature [22–24] discussed the analytical meanings of

TABLE 4. The limiting molar conductance (Λ_0), ion pair formation constant (K_A) and distance parameter (R) of [emim]BF₄ and [bmim]BF₄ in DMF and AN at different temperatures

| T/K | DMF | | | AN | | |
|--------|---|---|--------|---|---|--------|
| | Λ_0 (S.cm ² .mol ⁻¹) | K_A (dm ³ .mol ⁻¹) | R (nm) | Λ_0 (S.cm ² .mol ⁻¹) | K_A (dm ³ .mol ⁻¹) | R (nm) |
| 283.15 | 76.49 ±0.02 | 10.35 ±0.15 | 0.83 | 169.95 ±0.03 | 14.10 ±0.13 | 0.97 |
| 288.15 | 82.01 ±0.02 | 10.64 ±0.11 | 0.80 | 178.80 ±0.02 | 15.32 ±0.13 | 0.92 |
| 293.15 | 87.51 ±0.03 | 11.05 ±0.08 | 0.78 | 187.81 ±0.02 | 15.36 ±0.11 | 0.94 |
| 298.15 | 93.20 ±0.03 | 11.22 ±0.05 | 0.75 | 196.93 ±0.01 | 15.81 ±0.11 | 0.93 |
| 303.15 | 99.00 ±0.03 | 11.51 ±0.05 | 0.73 | 206.11 ±0.03 | 16.25 ±0.05 | 0.92 |
| 308.15 | 104.93 ±0.03 | 12.00 ±0.10 | 0.73 | 215.42 ±0.02 | 16.91 ±0.04 | 0.91 |
| 313.15 | 110.88 ±0.04 | 12.19 ±0.12 | 0.73 | 224.97 ±0.02 | 17.33 ±0.04 | 0.90 |
| 318.15 | 116.93 ±0.05 | 12.67 ±0.19 | 0.75 | 233.87 ±0.04 | 17.94 ±0.06 | 0.89 |
| | [bmim]BF ₄ | | | [bmim]BF ₄ | | |
| 283.15 | 72.90 ±0.02 | 9.65 ±0.11 | 0.83 | 163.23 ±0.03 | 14.25 ±0.04 | 0.80 |
| 288.15 | 78.49 ±0.02 | 9.84 ±0.05 | 0.75 | 171.77 ±0.03 | 15.11 ±0.04 | 0.76 |
| 293.15 | 84.06 ±0.02 | 10.15 ±0.06 | 0.70 | 180.30 ±0.03 | 15.41 ±0.11 | 0.75 |
| 298.15 | 89.71 ±0.02 | 10.33 ±0.11 | 0.69 | 189.08 ±0.02 | 15.61 ±0.10 | 0.77 |
| 303.15 | 95.29 ±0.02 | 10.73 ±0.11 | 0.62 | 197.94 ±0.01 | 16.00 ±0.08 | 0.77 |
| 308.15 | 100.95 ±0.02 | 11.05 ±0.11 | 0.63 | 206.96 ±0.03 | 16.43 ±0.09 | 0.77 |
| 313.15 | 106.50 ±0.03 | 11.34 ±0.05 | 0.69 | 216.33 ±0.05 | 17.12 ±0.07 | 0.78 |
| 318.15 | 112.12 ±0.01 | 11.86 ±0.05 | 0.76 | 225.41 ±0.04 | 17.69 ±0.06 | 0.79 |

In all measurements, $\Delta R = 0.04$ nm.

$J_{3/2}$, E, S and J parameters. Fuoss [20] method is used for the calculation of R, K_A and Λ_0 parameters and their values are tabulated in Table 4. The values of limiting molar conductance (Λ_0) obtained from Fuoss-Justice equation are found to be in agreement with the calculated value of Onsager plot. According to Fuoss-Edelson, we plot Λ versus $c^{1/2}$, which give straight line with intercept equal (Λ_0) and K_A were evaluated, and then iteration of this processes to fixed the value of (Λ_0) for all systems under study and the corresponding K_A values can be determined. The estimated values of the ion-pair association constant (K_A) of all systems under study were represented in Table 4. From association constant (K_A) values, it is observed that its values are very small comparing to other ionic solutions. This mean that these class of salts tend to be free ions more than associated ions inside used solvents DMF and AN. The ion pair formation constant (K_A) of [emim]BF₄ is higher than that of [bmim]BF₄ in the used solvents by $\sim 1 \text{ dm}^3.\text{cm}^{-1}$. The main reason of this behavior is related to the effect of alkyl chain length as discussed in the literature [25, 26]. The association constant is found to increase by the increase of temperature indicating that the association process of [emim]BF₄ and [bmim]BF₄ inside DMF and AN is endothermic process and required for energy that obtained from the surrounding solvent. We did not found any previous study for [bmim]BF₄ and [emim]BF₄ in DMF and AN so we can't compare our results with the literature.

Thermodynamic parameters of association

The standard free energy of association (ΔG_A°) was calculated for all salts under study using Eq. (6) and its values were listed in Table 5.

$$\Delta G_A^\circ(A) = -RT \ln K_A(T) \quad (6)$$

(T) can also be expressed by the polynomial

$$\Delta G_A^\circ = A_0 + A_1T + A_2T^2 \quad (7)$$

Standard enthalpy of association (ΔH_A°) and standard entropy of association (ΔS_A°) are determined according to Eq. (8&9).

$$\Delta S_A^\circ = -\left(\frac{\partial \Delta G_A^\circ}{\partial T}\right) - A_1 - 2A_2T \quad (8)$$

$$\Delta H_A^\circ = \Delta G_A^\circ + T\Delta S_A^\circ = A_0 - A_2T^2 \quad (9)$$

The values of Eq.7 parameters A_0 , A_1 and A_2 are tabulated in Table 6.

The negative values in all cases (Table 5), indicate that the association processes in all

studied systems were spontaneous processes [27, 33]. The negative value of ΔH_A° in case of AN solvent (Table 5) indicates the exothermic nature of the association processes. The negative value of ΔS_A° in case of AN solvent (Table 5) indicates that the enthalpy is the driving force of the association process. Additionally, unclear behaviors of entropy values in AN solvent may be result because the association process is very complicated. This unclear behavior approves that the enthalpic effect in AN solvent seem to dominate over the entropic effect. In case of DMF solvent, positive value of ΔH_A° indicating that the association process is endothermic. ΔH_A° values is higher in case of small cation [emim]BF₄ in the used solvents indicating easier association process. ΔH_A° values increase by increasing temperature in all cases indicating the tendency to form ion pairs by increasing temperatures.

The Eyring activation energy of charge transport (ΔH_A^\ddagger) can be calculated according to limiting molar conductance Λ_0 and temperature relation as in Eq.10

$$\ln \Lambda_0 + \frac{2}{3} \ln \rho_0 = -\frac{\Delta H_A^\ddagger}{RT} + B \quad (10)$$

Where B is an empirical constant. ΔH_A^\ddagger can be calculated from the slope of the relation between $\ln \Lambda_0 + \frac{2}{3} \ln \rho_0$ and $1/T$ as shown in Fig.3. ΔH_A^\ddagger value of [emim]BF₄ and [bmim]BF₄ in DMF are 8569 J.mol⁻¹ and 8691 J.mol⁻¹ respectively. ΔH_A^\ddagger value of [emim]BF₄ and [bmim]BF₄ in AN are 6150 J.mol⁻¹ and 6205 J.mol⁻¹ respectively. ΔH_A^\ddagger values showed that [bmim]BF₄ has higher value more than [emim]BF₄ with a difference equal to 122 units in DMF and 55 units in AN. This result may be arising from the presence of larger substituent [bmim]⁺ compared to [emim]⁺.

Walden product and hydrodynamic radii

From the point of view of ion-solvent interactions, Walden product ($\Lambda_0 \eta_0$) is an informative tool with a constant value [34, 35] because of limiting molar conductance of the ions depends up on its movement, thus the result of solvent viscosity by ion conductance must be independent of the nature of solvent. Thus in a series of mixed solvents with a uniform ion-solvent interactions, Walden product ($\Lambda_0 \eta_0$) will has a constant value for a certain electrolyte. Eq. (11) represents the formula of Walden product for 1:1 electrolytes. Table 7 is containing the calculated values of Walden product for ionic liquids in the used solvents.

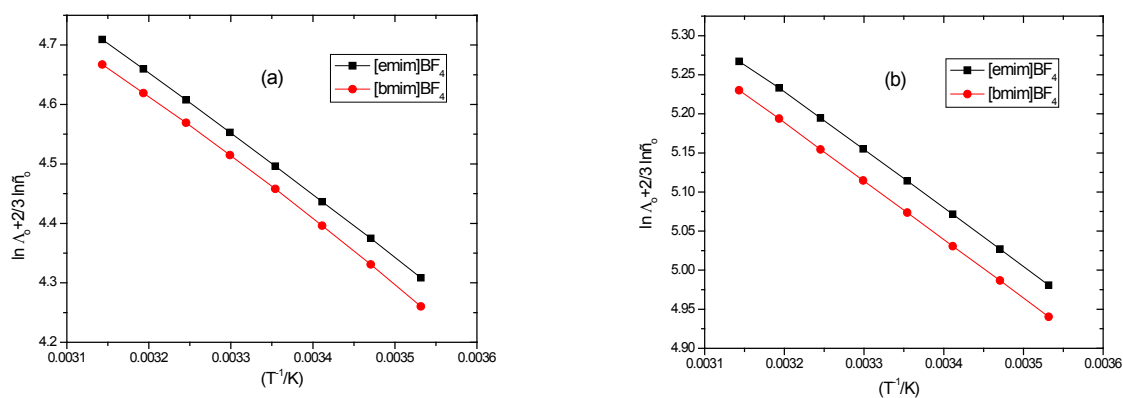
$$\Lambda_0 \eta_0 = \tau_s = 8.204 z_i / r_s \quad (11)$$

TABLE 5. The free energy of association (ΔG , kJ mol⁻¹), entropy of association and enthalpy of association of [emim]BF₄ and [bmim]BF₄ at different temperatures in the used solvents

| T/K | DMF | | | AN | | |
|--------|--|---|-------------------------|--|---|-------------------------|
| | [emim]BF ₄ (kJ.mol ⁻¹) | (J.mol ⁻¹ .K ⁻¹) | (kJ.mol ⁻¹) | [emim]BF ₄ (kJ.mol ⁻¹) | (J.mol ⁻¹ .K ⁻¹) | (kJ.mol ⁻¹) |
| 283.15 | -5.5015 | 29.96 | 2.982 | -6.2293 | 80.65 | -302.577 |
| 288.15 | -5.6648 | 35.38 | 4.530 | -6.5381 | 42.87 | -313.369 |
| 293.15 | -5.8553 | 40.80 | 6.105 | -6.6580 | 5.09 | -324.350 |
| 298.15 | -5.9930 | 46.22 | 7.708 | -6.8431 | -32.69 | -335.519 |
| 303.15 | -6.1578 | 51.64 | 9.337 | -7.0270 | -70.47 | -346.878 |
| 308.15 | -6.3662 | 57.06 | 10.994 | -7.2449 | -108.25 | -358.425 |
| 313.15 | -6.5104 | 62.48 | 12.678 | -7.4264 | -146.03 | -370.162 |
| 318.15 | -6.7165 | 67.90 | 14.388 | -7.6364 | -183.81 | -382.087 |
| | [bmim]BF ₄ | | | [bmim]BF ₄ | | |
| 283.15 | -5.3366 | 25.24 | 47.374 | -6.2543 | 59.16 | -144.158 |
| 288.15 | -5.4776 | 31.16 | 49.065 | -6.5051 | 41.16 | -149.299 |
| 293.15 | -5.6482 | 37.08 | 50.786 | -6.6659 | 23.16 | -154.531 |
| 298.15 | -5.7881 | 43.00 | 52.536 | -6.8115 | 5.16 | -159.853 |
| 303.15 | -5.9809 | 48.92 | 54.316 | -6.9880 | -12.84 | -165.265 |
| 308.15 | -6.1549 | 54.84 | 56.125 | -7.1712 | -30.84 | -170.766 |
| 313.15 | -6.3222 | 60.76 | 57.964 | -7.3946 | -48.84 | -176.358 |
| 318.15 | -6.5417 | 66.68 | 59.833 | -7.5993 | -66.84 | -182.040 |

TABLE 6. Eq.7 coefficients A₀, A₁ and A₂ of [emim]BF₄ and [bmim]BF₄ in acetonitrile and dimethyl formamide.

| System | A ₀ /kJ.mol ⁻¹ | A ₁ (J.mol ⁻¹ .K ⁻¹) | A ₂ (J.mol ⁻¹ .K ⁻²) |
|-----------------------|--------------------------------------|--|--|
| [emim]BF ₄ | DMF | | |
| | -40.472 | 276.974 | -0.542 |
| [bmim]BF ₄ | -88.368 | 310.009 | -0.592 |
| [emim]BF ₄ | AN | | |
| | 319.503 | -2220.131 | 3.778 |
| [bmim]BF ₄ | 154.809 | -1078.500 | 1.800 |

**Fig.3.** versus 1/T for [bmim]BF₄ and [emim]BF₄ in (a) DMF, (b) AN solvents.

The z_i is the ion charge number and η_0 is the viscosity of the used solvent. Walden product values as seen in Table 7 show a small change of its value and approve the relation in Eq.11 that the temperature has a minor effect on Walden product and the viscosity of the solvent is the major factor. As seen in Walden product results $[\text{bmim}]^+$ has ion effective size larger than that of $[\text{emim}]^+$ at all used temperatures. Walden product results follow the series:

$$\Lambda_0 \eta_0 (\text{DMF}) > \Lambda_0 \eta_0 (\text{AN}),$$

$$\Lambda_0 \eta_0 [\text{emim}]\text{BF}_4 > \Lambda_0 \eta_0 [\text{bmim}]\text{BF}_4$$

The Walden product suggestion that $[\text{bmim}]^+$ has higher effective radius is in good agreement with the results of Eyring activation enthalpy of charge transfer in which $[\text{bmim}]^+$ has higher value.

Conclusions

Conductance study of $[\text{emim}]\text{BF}_4$ and $[\text{bmim}]\text{BF}_4$ has been reported in DMF and AN solvents. The data was analyzed using Fuoss-Justice equation. We can conclude that, the extent of ion-pairing in salt solutions

under study depends upon the nature of the ion-solvent interaction taking place in the solution. Moreover, it depends on the dielectric constant and the properties of the medium. The association of both ionic liquids increase as the temperature increase and the ion pair constant of $[\text{emim}]\text{BF}_4$ is higher than that of $[\text{bmim}]\text{BF}_4$ in the used solvents due to effect of alkyl chain length. Also, it was found that the predominant order of the association constant is in DMF < in AN. Also, the low cost and effective conductance method is used to determine Walden product and activation enthalpy of charge transfer.

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TABLE 7. The Walden product ($\Lambda_0 \eta_0$, S.mol⁻¹.cm². mPa.s) of $[\text{emim}]\text{BF}_4$ and $[\text{bmim}]\text{BF}_4$ at temperatures and solvents used

| T/K | DMF | AN |
|--------|--|--|
| | $[\text{emim}]\text{BF}_4$ $10^{-2} \Lambda_0 \eta_0$ | $[\text{emim}]\text{BF}_4$ $10^{-2} \Lambda_0 \eta_0$ |
| 283.15 | 0.777 | 0.676 |
| 288.15 | 0.783 | 0.674 |
| 293.15 | 0.786 | 0.674 |
| 298.15 | 0.788 | 0.672 |
| 303.15 | 0.791 | 0.671 |
| 308.15 | 0.793 | 0.669 |
| 313.15 | 0.795 | 0.667 |
| 318.15 | 0.798 | 0.659 |
| | $[\text{bmim}]\text{BF}_4$ $10^{-2} \Lambda_0 \eta_0$ | $[\text{bmim}]\text{BF}_4$ $10^{-2} \Lambda_0 \eta_0$ |
| 283.15 | 0.740 | 0.649 |
| 288.15 | 0.749 | 0.648 |
| 293.15 | 0.755 | 0.647 |
| 298.15 | 0.758 | 0.645 |
| 303.15 | 0.761 | 0.644 |
| 308.15 | 0.762 | 0.643 |
| 313.15 | 0.764 | 0.642 |
| 318.15 | 0.765 | 0.635 |

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معاملات الديناميكا الحرارية لذوبان ١-إيثيل-٣-ميثيل إيميدازوليوم رباعي بورات الفلور و ١-بيوتيل-٣-ميثيل إيميدازوليوم رباعي بورات الفلور في مذيب ثنائي ميثيل الفورمايدول والأسيتونيترييل عند درجات الحرارة المختلفة

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يهدف البحث إلي تعيين تداخلات الأيون والمذيب البينييه لمجموعه جديده من المذيبات هي الأملاح الأيونيه السائله مثل-إيثيل-٣-ميثيل إيميدازوليوم رباعي بورات الفلور و ١-بيوتيل-٣-ميثيل إيميدازوليوم رباعي بورات الفلور في مذيب ثنائي ميثيل الفورمايدول والأسيتونيترييل في نطاق درجة حراره من ٢٨٣,١٥ إلي ٣١٨,١٥ درجة كلفن عن طريق استخدام التوصيليه الكهربيه. تم تحليل بيانات التوصيليه الكهربيه باستخدام معادله فوس-جوستيس وتم حساب التوصيل المولي (A) والتوصيل المولي المحدد (A_0) وثابت التجمع وناتج والذن وطاقة تنشيط ايرنج ومعاملات الديناميكا الحراريه للتجمع وهي الطاقه الحره للتجمع والإنثالي والإنتروبي وقد أظهرت النتائج أن التوصيل المولي والتوصيل المولي المحدد قد نقص عند نقص السماحيه النسبييه للمذيب ولكن زاد ثابت التجمع. أظهرت النتائج أن التوصيل المولي والتوصيل المولي المحدد زاد بزيادة درجة الحراره وكذلك زاد ثابت التجمع مما يدل أن عملية التجمع ماصه للحراره كما هو مبين من نتائج الإنتروبي والإنثالي. كما تم دراسة تأثير طول سلسله الألكيل علي معاملات الديناميكا الحراريه وخصائص الارتباط.