# Effect of the Alkyl Chain Length of the Cation on the Interactions between Water and Ammonium-Based Ionic Liquids: Experimental and COSMO-RS Studies

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# Evaluation of Thermophysical Properties of Ionic Liquids with Polar Solvent: A Comparable Study of Two Families of Ionic Liquids with Various Ions

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**Ⓢ** *Supporting Information*

**ABSTRACT:** In this work, we explore and compare the role of the ion effect on the thermophysical properties of two families of ionic liquids (ILs), namely, tetra-alkyl ammonium cation $[R_4N]^+$ with hydroxide $[OH]^-$ anion and 1-alkyl-3-methyl imidazolium cation $[amim]^+$ with different anions (chloride, methyl sulfate, and tetrafluoroborate), with polar solvent such as dimethylsulfoxide (DMSO) in the temperature range from 25 to 40 °C and over the whole concentration range of ILs. Two families of ILs, namely, tetramethyl ammonium hydroxide $[(CH_3)_4N][OH]$ (TMAH), tetraethyl ammonium hydroxide $[(C_2H_5)_4N][OH]$ (TEAH), tetrapropyl ammonium hydroxide $[(C_3H_7)_4N][OH]$ (TPAH), and tetrabutyl ammonium hydroxide $[(C_4H_9)_4N][OH]$ (TBAH) from ammonium-based ILs and 1-ethyl-3-methylimidazolium chloride $[Emim][Cl]$, 1-ethyl-3-methylimidazolium methylsulfate $[Emim][MeSO_4]$, 1-butyl-3-methylimidazolium tetrafluoroborate $[Bmim][BF_4]$, and 1-butyl-3-methylimidazolium chloride ($[Bmim][Cl]$) from imidazolium family of ILs, are used in the present study. To address the molecular interactions of ILs with DMSO, densities ($\rho$), ultrasonic sound velocities ($u$), and viscosities ($\eta$) have been measured over the entire composition range and at four temperatures, 25, 30, 35, and 40 °C, under atmospheric pressure. From these experimental data, the excess molar volume ($V^E$), the deviation in isentropic compressibility ($\Delta\kappa_s$), and the deviation in viscosity ($\Delta\eta$) were calculated and were adequately correlated by using the Redlich−Kister polynomial equation. The measured and predicted data were interpreted on the basis of intermolecular interactions and structural effects between like and unlike molecules upon mixing. The hydrogen-bonding features between ammonium-based ILs and DMSO were analyzed using molecular modeling program by HyperChem 7.
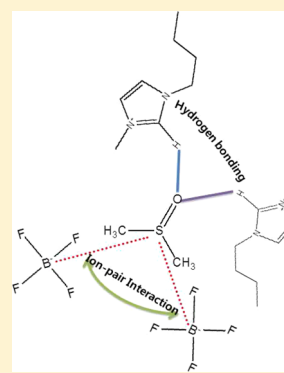
## ■ INTRODUCTION

Dimethylsulfoxide (DMSO) is a colorless, odorless, hygroscopic liquid with a slightly bitter taste. It is a versatile, powerful, biodegradable, and nontoxic solvent. DMSO is an extraordinary dipolar solvent, completely miscible with water and with a very wide range of organic and inorganic substances.[1,2] DMSO has a unique position among the polar solvents and is extensively used in chemistry, biology, and medicine.[3−6] DMSO is a self-associated liquid over a wide range of temperatures and has the ability to participate in hydrogen bonding. Moreover, it is a strong electron donor and has a high polarity. On the other hand, the structure of DMSO, with a hard oxygen atom and a soft sulfur atom, leads to good solvation of cations and poor solvation of anions.[2] The resonance structure of DMSO is shown below.
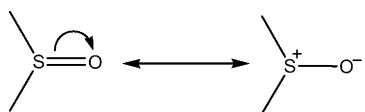
DMSO is best formulated as a resonance structure and as having a polarized S−O bond, which is a $(P{\rightarrow}d)_\pi$ SO double bond character compound. The enhancement of its donor ability in liquid mixtures may result from rupture of the DMSO structure by another solvent.

Over the last couple of decades, ionic liquids (ILs) have received a great deal of attention as a class of solvents with limitless applications in a wide range of disciplines and are growing rapidly because of their tunable and unique properties.[7−10] The most notable characteristics of many ILs are their low vapor pressure, nonflammability, low melting point, wide liquid range, and solvating properties for diverse substances.[11−15] A few characteristic features of ILs are the ability to form hydrogen bonds and the ability to mediate hydrocarbon−solvent interactions. Moreover, ILs appear as alternative and complementary solvents to the conventional organic solvents.

Knowledge of structure and properties of ILs is essential for understanding their molecular interactions in the binary mixtures. For the applications in chemical industrial processes, the knowledge of the thermophysical properties of ILs is necessary as they represent the basis for the chemical and

**Table 1. Specifications of Pure Components and Comparison of Experimental Densities ($\rho$), Ultrasonic Sound Velocities ($u$), and Viscosities ($\eta$) with the Literature Values for DMSO and ILs at 25 °C**

| solvent | MW/(g.mol$^{-1}$) | mass fraction purity | $\rho$/(g.cm$^{-3}$) | | $u$/(m.s$^{-1}$) | | $\eta$/(mPa.s) | |
|---|---|---|---|---|---|---|---|---|
| | | | exptl | lit. | exptl | lit. | exptl | lit. |
| DMSO | 78.13 | 0.99 | 1.095 | 1.09537[a] | 1496 | 1485[b] | 1.99 | 1.99[b] |
| | | | | 1.09530[b,c] | | 1489[f] | | 1.97[i] |
| | | | | 1.09536[d] | | | | |
| | | | | 1.09527[e] | | | | |
| | | | | 1.09533[f] | | | | |
| | | | | 1.09540[g] | | | | |
| | | | | 1.09574[h] | | | | |
| TMAH | 91.1 | 0.99 | 1.018 | 1.01797[j] | 1828 | 1828[j] | 2.77 | 2.77[j] |
| TEAH | 147.26 | 0.99 | 1.009 | 1.00881[j] | 1814 | 1814[j] | 4.94 | 4.94[j] |
| TPAH | 203.25 | 0.99 | 0.996 | 0.99594[j] | 1801 | 1801[j] | 6.1 | 6.10[j] |
| TBAH | 259.34 | 0.99 | 0.994 | 0.99358[j] | 1798 | 1798[j] | 6.69 | 6.69[j] |
| [Emim][Cl] | 146.06 | 0.99 | | | | | | |
| [Emim][MeSO$_4$] | 222.26 | 0.99 | 1.28 | 1.2873[k] | 1730 | | 84.3 | 83.885[k] |
| | | | | 1.2629[l] | | | | |
| [Bmim][BF$_4$] | 226.13 | 0.99 | 1.201 | 1.20150[m] | 1566 | | 101 | 103.4[n] |
| | | | | 1.201129[n] | | | | 103.8[s] |
| | | | | 1.20057[o] | | | 80.66[t] | 81.40[t,h] |
| | | | | 1.20110[p] | | | | 80.60[s] |
| | | | | 1.20100[q] | | | | 100.66[r] |
| | | | | 1.20089[h] | | | | |
| | | | | 1.20030[r] | | | | |
| [Bmim][Cl] | 174.67 | 0.99 | 1.074 | 1.08[u,v] | | | | |

[a]Reference 16. [b]Reference 17. [c]Reference 18. [d]Reference 19. [e]Reference 20. [f]Reference 21. [g]Reference 22. [h]Reference 23. [i]Reference 24. [j]Reference 25. [k]At 0.0023 mol fraction ref 26. [l]Reference 27. [m]Reference 28. [n]Reference 29. [o]Reference 30. [p]Reference 31. [q]Reference 32. [r]Reference 33. [s]Reference 34. [t]At 30 °C. [u]Reference 35. [v]Reference 36

biological process.[7] The experimental values of thermophysical properties allow us to establish new predictive interactions and information about the molecular level structure of the mixtures that are desirable for industry. Therefore, a deep knowledge of thermophysical properties of liquid mixtures containing ILs is essentially required for the scientific community. Apparently, the physicochemical properties of ILs are quite sensitive toward the structure and nature of cations and anions. The variations in thermophysical properties of ILs, such as density ($\rho$), speed of sound ($u$), and viscosity ($\eta$), are observed to be very sensitive to the change in ion mainly because of microscopic level interactions between solvent molecules. Studies on thermophysical properties of the ILs and their mixtures with polar solvents have shown better media for chemical processes. However, until now, there is no comprehensive and comparative study available on the properties and structure relation of mixtures of the ammonium family of ILs or imidazolium-based ILs with DMSO mixtures that covers the impact of different factors such as cation size, temperature, and composition and also ion−ion pair interactions.

In this work, we explore and compare the measurements of three thermophysical properties such as $\rho$, $u$, and $\eta$ of binary mixtures involving DMSO with tetramethyl ammonium hydroxide [(CH$_3$)$_4$N][OH] (TMAH), tetraethyl ammonium hydroxide [(C$_2$H$_5$)$_4$N][OH] (TEAH), tetrapropyl ammonium hydroxide [(C$_3$H$_7$)$_4$N][OH] (TPAH), tetrabutyl ammonium hydroxide [(C$_4$H$_9$)$_4$N][OH] (TBAH), 1-ethyl-3-methylimidazolium chloride [Emim][Cl], 1-ethyl-3-methylimidazoliummethylsulfate [Emim][MeSO$_4$], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$], and 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) over a complete mole fraction range at various temperatures. Further, the excess molar volume ($V^E$),

the deviation in isentropic compressibilities ($\Delta\kappa_s$), and the deviation in viscosity ($\Delta\eta$) were calculated from the experimental data by using the standard equations. These deviations in physical parameters have been explained in terms of intermolecular interactions between DMSO and ILs. Moreover, the hydrogen-bonding features between ammonium-based ILs and DMSO were carried out to get a deeper insight into intermolecular interactions for these mixtures. These studies were performed according to the semiempirical calculations by using HyperChem 7.

■ **EXPERIMENTAL PROCEDURE**

**Materials.** DMSO (Merck >99% of purity) was stored over freshly activated 3 Å molecular sieves and was purified by the standard method described by Riddick et al.[1] The purity of the DMSO was checked by comparing the measured $\rho$, $u$, and $\eta$ which were in good agreement with literature values.[16−24] All of the ammonium family of ILs, namely, TMAH, TEAH, TPAH, and TBAH of general type [amine][anion], used in the present study were synthesized in our laboratory. The procedure for synthesis of ILs was delineated in our previous paper in detail.[25] All imidazolium-based ILs such as [Emim][Cl], [Emim]-[MeSO$_4$], [Bmim][BF$_4$], and [Bmim][Cl] were obtained from Sigma−Aldrich chemical company (U.S.). Among the ILs, TMAH, TEAH, TPAH, and TBAH had low levels of water (below 70 ppm) analyzed by Karl Fischer titration. Further, we found low levels of water (below 75 ppm) for [Emim][Cl], [Emim][MeSO$_4$], [Bmim][BF$_4$], and [Bmim][Cl] which were analyzed by Karl Fischer titration. A comparison is made for the pure solvents in Table 1 between the experimental $\rho$, $u$, and $\eta$ values determined in the present study and those reported in the literature.[16−36] It can be seen that the values of the
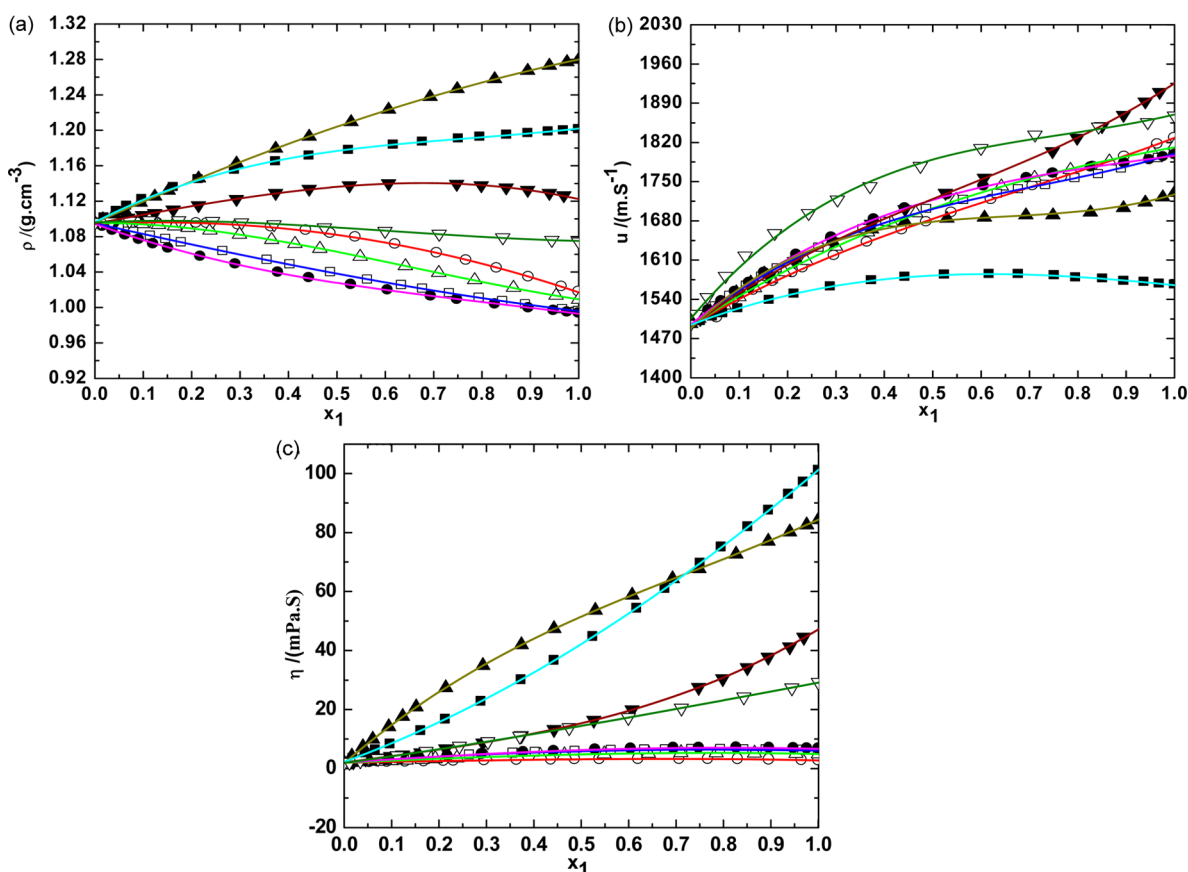
**Figure 1.** (a) Densities ($\rho$), (b) ultrasonic sound velocity ($u$), and (c) viscosities ($\eta$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL data: ○, TMAH (1) + DMSO (2); △, TEAH (1) + DMSO (2); □, TPAH (1) + DMSO (2); ●, TBAH (1) + DMSO (2); ▲, [Emim][MeSO$_4$] (1) + DMSO (2); ■, [Bmim][BF$_4$] (1) + DMSO (2); ▽, [Bmim][Cl] (1) + DMSO (2); and ▼, [Emim][Cl] (1) + DMSO (2) at 25 °C and atmospheric pressure. The solid line represents the smoothness of these data.

properties of DMSO well agree with those reported in the literature.[16−24] However, it is expected that there are discrepancies between values reported in the literature for the $\rho$ and $\eta$ of imidazolium-based ILs by different groups because of impurities such as water. Impurities in ILs may have a dramatic effect on its thermophysical properties. No comparable $\rho$ data were found in the literature for ammonium ILs studied in this work.

■ **METHODS AND PROCEDURE**

The binary mixtures of DMSO and IL were prepared by mass using a high-precision analytical balance (Mettler Toledo) with an uncertainty of $\pm 1 \times 10^{-4}$ g. All of the samples were prepared immediately before the measurements to avoid variations in composition because of evaporation of the solution. The detailed procedure for all three measurements was described in detail elsewhere.[25,37,38] The estimated uncertainty in the mole fraction composition was found to be less than $5 \times 10^{-4}$. After mixing the sample, the bubble-free homogeneous sample was transferred into the U-tube of the densimeter or the sample cell of ultrasonic interferometer through a medical syringe. A bubble-free sample was introduced into the sample cell, and the cell was placed under the sensor plates of the viscometer. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled to ±0.01 K was used for all the $u$ and $\eta$ measurements.

**Density Measurements.** Solution densities were determined in the temperature range of 25−40 °C at atmospheric

pressure with an Anton-Paar DMA 4500 M vibrating-tube densimeter equipped with a built-in solid-state thermostat and a resident program with an accuracy of temperature of ±0.03 °C. The instrument was calibrated once a day with double-distilled, deionized water and with air at 20 °C as standards. The uncertainty in the density experimental measurements was ±0.00005 g cm$^{-3}$. The excess molar volumes ($V^E$) of ILs with DMSO systems over the IL concentration range at different temperatures have been deduced from the $\rho$ of the pure compounds and the mixture ($\rho_m$) using the standard equations. The $V^E$ values are accurate to ±0.003 cm$^3$ mol$^{-1}$.

**Ultrasonic Sound Velocity Measurements.** Ultrasonic sound velocity measurements were measured using a commercially available single crystal ultrasonic interferometer (model F-05) operating at 2 MHz frequency supplied by Mittal Enterprises, New Delhi, India. The uncertainty in sound velocity was 0.2%.

**Viscosity Measurements.** The viscosity of the studied pure solvents and of all the binary mixture solutions was measured by using SV-10 sine wave vibro viscometer (A&D Co. Ltd. Japan) by detecting the driving electric current necessary to resonate the two sensor plates at a constant frequency of 30 Hz and at a amplitude of less than 1 mm. All $\eta$ measurements of the samples were collected at a heating rate of 1 K/15 min after reaching the thermodynamic equilibrium. Typically, the uncertainty in $\eta$ is 1%.

The deviation in isentropic compressibility ($\Delta\kappa_s$) and the deviation in viscosities ($\Delta\eta$) of ILs with DMSO over the entire
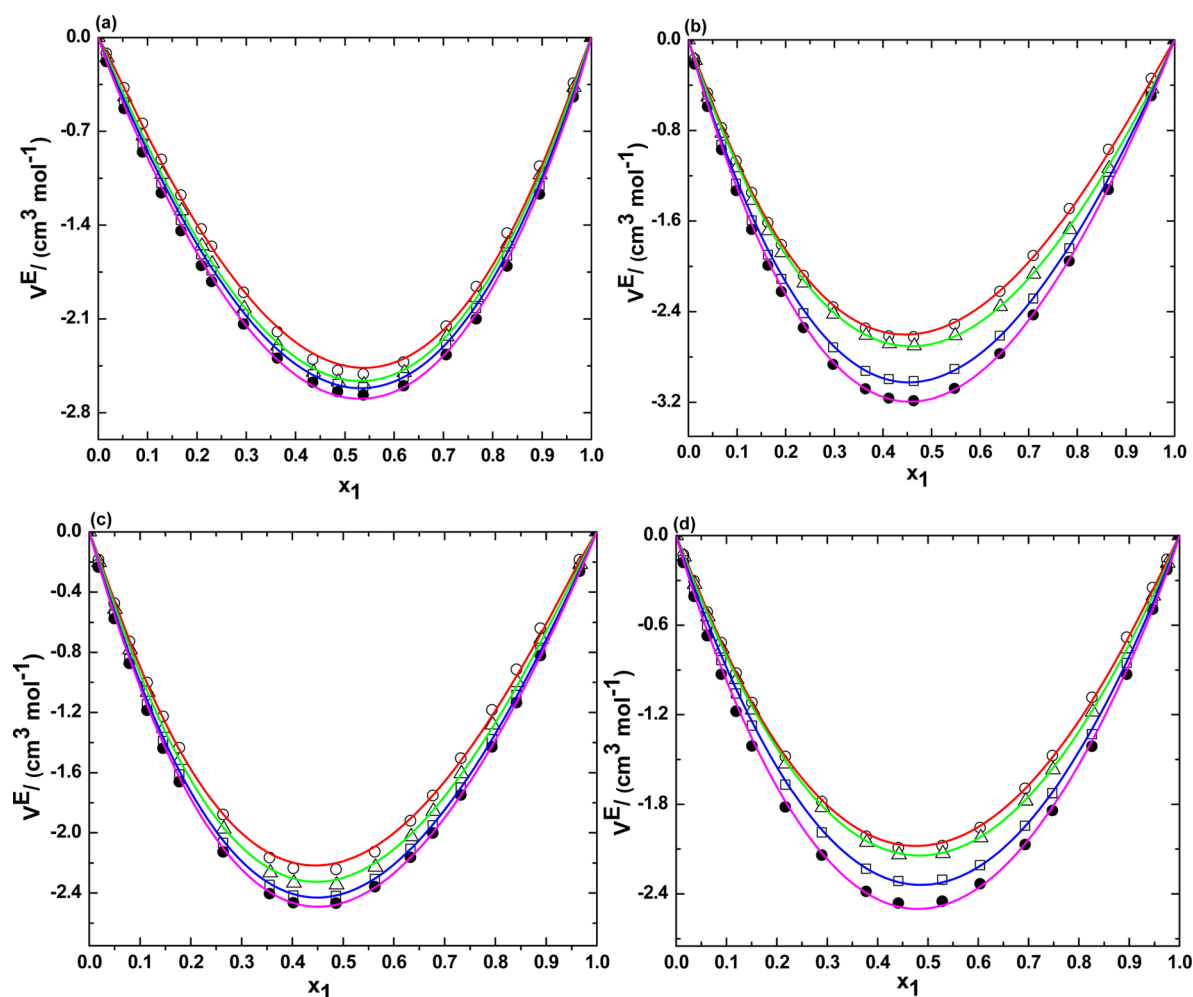
**Figure 2.** Excess molar volumes ($V^E$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) TMAH (1) + DMSO (2); (b) TEAH (1) + DMSO (2); (c) TPAH (1) + DMSO (2); (d) TBAH (1) + DMSO (2) at (○) 25, (△) 30, (□) 35, and (●) 40 °C at atmospheric pressure. The solid curves are correlated by Redlich−Kister equation.

composition range were obtained from the experimental data according to well-known thermodynamic expressions at temperatures from 25 to 40 °C and at atmospheric pressure.

**Hydrogen Bonding through Molecular Modeling Program.** The structures of ammonium ILs and DMSO were optimized on the basis of molecular mechanics and semiempirical calculations using the HyperChem 7 molecular visualization and simulation program.[39−41] Initial molecular geometries of DMSO and ILs were optimized with the AM1 semiempirical calculations, and single-point calculations were carried out to determine the total energies. The optimized molecules of DMSO and IL were chosen and then were placed on top of each other symmetrically (parallel) with a starting interplanar distance of 2.3 Å, and the angle made by covalent bonds to the donor and acceptor atoms was less than 120°. Further, the geometries were optimized using geometry optimizations on the basis of molecular mechanics (using the MM + force field) and AM1 semiempirical calculations; the Polak-Ribiere routine with root mean square (rms) gradient of 0.01 as the termination condition was used. Hydrogen bonds were obtained using HyperChem show hydrogen bonds and recompute hydrogen bond options. Further, we calculated the heat of formation (ΔHf) and binding energies (E) of the pure components and their mixtures. Using this calculation, we

examined that the ammonium ILs are engaged in the H-bonding with the DMSO.

## RESULTS AND DISCUSSION

The thermophysical properties of ILs and their mixtures with polar solvent are of fascinating and great practical importance in understanding the intermolecular interactions of mixed solvents. The knowledge of the thermophysical properties of polar solvent with IL mixtures is important for many chemical

**Table 2. Calculated Binding Energies (E) and Heat of Formation (ΔHf) of Pure Components and Their Mixtures Optimized with HyperChem 7**

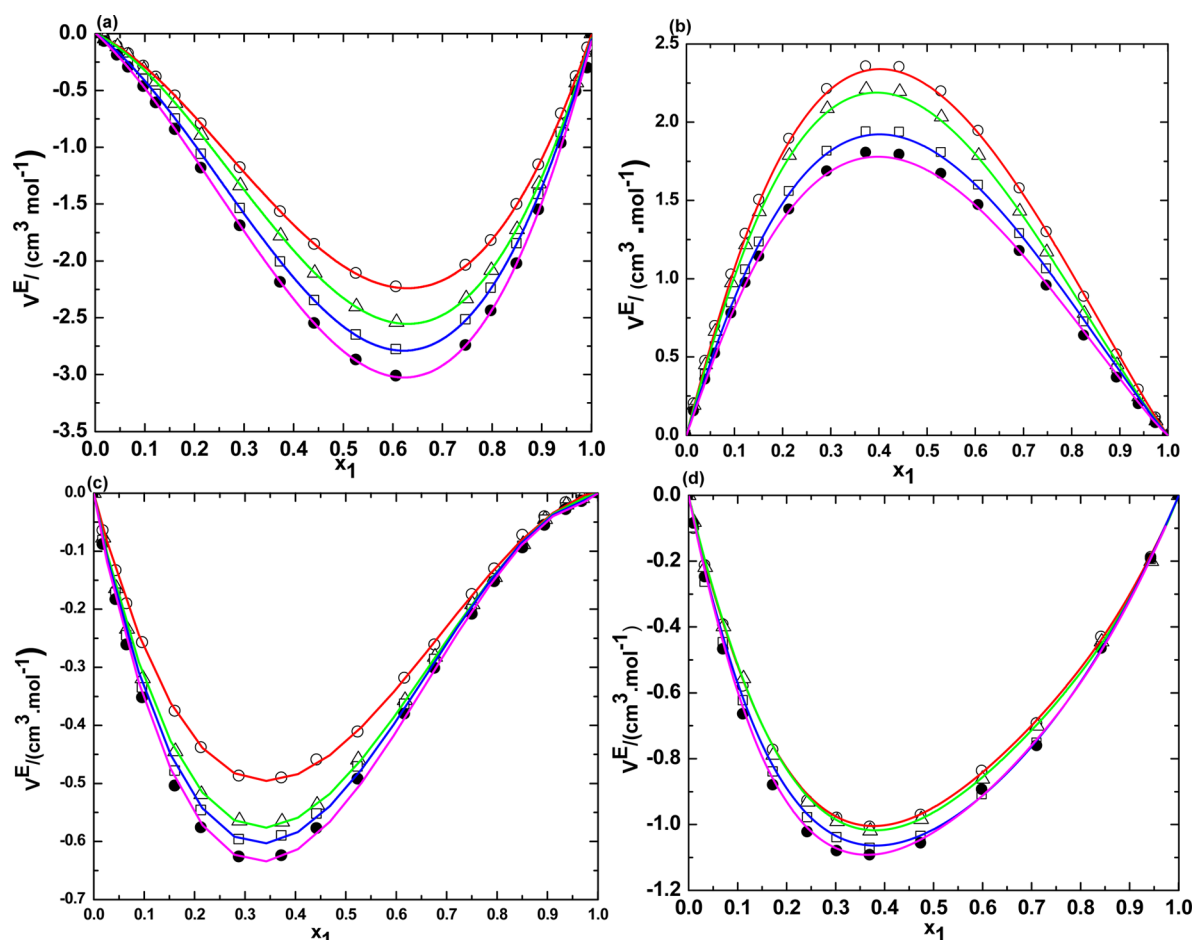| compound or mixture | E (kcal/mol) | ΔHf (kcal/mol) |
|---|---|---|
| DMSO | −820.31 | −39.96 |
| TMAH | −1510.41 | −23.03 |
| TEAH | −2658.98 | −25.17 |
| TPAH | −3784.96 | −50.76 |
| TBAH | −4907.84 | −73.27 |
| TMAH + DMSO | −2362.50 | −48.71 |
| TEAH + DMSO | −3475.03 | −60.86 |
| TPAH + DMSO | −4607.08 | −88.53 |
| TBAH + DMSO | −5733.18 | −112.25 |

**Figure 3.** Excess molar volumes ($V^E$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) [Emim][Cl] (1) + DMSO (2); (b) [Emim][MeSO$_4$] (1) + DMSO (2); (c) [Bmim][BF$_4$] (1) + DMSO (2); and (d) [Bmim][Cl] (1) + DMSO (2) at (○) 25, (△) 30, (□) 35, and (●) 40 °C at atmospheric pressure. The solid curves are correlated by Redlich−Kister equation.

processes in which these mixtures are potential replacement for conventional solvent media.[42−45] As a consequence, great effort is being made for determining these properties either experimentally[25,39,40,42−45] or by modeling and simulation estimations.[46−49]

To provide insight into a molecular picture of the interactions between polar solvent DMSO with two different families of ILs, we have measured $\rho$, $u$, and $\eta$ properties over the whole composition range at four temperatures, 25, 30, 35, and 40 °C under atmospheric pressure. Because [Emim][Cl] is solid, the measurements were performed only up to 0.9929 mol fraction of IL ($x_1$). Interestingly, this IL is liquefying with the addition of DMSO. The properties of [Bmim][Cl] with DMSO were previously reported by us.[38] For the sake of clarity and comparison between imidazolium-based ILs, we have discussed the data of this system in the present study also. However, $\rho$, $u$, and $\eta$ of pure overcooled liquid [Emim][Cl] or [Bmim][Cl] were calculated from the binary data via extrapolation, which may be quite credible as the highest concentration of [Emim][Cl] is 0.9920, which is almost pure compound. The experimental $\rho$, $u$, and $\eta$ values of all the ammonium family ILs and all of the imidazolium-based ILs with DMSO are presented as a function of IL concentration in Tables 1S and Table 2S of the Supporting Information (SI), respectively. Further, Figures 1S−6S of the SI show the measured $\rho$, $u$, and $\eta$ values for the binary mixtures involving DMSO with all ILs at all studied

temperatures. Figure 1 reveals the measured properties of $\rho$, $u$, and $\eta$ values of binary mixtures for all ILs with DMSO as function of IL concentration at 25 °C.

The $\rho$ values of ammonium ILs with DMSO do not follow a similar trend. The mixture of TMAH or TEAH with DMSO shows a slight increase in $\rho$ values up to $x_1 \approx 0.1000$ at all experimental temperatures; later, the values decrease with increasing the IL concentration as displayed in Figure 1Sa or b of the SI, respectively. This may be due to the progressive weakening of the ion−ion pair interactions between TMAH or TEAH with DMSO and also to the self-interaction occurring between the ions of IL above the $x_1 \approx 0.1000$. On the other hand, it is found that the $\rho$ values of the mixtures of TPAH or TBAH with DMSO decrease with increasing mole fraction of the IL as shown in Figure 1a and 1Sc or d of the SI, respectively.

The results reveal that the $\rho$ of ammonium ILs with DMSO decreases slowly as the alkyl chain length increases from methyl to butyl chain of IL as shown in Figure 1S of the SI. It was found that the $\rho$ for the mixtures of ammonium ILs with DMSO decreases as both temperature and concentration of the ILs increase as shown in Figure 1S of the SI. The data in Figure 1 and 1S of the SI indicate that the $\rho$ values of the ILs follow the order TMAH > TEAH > TPAH > TBAH, which indicates that the lower alkyl chain length of cation of ILs is much denser than higher alkyl chain length of ILs. It can be known from the

**Scheme 1. Existence of a Strong Interaction between the Cation (+) of [Bmim][BF$_4$] and the Negatively Charged Oxygen (−) of DMSO and Also the Anion (−) of [Bmim][BF$_4$] and the Positively Charged S Atom (+) of DMSO**
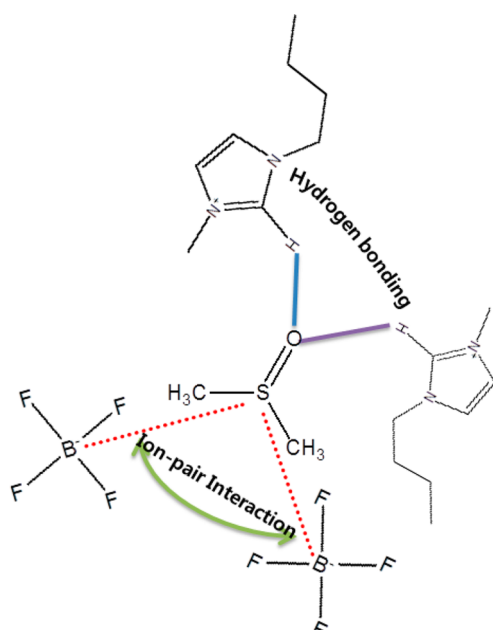


$\rho$ values in Figure 1a and 1S of the SI that the $\rho$ is quite sensitive to the size of the cation of ammonium ILs, temperature, and also the composition of mixture. This has been attributed to the modification of the cation–anion interaction because of the increase in the cation size.[7,50,51]

However, in imidazolium-based ILs with DMSO, we observed an opposite trend as compared to ammonium ILs. Figure 1a and 2Sa or d of the SI reveal that the $\rho$ values for [Emim][Cl] or [Bmim][Cl] + DMSO system increase up to the $x_1 \approx 0.6000$ or 0.1700 on addition of [Emim][Cl] or [Bmim][Cl] to DMSO, respectively. Later, the $\rho$ values decrease with increasing the mole fraction of IL at all experimental temperatures. This may be due to the diminished ion–ion pair interactions between the IL and DMSO and also to the self-interaction between the ions of IL above ≈0.6000 or ≈0.1700$x_1$ of [Emim][Cl] or [Bmim][Cl], respectively. The $\rho$ values for the mixtures of [Emim][MeSO$_4$] or [Bmim][BF$_4$] + DMSO show an increase for entire mole fractions as depicted in Figure 2Sb or c of the SI, respectively. On the other hand, 1-alkyl-3-methylimidazolium cation with chloride anion IL systems exhibit a systematic decrease of $\rho$ values with increasing the alkyl side chain in the cation (Figure 2Sa and d of the SI).

It can be seen from Figure 1a that the two IL families with DMSO have opposite trends in the $\rho$ values: for ammonium ILs with DMSO, the $\rho$ values decrease as the mole fraction of IL increases, whereas for imidazolium ILs, $\rho$ values increase with increasing the concentration of ILs. Moreover, from the obtained results, the ammonium-based IL + DMSO are less dense than imidazolium-based IL + DMSO. It is apparent that the $\rho$ values of ILs mainly depend on how the ions can be packed together and on the size and shape of the ions as well as on the ion–ion interactions. As expected, $\rho$ decreases as the temperature increases for all ILs with DMSO.

Figure 1b shows the $u$ values of the mixtures of ILs with DMSO at 25 °C over the whole composition range. The values

of $u$ are found to increase with increasing the mole fraction of ammonium-based ILs with DMSO at all studied temperatures (Figure 3S of the SI). The $u$ values decrease as the temperature increases in ammonium IL with DMSO systems as displayed in Figure 3S of the SI. As seen from the experimental results in Figure 1b, the $u$ values slightly increase when the alkyl substituent size of the cation increases. The data in Table 1S of the SI and Figure 1b show that at the same temperature the $u$ values of ILs + DMSO follow the order TBAH > TPAH > TEAH > TMAH.

In other words, the temperature-dependent $u$ values of imidazolium-based ILs with DMSO show different behaviors for each system as displayed in Figure 4S of the SI. For the [Emim][Cl] or [Bmim][Cl] with DMSO mixture, the $u$ values increase as the concentration of IL increases in DMSO at all studied temperatures as shown in Figure 1b and 4Sa or d of the SI. As it can be seen from Figure 4Sb of the SI, the $u$ values increase as the concentration of [Emim][MeSO$_4$] increases in the DMSO system up to $x_1 \approx 0.7000$. Later, the values of $u$ become constant up to ≈0.8000; finally, the values increase above $x_1 \approx 0.8000$ at all studied temperatures. In the case of [Bmim][BF$_4$] with DMSO, $u$ values increase up to $x_1 \approx 0.6500$ of IL, and later, a slight decrease is observed in the $u$ values up to $x_1 \approx 1.000$ at all investigated temperatures as shown in Figure 4Sc of of the SI. As shown in Figure 4S of the SI, the $u$ values decrease with increasing the temperature in all of the ILs with DMSO systems. Our experimental results clearly reveal that $u$ decreases as the temperature increases for both families of the ILs with DMSO.

ILs are viscous solvents that can be mixed with other less viscous organic compounds. Therefore, the $\eta$ of pure ILs and their mixtures with organic solvents is an important property and is more useful in industrial applications. It is clear that the $\eta$ values increase with increasing the mole fraction of ammonium IL up to ≈0.7000, 0.7100, 0.7500, and 0.8200; later values decrease at all studied temperatures for the systems of TMAH + DMSO, TEAH + DMSO, TPAH + DMSO, and TBAH + DMSO, respectively, as displayed in Figure 1c and Figure 5S of the SI. These results have been interpreted by the fact that the strong interaction between the ions strengthens upon mixing with the polar solvent leading to a higher $\eta$ up to $x_1 \approx 0.7000$–0.8000; later, at a higher concentration of IL, there is a decrease in the molecular interactions (Figure 5S of the SI). The reason for the higher $\eta$ in the case of TPAH or TBAH is that the size of cation is large enough to facilitate the interactions between DMSO and IL. The highest $\eta$ of the IL containing the [TBA]$^+$ cation can be explained by strong molecular interactions because of hydrogen bonding. Usually, a low molecular weight of IL has lower $\eta$ values in which the cation has sufficient side chain mobility.[7]

As can be seen from Figure 6S of the SI, the $\eta$ increased with increasing the mole fraction of imidazolium ILs in DMSO, whereas the $\eta$ values decreased as the temperature increased in the four systems. The results of Figure 1c seem to indicate that the geometry and molar mass of the anions have a strong influence on the $\eta$ of the imidazolium class of ILs, since [Emim]$^+$ combined with either Cl$^-$ or MeSO$_4$$^-$ produces ILs with significantly different $\eta$ in their mixtures. The lower $\eta$ of the [Emim][Cl] can be justified by the lower molar mass Cl$^-$ anion as compared to the higher molar mass of the MeSO$_4$$^-$ anion of the IL system. Analogously, the $\eta$ for the [Bmim]-[BF$_4$] + DMSO system is higher than that of the [Bmim][Cl] system mainly because the molar mass of the BF$_4$$^-$ anion with
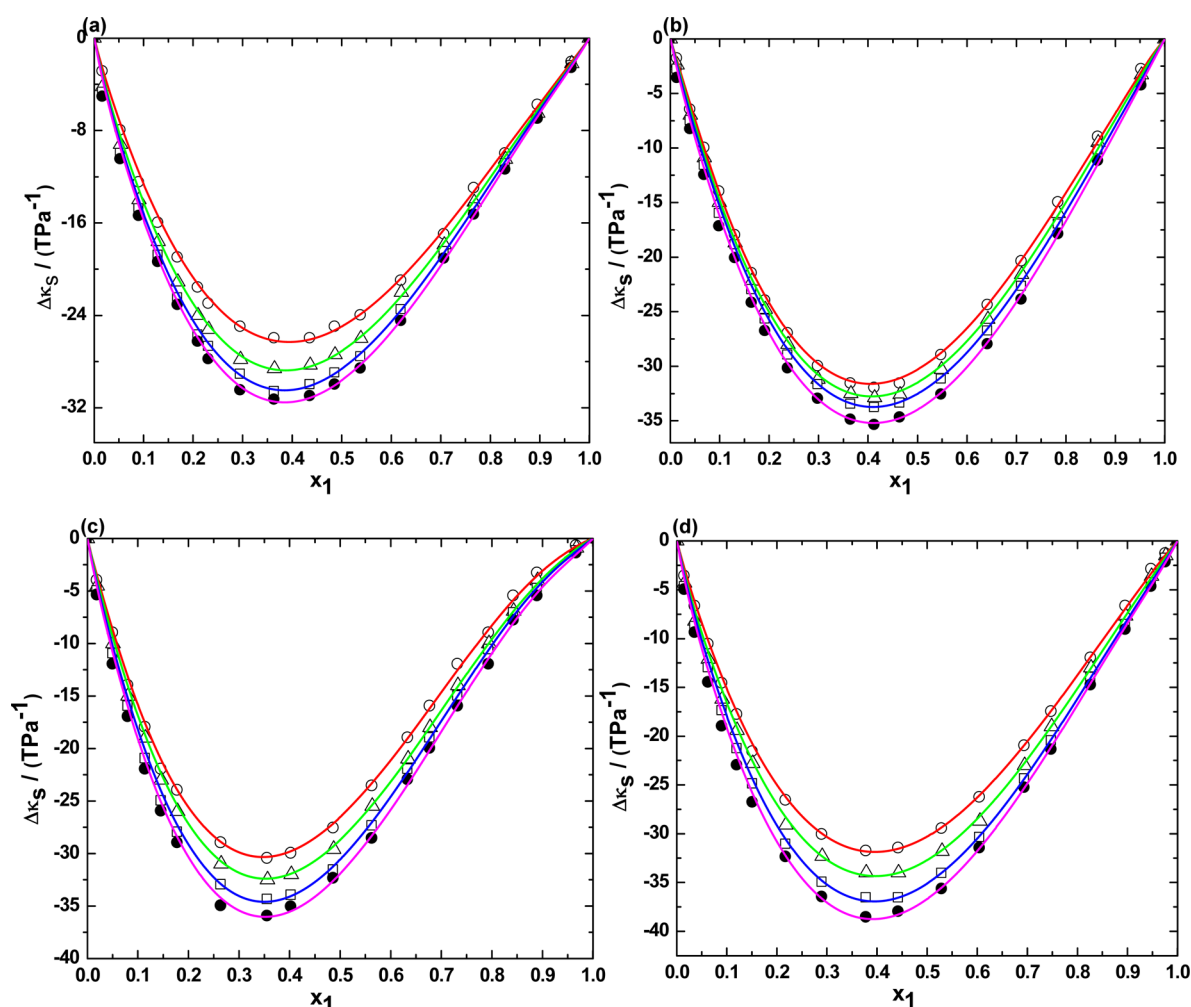
**Figure 4.** Deviation in isentropic compressibility ($\Delta\kappa_s$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) TMAH (1) + DMSO (2); (b) TEAH (1) + DMSO (2); (c) TPAH (1) + DMSO (2); (d) TBAH (1) + DMSO (2) at (○) 25, (△) 30, (□) 35, and (●) 40 °C at atmospheric pressure. The solid curves are correlated by Redlich–Kister equation.

the Bmim$^+$ cation is higher than the molar mass of the Cl$^-$ anion with same cation. These observed results clearly conclude that an increase in the size of the anion causes an increase of $\eta$, and this trend is observed in Figure 1c and 6S of the SI particularly for imidazolium-based IL systems. As can be observed from Figure 1c, the $\eta$ values of imidazolium ILs with DMSO are much greater than that of ammonium ILs with DMSO mixtures, and the high $\eta$ of imidazolium ILs systems is due to strong interactions between the imidazolium ILs and DMSO.

The obtained $V^E$, $\Delta\kappa_s$, and $\Delta\eta$ values of all the ammonium-based ILs or of all the imidazolium family ILs with DMSO as a function of the mole fraction of IL at various temperatures are also incorporated in Tables 1S and 2S of the SI, respectively. The $V^E$, $\Delta\kappa_s$, and $\Delta\eta$ values of the studied binary mixtures as a function of composition of ILs are plotted in Figures 2–7 at several temperatures. Moreover, for the sake of clarity, presentation, and comparison between the two families of ILs, the values of $V^E$, $\Delta\kappa_s$, and $\Delta\eta$ for IL with DMSO over the whole composition range at 25 °C are graphically displayed in Figure 8. The following Redlich–Kister expression was used to fit these properties:

$$Y = x_1 x_2 \left( \sum_{i=0}^{n} a_i (x_1 - x_2)^i \right)$$

(1)

$$\sigma = \left[ \frac{\sum_{i=1}^{n} (Y_i^{exp} - Y_i^{cal})^2}{n} \right]^{1/2}$$

(2)

where $Y$ refers to $V^E$ or $\Delta\kappa_s$ or $\Delta\eta$ and where $x_i$ and $Y_i$ are the mole fraction and the molar properties of pure compounds, respectively. $a_i$ is an adjustable parameter that can be obtained by least-squares analysis. Values of the fitted parameters are listed in Table 3S of the SI along with the standard deviations of the fit.

The obtained $V^E$ of the binary mixture of the ammonium family of ILs with DMSO is negative in the entire composition range with a minimum at higher mole fractions of the IL ≈ 0.4700−0.5400 as illustrated in Figure 2. The deviation becomes more negative with increasing temperature from 25 to 40 °C for all the mixtures. The negative values indicate more attractive interactions in the mixtures than in the pure components. The negative $V^E$ reveals that the systems have a strong packing effect by heteroassociations between both molecules through hydrogen bonding. Further, the interactions
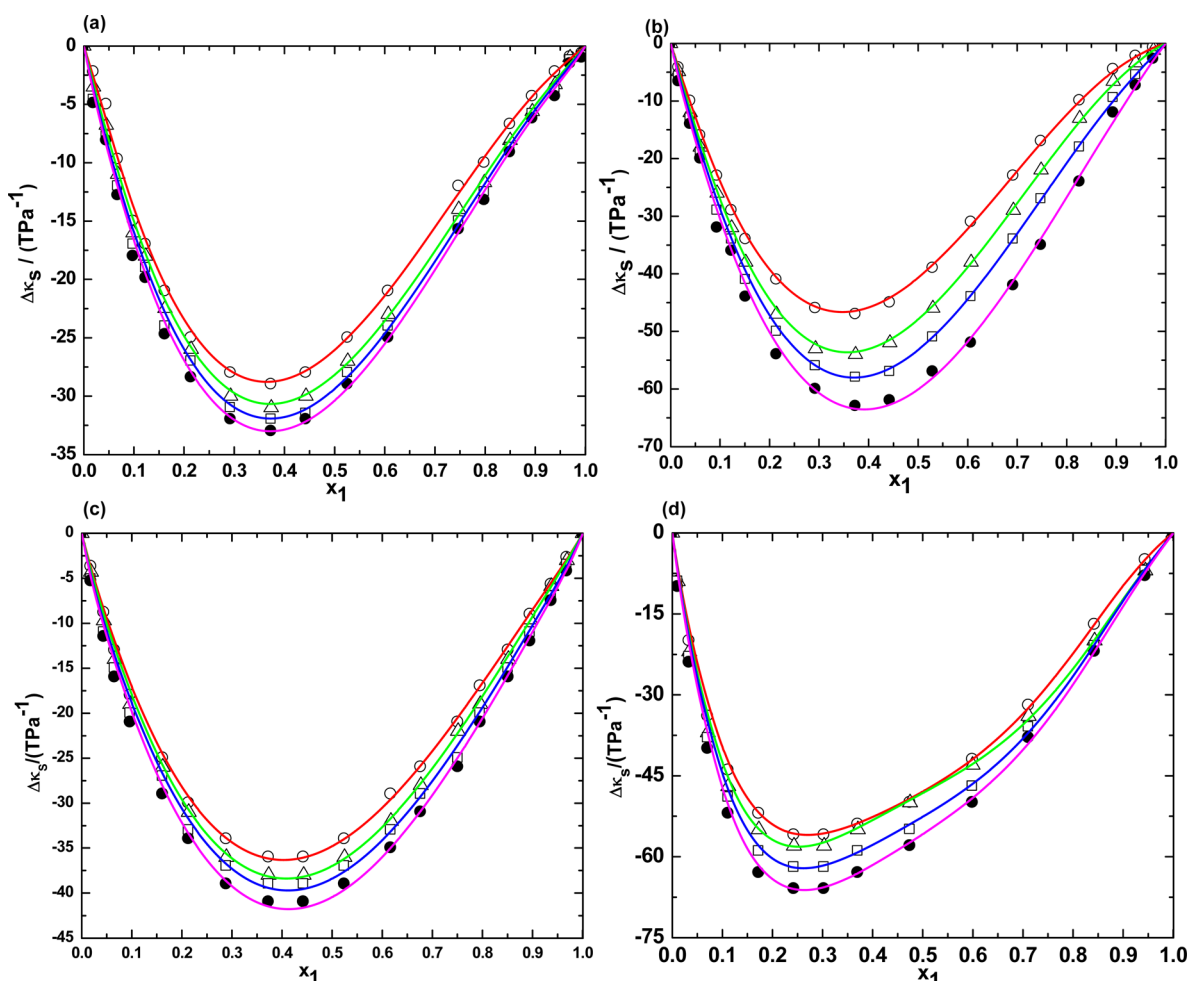
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**Figure 5.** Deviation in isentropic compressibility ($\Delta\kappa_s$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) [Emim][Cl] (1) + DMSO (2); (b) [Emim][MeSO$_4$] (1) + DMSO (2); (c) [Bmim][BF$_4$] (1) + DMSO (2); and (d) [Bmim][Cl] (1) + DMSO (2) at (○) 25, (△) 30, (□) 35, and (●) 40 °C at atmospheric pressure. The solid curves are correlated by Redlich−Kister equation.

between the DMSO molecules and the ions of IL are due to ion−dipole interactions.

Interestingly, the TEAH + DMSO mixture exhibits higher negative $V^E$ values as compared to other ammonium-based ILs. The large negative $V^E$ in TEAH system is due to the strong +inductive (+I) effect that is produced by the longer alkyl chain. The +I effect is lesser in TMAH when compared to the TEAH because of the shorter alkyl chain length. On the other hand, when increasing the alkyl chain from TEAH to TPAH or TBAH, this leads to variation in the hydrogen bond between the cation and the anion. These results explicitly demonstrate that higher alkyl chain molecules decrease the hydrogen-bonding tendency between TPAH or TBAH with DMSO. Therefore, we might expect moderate steric hindrance of the alkyl chain in TPAH or TBAH molecules. After consideration of both the factors, TEAH has more ability to form hydrogen bonding with DMSO; therefore, we observed more negative $V^E$ in the TEAH system.

To achieve a molecular picture of the interactions between ammonium-based ILs and DMSO, we predicted semiempirical calculations with the help of HyperChem 7. Table 2 collects the results of molecular mechanics and semiempirical calculations carried out for ammonium ILs, DMSO, and their mixtures. It is clear from Table 2 that ΔHf of the complex of the resulting

hydrogen bonding was smaller than the sum of ΔHf of DMSO and ILs at all the cases. The binding energies and the heat of formation values increase as the size of the IL increases. Figures 7S−10S of the SI demonstrate that the hydrogen bonding clearly appears between ions of the ammonium family of ILs and the oxygen atom of DMSO. Our semiempirical calculations are very well correlated with our experimental results, clearly affirming that there is an interaction between the DMSO and the ammonium ILs. The structural changes upon mixing are remarkable for IL and DMSO despite the dipolar ordering in their pure compounds.

The results in Figure 2c and d clearly show that TPAH + DMSO and TBAH + DMSO have almost the same negative $V^E$ values. Hence, we can predict that at higher alkyl chain length, cation ILs interact equally with DMSO. These results are strengthened by our Hyperchem data in Figures 9S and 10S of the SI that the OH ion of both TPAH and TBAH interacts with the sulfur atom rather than the oxygen atom of DMSO. This shows that ion-pair interaction is dominated more in TPAH and TBAH as compared to the rest of the ILs (lower alkyl chain ILs).

On the other hand, as seen from results in Figure 3b, the values of $V^E$ for the [Emim][MeSO$_4$] + DMSO mixture are positive throughout the whole range of composition. The
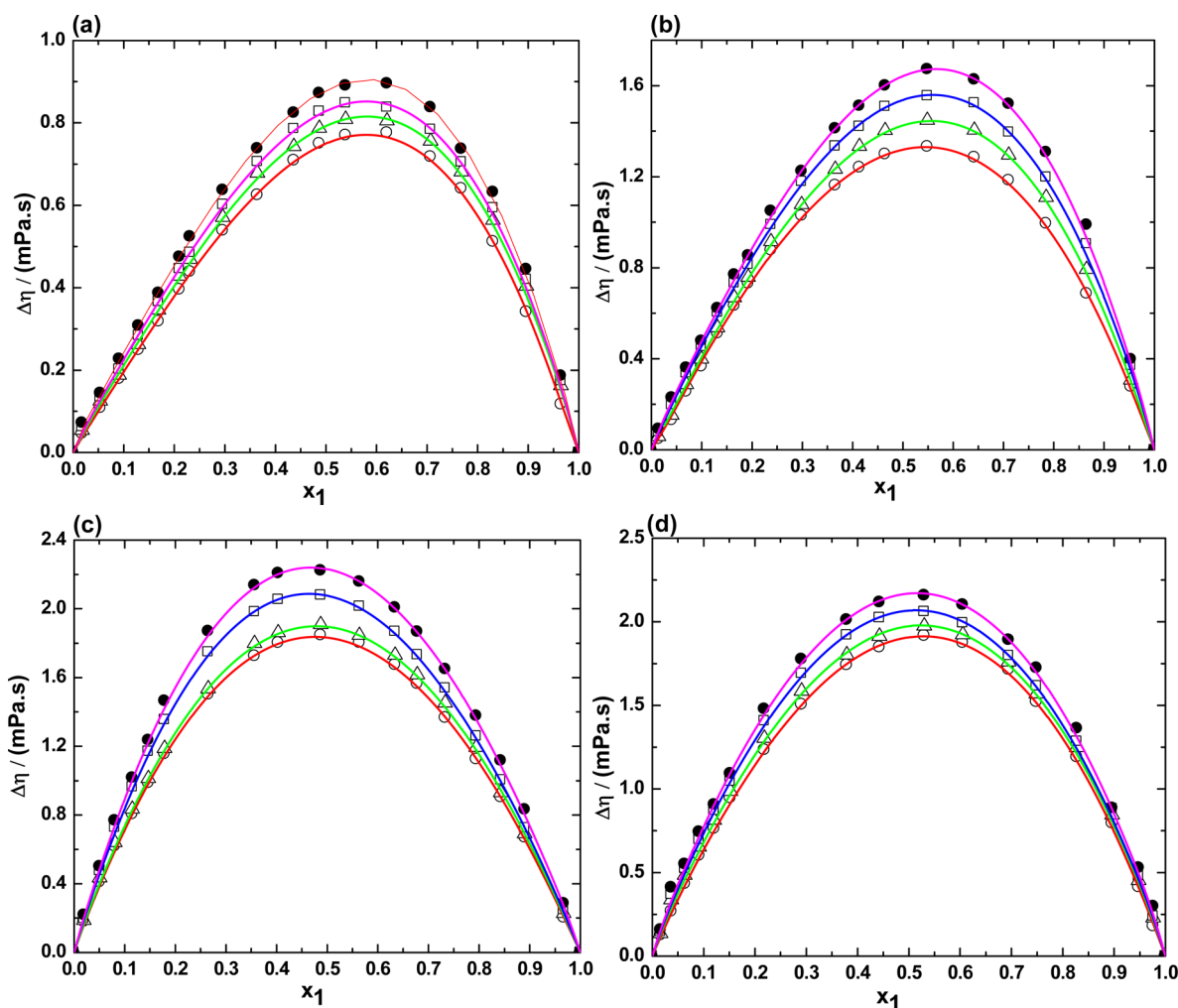
**Figure 6.** Deviation in viscosity ($\Delta\eta$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) TMAH (1) + DMSO (2); (b) TEAH (1) + DMSO (2); (c) TPAH (1) + DMSO (2); (d) TBAH (1) + DMSO (2) at (○) 25, (△) 30, (□) 35, and (●) 40 °C at atmospheric pressure. The solid curves are correlated by Redlich−Kister equation.

observed positive values show that there exist no specific interactions between unlike molecules and also that the compact structure of the polar component (DMSO) due to dipolar association has been broken by this IL. The magnitude and sign of $V^E$ values are a reflection of the type of interactions taking place in the mixture, which are the result of different effects containing the loss of the ion−dipole interaction between IL and DMSO (positive $V^E$). In other words, the interaction between the ion-pair of ILs is more as compared to IL + DMSO interactions, which leads to positive contribution. The maximum decreases as temperature increases for $V^E$ values of [Emim][MeSO$_4$] + DMSO systems.

Figure 3 (a, c, d) shows that the $V^E$ values for [Emim][Cl] or [Bmim][BF$_4$] or [Bmim][Cl] + DMSO are negative throughout the entire concentration range and at all experimental temperatures. As mentioned earlier, the negative contribution reveals that interactions between unlike molecules such as formation of hydrogen bonds and charge-transfer complexes resulted in decrease of volume. For the $V^E$ of [Emim][Cl] + DMSO system (Figure 3), the magnitude is comparatively larger than that of [Bmim][Cl] or [Bmim][BF$_4$] + DMSO system under the same experimental condition. The sign and magnitude of $V^E$ of the system depend on the type of interactions taking place in the mixtures. On the other hand,

the [Emim][Cl] + DMSO mixture reveals more negative values of $V^E$ than the [Bmim][Cl] or [Bmim][BF$_4$] + DMSO system mixture, which implies that [Emim][Cl] ion−dipole interactions and packing effects with DMSO are stronger than those in the [Bmim][Cl] or [Bmim][BF$_4$] system, and these effects depend strongly on the nature of IL.

Imidazolium ILs such as [Bmim][BF$_4$] can be described by the association of the imidazolium cation with the anion through hydrogen bonds. The introduction of DMSO occurs with the disruption of these extended networks of anion [BF$_4$]$^-$ and cation [Bmim]$^+$, and ILs can thus act as both hydrogen-bond acceptors (anion) and donors (imidazolium cation), and as expected, they interact with substances with both accepting and donating sites. Meanwhile, the negative pole in DMSO is an oxygen atom that juts out from the rest of the molecule, which is the position of highest electron density, and this oxygen atom is the best hydrogen-bond acceptor and **S** atom of DMSO, which has positive character, and associates with the anion of IL. The $V^E$ data in Figure 3c show the existence of a strong interaction between the cation (+) of IL and the negatively charged oxygen (−) of DMSO and also the anion (−) of IL and the positively charged S atom (+) of DMSO. These interactions are shown schematically in Scheme 1. Moreover, our results are consistent with Zhang et al.'s[52]
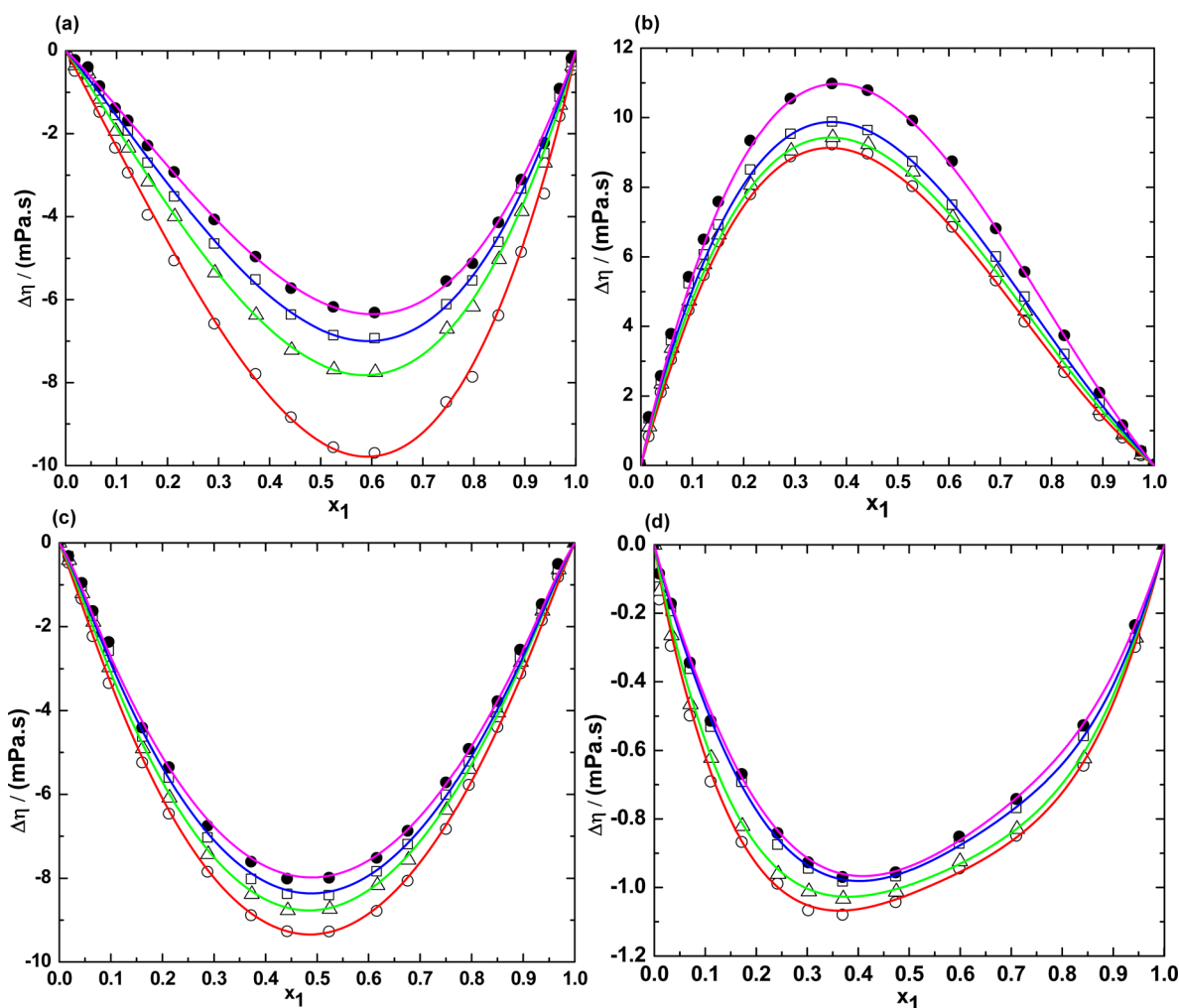
**Figure 7.** Deviation in viscosity ($\Delta\eta$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL for (a) [Emim][Cl] (1) + DMSO (2); (b) [Emim][MeSO$_4$] (1) + DMSO (2); (c) [Bmim][BF$_4$] (1) + DMSO (2); and (d) [Bmim][Cl] (1) + DMSO (2) at (○) 25, (△) 30, (□) 35, and (●) 40 °C at atmospheric pressure. The solid curves are correlated by Redlich−Kister equation.

infrared spectroscopic studies in which it was found that hydrogen-bond interactions are formed between the hydrogen atom at position 2 of the imidazole ring and the functional groups of DMSO. According to our present investigation, when DMSO is mixed with [Bmim][BF$_4$], ion−dipole interactions will occur between the DMSO molecules and the imidazolium ring of the IL leading to the negative $V^E$. The filling effect of organic molecular liquids in the interstices of ILs and the ion−dipole interactions between the organic molecular liquid and the imidazolium ring of the ionic liquids all contribute to the negative values of the $V^E$.[53,54]

As seen in Figures 4 and 5, $\Delta\kappa_s$ values of all ILs + DMSO are negative over the full composition range at various temperatures as a function of IL concentration. The behavior of $\Delta\kappa_s$ implies that these mixtures are less compressible than the ideal mixture. This is due to a closer approach of unlike molecules and to a stronger interaction between components of mixtures that leads to a decrease in compressibility at all temperature ranges. The negative $\Delta\kappa_s$ values of IL + DMSO are attributed to the strong attractive interactions, which are due to the solvation of the ions in these solvents. Clearly, we observed higher $\Delta\kappa_s$ values for imidazolium ILs with DMSO than for ammonium ILs with DMSO at all studied temperatures (Figures 4 and 5).

The experimental $\Delta\eta$ values for the investigated systems, together with the curves obtained using eq 1, are shown in Figures 6 and 7. An examination of the curves in Figure 6 shows that for the $\Delta\eta$ values for ammonium ILs + DMSO, a peak appears between the DMSO region and the IL region, although it is not at all symmetrical at all temperatures. It is evident from Figure 6 that the $\Delta\eta$ values for ammonium ILs + DMSO are positive throughout the whole range of composition at all investigated temperatures. It is obvious that the $\Delta\eta$ values increase with increasing the temperatures for all ammonium-based ILs with DMSO (Figure 6). The positive deviation for these systems indicates strong interaction between ammonium IL and DMSO. Further, the positive values of $\Delta\eta$ for the investigated ammonium IL binary systems suggest that the $\eta$ values of associates formed between unlike molecules are relatively more than those of the pure components.

The positive deviation is a characteristic of mixtures containing hydrogen bonding between ions of IL as well as structural arrangement of IL and solvent. Therefore, the $\Delta\eta$ value depends on molecular interactions as well as on the size and the shape of the molecules. The highest $\Delta\eta$ was observed for TPAH and TBAH with DMSO at all studied temperatures. These variations in $\Delta\eta$ could be attributed to relatively larger
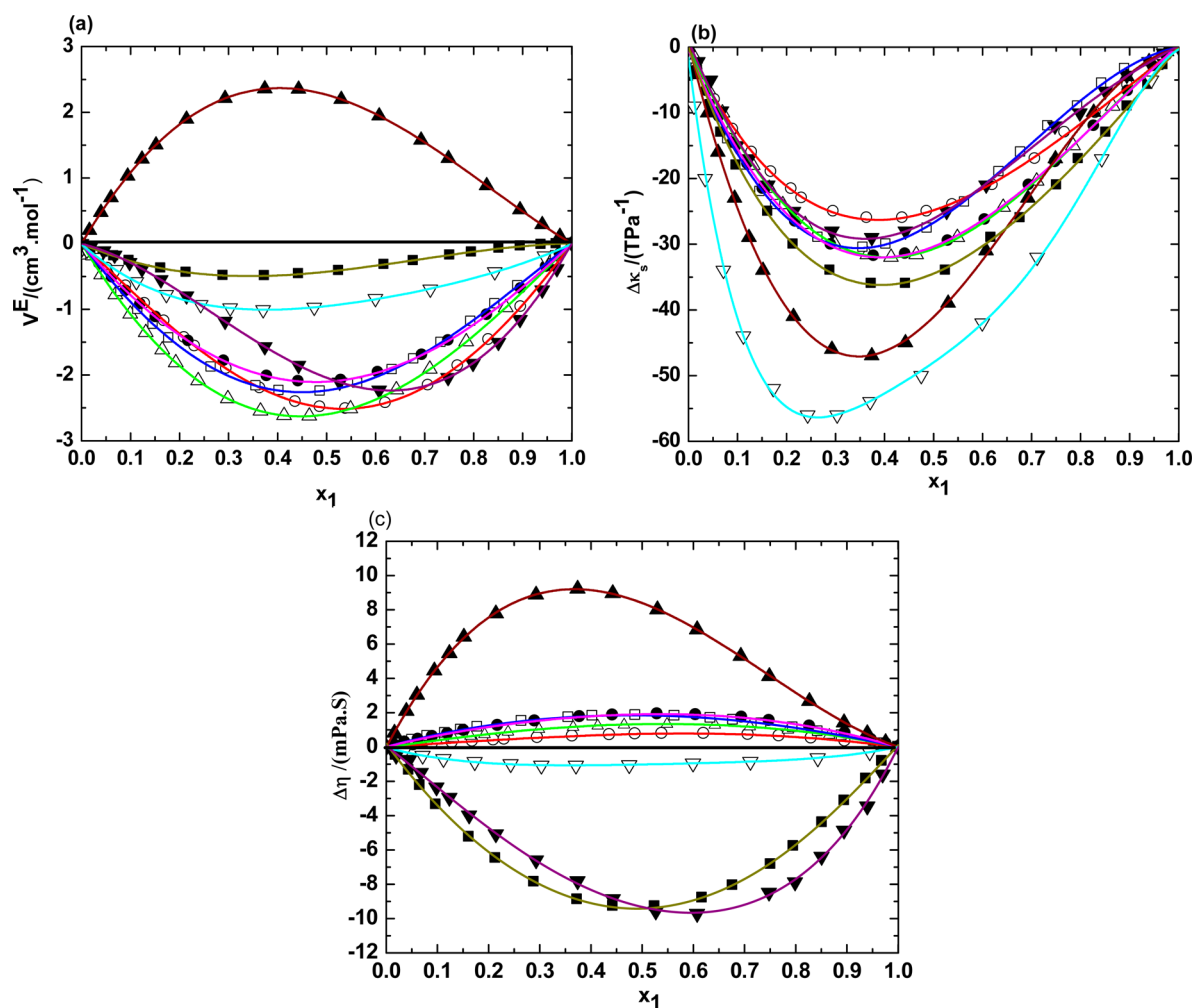
**Figure 8.** (a) Excess molar volume ($V^E$), (b) deviation in isentropic compressibility ($\Delta\kappa_s$), and (c) deviation in viscosity ($\Delta\eta$) for the mixtures of ILs + DMSO as a function of the composition expressed in the mole fraction ($x_1$) of IL data: ○, TMAH (1) + DMSO (2); △, TEAH (1) + DMSO (2); □, TPAH (1) + DMSO (2); ●, TBAH (1) + DMSO (2); ▲, [Emim][MeSO$_4$] (1) + DMSO (2); ■, [Bmim][BF$_4$] (1) + DMSO (2); ▽, [Bmim][Cl] (1) + DMSO (2); and ▼, [Emim][Cl] (1) + DMSO (2) at 25 °C and atmospheric pressure. The solid curves are correlated by Redlich−Kister equation.

hydrogen bonding interactions of the ion with DMSO as compared with the rest of the ions of IL with DMSO.

The $\Delta\eta$ values of [Emim][MeSO$_4$] + DMSO system at different temperatures are positive throughout the whole range of composition (Figure 7b). The positive deviation of $\Delta\eta$ values increases with increasing the temperature. The results in Figure 7 a or c or d reveal that the $\Delta\eta$ values are negative for [Emim][Cl] + DMSO or [Bmim][BF$_4$] + DMSO or [Bmim][Cl] + DMSO system, respectively, over the entire range of composition at all studied temperatures. As the temperature increases, the negative $\Delta\eta$ values decrease for these systems. An elementary difference in the behavior of $\Delta\eta$ values observed is that the values are found to be positive for [Emim][MeSO$_4$] + DMSO, whereas these are negative for systems containing [Emim][Cl] + DMSO or [Bmim][BF$_4$] + DMSO or [Bmim][Cl] + DMSO under the same experimental conditions. One general conclusion that can be reached from analysis of these systems is that the $\Delta\eta$ values increase or decrease with increase of temperature because of the variation of size and shape of molecules as well as because of different types of interactions between the components of the mixture.

The differences in $V^E$ values between ammonium-based ILs with DMSO and imidazolium family ILs with DMSO are compared in Figure 8a under the same experimental conditions. From close observation of Figure 8a, one can see that the $V^E$ of mixing of all the mixtures of ILs with DMSO is negative over the entire range of compositions at 25 °C except for [Emim][MeSO$_4$] with DMSO that exhibits positive $V^E$ values. The negative $V^E$ values for lower alkyl chain length of IL systems ($V^E = -2.515$ cm$^3$ mol$^{-1}$ at $x_1 = 0.5388$ for TMAH + DMSO; $V^E = -2.626$ cm$^3$ mol$^{-1}$ at $x_1 = 0.4647$ for TEAH + DMSO) are higher than those for higher alkyl chain length of IL systems ($V^E = -2.247$ cm$^3$ mol$^{-1}$ at $x_1 = 0.4872$ for TPAH + DMSO; $V^E = -2.096$ cm$^3$ mol$^{-1}$ at $x_1 = 0.4429$ for TBAH + DMSO) as depicted in Figure 8a. Therefore, the less negative $V^E$ values for higher alkyl chain length of IL mixtures serve as evidence that the interactions between higher alkyl chain length of IL (TPAH or TBAH) with DMSO are notably weaker than those between lower alkyl chain length of IL (TMAH or TEAH) with DMSO. This suggests that the O−H···O=S hydrogen-bonding interactions between the ammonium ILs with DMSO are decreasing when extending the alkyl chain of the cation. The reason for strong interaction between lower

alkyl chain of IL and DMSO is that DMSO molecules fit into the interstices of the ILs upon mixing, whereas higher alkyl chain ILs weakly interact with DMSO molecules because of the larger steric hindrance of the bulky group of the higher alkyl chain of IL. Therefore, it is important to note that the nature of interactions in IL + DMSO system is highly dependent on the alkyl chain length of ammonium IL. The results in Figure 8a clearly show that the negative $V^{E}$ values of ammonium-based ILs with DMSO are higher than those of imidazolium family ILs [Bmim][BF$_4$] or [Bmim][Cl] with DMSO. Therefore, the ammonium IL interacts with DMSO more strongly than the imidazolium family IL. However, the interactions between [Emim][Cl] and DMSO are stronger than ammonium-based ILs in the rich-[Emim][Cl] IL mole fraction region (Figure 8a).

The $\Delta\kappa_s$ values of ammonium ILs with DMSO and imidazolium ILs with DMSO are compared in Figure 8b at 25 °C, and the values are negative over the whole mole fraction range. The negative $\Delta\kappa_s$ values for imidazolium ILs with DMSO are higher than those of ammonium ILs with DMSO mixtures except in the case of [Emim][Cl] and DMSO system. It is obvious that the difference in $\Delta\kappa_s$ between these two families is caused mainly because of conformational changes in the structural interactions and in the ion−ion pair interactions and because of size and also shape of the components.

The curves in Figure 8c show that the $\Delta\eta$ values for ILs + DMSO are positive at 25 °C except for [Emim][Cl] or [Bmim][BF$_4$] or [Bmim][Cl] with DMSO system in which negative values are observed. The $\Delta\eta$ values increase with increasing the alkyl chain length of the cation of ammonium IL. Considering the fact that similar factors have opposite effects on the $V^{E}$ and $\Delta\eta$ properties, increasing the temperature will lead to more negative $V^{E}$ and less positive $\Delta\eta$ values as one can see in Figures 2, 6, and 8. A close examination of Figure 8 concludes that the main factor for a negative $V^{E}$ and a positive $\Delta\eta$ may be association or complex formation between the components of ammonium ILs with DMSO mixtures. However, this general conclusion is not observed in the imidazolium family of ILs with DMSO because the imidazolium IL contains a bigger cation than that of ammonium IL. It is obvious that the difference in these properties between these two families is mainly because of conformational changes in the structural interactions and in the ion−ion pair interactions and because of size and also shape of the components. Moreover, the structure and nature of cations and anions greatly influence the physicochemical properties of ILs.

It is noticeable that the maximum values of $\Delta\eta$ are observed at about mole fractions of the IL ≈ 0.4700−0.5400; this is just the mole fraction as the $V^{E}$ values have the minimum values (mole fractions of the IL ≈ 0.4700−0.5400 as illustrated in Figure 2) for the systems of ammonium ILs with DMSO. From these observations, it seems possible to suggest that an unusual structure occurs in the vicinity of this particular composition of the mixtures.

## CONCLUSIONS

We have measured and compared thermophysical properties of $\rho$, $u$, and $\eta$ for binary mixture of ammonium-based ILs or imidazolium family ILs with DMSO over the whole composition range at various temperatures. The $\rho$ and $u$ values decrease while the $\eta$ values increase with increasing the cation alkyl chain length of ammonium ILs. Apparently, ILs that possess a higher cation side chain is accompanied by lower $\rho$, lower $u$, and larger $\eta$. Clearly, our results might imply that the

cation size was responsible for the alteration of the thermophysical properties of ILs. To measure the nonideality of the mixtures, we determined $V^{E}$, $\Delta\kappa_s$, and $\Delta\eta$ at each temperature as a function of IL concentration. Ion−dipole and hydrogen-bonding interactions between the polar solvent molecules and the ions of the ILs are suggested to be mainly responsible for the $V^{E}$, $\Delta\kappa_s$, and $\Delta\eta$ of the mixtures. Our studies demonstrate that these properties absolutely depend on alkyl chain length of the cation of ammonium-based ILs as well as of the anion of imidazolium family ILs. These observed interactions are supported by our molecular modeling calculations, which are obtained by HyperChem 7. Our findings provide a better understanding of the molecular interactions for the mixing of the solvents and better analysis of the solvation process. Apparently, an understanding of how the nature of ILs can affect the molecular interactions with molecular solvents that occur in them remains to be achieved.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The experimental $\rho$, $u$, and $\eta$ values of all the ammonium family ILs and all of the imidazolium-based ILs with DMSO are presented as a function of IL concentration and at all studied temperatures. Values of the fitted parameters along with the standard deviations of the fit. Figures of hydrogen-bonding interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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