A density functional theory study on the water aggregation behaviour of fatty acid-based anionic surface active ionic liquids

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Abstract

The hydrogen bond interactions between methyl-imidazolium cation (MIM+) and fatty acid anions (CmHnCOO–, where m = 1–6; n = 3–13) of ionic liquids are studied in both gas phase and water phase using density functional theory. The structural properties show that the presence of N–H···O and C–H···O hydrogen bonds between [MIM]+ and [CmHnCOO]– (m = 1–6; n = 3–13) ionic liquids. From the vibrational frequency analysis, it was found that the hydrogen bond interaction between [MIM]+ and [CmHnCOO]– (m = 1–6; n = 3–13) ionic liquids are red-shifted in frequency. The natural bond orbital analysis show that the N–H···O hydrogen bond associated with the large charge transfer which has the higher stabilization energy (i.e. E(2) ~ 38 kcal/mol). Further, the cation/anion–water cluster (H2O)1–3 interactions show that the water molecules are preferred to interact with anions. In the case of ionic liquid–water cluster interaction, the water molecules occupies the interstitial space between cation and anion of ionic liquids which results in weakening the cation–anion interaction.

Keywords Ionic liquids · Methyl-imidazolium cation · Fatty acid anion · Density functional theory · Water cluster

Introduction

Ionic liquids (ILs) are a class of organic salts composed of ions that are exist in the liquid state at low temperatures (below 100 °C) [1–8]. Generally, ILs consist of organic cation (for example, imidazolium, pyridinium, phosphonium) and organic/inorganic anion (for example, acetate, nitrate, tetrafluoroborate, alkyl-sulfate) [9–19]. Because of their unique properties, they have attracted research interests in both academia and industries as they applied in organic/inorganic synthesis, catalysis, electrochemical devices and so on [20–26]. Different kinds of ILs are developed and studied for various applications such as room-temperature ILs (RTILs) [2, 16, 27], poly- ILs (PILs) [28, 29], amino acid ILs (AAILs) [30–32] and task-specific ILs (TSILs) [33, 34]. Similarly, a new class of ILs called surface active ionic liquid (SAILs) has possessed diverse applications in organic synthesis, biotechnology, nanotechnology, surfactant flooding and so on [35–39]. It is considered that the SAILs have both the properties of ILs and surfactant. Based on the structural property, SAILs can be divided into three categories: (i) cationic SAILs (like imidazolium, pyridinium with long alkyl chain), (ii) anion SAILs (like carboxylate anion, sulphate anion and sulfonate anion) and (iii) catanionic SAILs (cations and anions showing surface active properties) [38, 39]. The nature of SAILs can be tuned by the choice of cation and anion, and the properties of SAILs are studied extensively in colloidal chemistry, supramolecular chemistry, electrochemistry, pharmaceutical industry and etc. [40–43].

The presence of hydrogen bond (H bond) between cation and anion of ILs plays a vital role in the behaviour of ILs [44–48]. In general, the H bond is denoted as X–H···Y interaction in which X (usually, C, N and O) and Y (usually, N and O) are strong electronegative atoms. It was found that the cations are the active H bond donors and anions are the active H bond acceptors. Based on the strength of the H bond, the ILs are divided into two types: (i) protic ILs and (ii) aprotic ILs. In protic ILs, H bond is formed by proton transfer from a Brønsted acid to a Brønsted base; whereas in aprotic ILs, the cationic C–H unit is the major H bond donor unit [48]. Since ILs have large numbers of cations and anions, the H bonding in ILs is highly system dependent. Unlike
the H bonding in traditional neutral system, the H bonding present in the ILs has different interesting behaviours.

Nowadays, the water aggregation or micellization properties of SAILs are actively studied by both experimental and theoretical studies [38, 49, 50]. Experimentally, surface tension, conductivity, steady state fluorescence spectra, viscosity and dynamic light scattering measurements are used to determine the water aggregation properties of SAILs. Theoretically, density functional theory (DFT) is used to study the water aggregation properties of SAILs. Mostly, the studies are performed on water aggregation properties of imidazolium cations with sulfonate anions of SAILs [39, 51]. It promoted us to study the water aggregation properties of SAILs. Here, we have studied the water aggregation properties of the methyl-imidazolium cation with six fatty acid anion of SAILs with different water molecules (1–3) using DFT. This study will be useful to understand the interactions of cation–water, anion–water, cation–anion and ionic liquid–water towards the water aggregation properties of SAILs.

Computational details

The hybrid M06-2X density functional [52] along with 6-311++G (d,p) basis set [53] is used to optimize the structures of methyl-imidazolium cation [MIM]⁺, fatty acid-based anions [CₘHₙCOO]⁻ (where m = 1–6; n = 3–13) and ILs [MIM⁺–CₘHₙCOO⁻] (m = 1–6; n = 3–13) and ILs with water molecules (H₂O)ₓ (where x = 1–3) respectively. The solvent effects on the stability of ILs are examined through self-consistent reaction field (SCRF) using polarizable continuum model (PCM) in water [54, 55]. Vibrational frequency analysis used to found the global minimum structures with no imaginary frequency values. The strength of H bond between cation and anion of ILs is studied by atoms in molecule (AIM) analysis using the MORPHY98 program package [56, 57]. Further, the natural bond orbital (NBO) analysis is used to understand the charge transfer between ILs [58]. All of the above calculations are performed with Gaussian09 Rev. A.02 package [59].

Results and discussion

Structures of [MIM]⁺ cation and [CₘHₙCOO]⁻ anions

The optimized structures of methyl-imidazolium cation [MIM]⁺ and fatty acid anions [CₘHₙCOO]⁻ (where m = 1–6; n = 3–13) are shown in Fig. 1. In the case of [MIM]⁺ cation, a three-center (N1-C2-N3) four-electron ∏ system is observed [60]. The bond lengths of N1=C2 and C2=N3 are predicted to be 1.327 and 1.333 Å and the bond lengths of N3-C4 and C5-N is to be 1.376 and 1.381 Å respectively, while for C4=C5, it is of 1.357 Å. From the NBO charge analysis, it is found that the negative charge is located on the
two N atoms (N1 = –0.35 e and N3 = –0.50 e) and positive charge is located on the C2 atom while C4 and C5 atoms have nearly neutral charge. In the case of fatty acid anions (i.e. [CmHnCOO]–, where m = 1–6; n = 3–13), as the chain length increases (i.e. C1 to C6), the anions prefer to form bent structure. The natural charge value of –0.81 e is found on the two O atoms (COO–) in the fatty acid anions. The length of the hydrophobic chain in fatty acid anion is in the range of 2.66–9.65 Å which is in agreement with the theoretically calculated value (2.76–9.09 Å) by Tanford equation, L = 1.5 + 1.265n (where n is the number of carbon atom) [61].

Structures of cation–water and anion–water interactions

The optimized structures of water clusters (H2O)x (x = 1–3), [MIM]+ cation and [CmHnCOO]– anions with different water molecules (H2O)x (x = 1–3) are shown in Figs. 2, 3, and 4 respectively. The purpose of this study is to analyze the changes in the natural charge values of cation and anions of ILs during the interactions with water molecule and also to find the water aggregation property of cation and anions of ILs with water molecule. Previously, Roohi and Khyrkha studied the water aggregation property of [MIM]+ cation [62]. The O atom in H2O molecule forms H bond with [MIM]+ cation in three ways 1:1, 2:1 and 3:1 ratio. That is, the number of H bonds between [MIM]+ cation and water molecule is increased with increase of number of water molecules from 1 to 3. The bond length of N3–H13 is elongated from 1.012 Å (isolated cation) to 1.030 Å (cation–water) because of the electron absorption effect of H2O. The negative charge of N3 atom in [MIM]+ cation is increased from –0.498 to –0.513 e during the interactions with water molecules (H2O)1–3. Figure 4 shows the optimized structures of interactions between fatty acid anion with different water molecules (H2O)1–3. Recently, Ali et al. have studied the aggregation behaviour of choline fatty acid-based ILs by experimentally [63]. Here, the H atom in H2O molecule forms H bond with O atom of [CmHnCOO]– (m = 1–6; n = 3–13) anions in three ways 2:1, 3:1 and 4:1 ratio. The O–C bond of [CmHnCOO]– (m = 1–6; n = 3–13) anions is increased from 1.249 to 1.257 Å during the interactions with water molecule (H2O)1–3. This means that the hydrate formation weakens the O–C bond in the fatty acid anions. Also, the negative charge of O atom in [CmHnCOO]– (m = 1–6; n = 3–13) anions is increased from –0.81 to –0.84 e on interactions with H atom of water molecules (H2O)1–3.

Structures of cation–anion interactions

The optimized structures of ILs [MIM]+–[C1H3COO]–, [MIM]+–[C2H5COO]–, [MIM]+–[C3H7COO]–, [MIM]+–[C4H9COO]–, [MIM]+–[C5H11COO]– and [MIM]+–[C6H13COO]– are shown in Figs. 5 and S1–S3. The methyl-imidazolium cation [MIM]+ shows different interaction sites for the fatty acid anions [CmHnCOO]– (m = 1–6; n = 3–13). In this study, four different interaction sites are considered (site i) C2–N3, (site ii) N3–C4, (site iii) N3 and (site iv) N1–C2 (Figs. 5 and S1–S3). Further, the optimized structures of ion pairs in water phase and ion pair without proton transfer is shown in Figs. S4 and S5. Among that, the C2–N3 site of [MIM]+ cation is the preferred site for the interaction of fatty acid anions (Fig. 5). From the NBO natural charge analysis, it is evident that the C2 atom in the

**Fig. 2** The optimized water cluster (H2O)ₙ (x = 1–3) at M06-2X/6-311++G** level of theory

**Fig. 3** The optimized structures of methyl-imidazolium cation [MIM]+ with water cluster (H2O)ₙ (where x = 1–3) at M06-2X/6-311++G** level of theory

**Fig. 5** The optimized structures of ILs [MIM]+–[CmHnCOO]– (where m = 1–6; n = 3–13) at M06-2X/6-311++G** level of theory
C2-N3 site has more positive charge compared to the other possible sites which leads to the much stronger interactions with the anions. As shown in Fig. 5, there are two H bonds are formed (i.e. N–H···O and C–H···O) between [MIM]+ and \([\text{C}_m\text{H}_n\text{COO}]^-(m=1–6; n=3–13)\). The calculated bond length, bond angle values of H bond between [MIM]+ and \([\text{C}_m\text{H}_n\text{COO}]^-(m=1–6; n=3–13)\) are listed in Table 1. The H bond distances of N–H···O and C–H···O are in the range of 1.692–1.704 Å and 2.300–2.310 Å respectively. During cation–anion interaction, the N3–H13 and C2–H9 bonds in the [MIM]+ cation are elongated by 0.692 and 0.020 Å. The obtained result is in agreement with the previous result in which the N–H bond of [MIM]+ cation is elongated by 0.670 Å while interacting with \([\text{C}_1\text{H}_3\text{COO}]^-\) anion [62]. This result shows that the proton transfer takes place from N–H bond of [MIM]+ cation to \([\text{C}_m\text{H}_n\text{COO}]^-\) anion (m = 1–6; n = 3–13). The optimized ion pairs without proton transfer are shown in Fig. S5. The calculated relative energy values in Table S1 show that the ion pairs with proton transfer are much lower in energy compared to the ion pairs without proton transfer. The bond angle values show that the N–H···O bond is almost linear with the bond angle of 175° and the C–H···O bond has a bond angle of 122°. The calculated NBO natural charge values shows that the negative charge in the N3 atom of [MIM]+ cation is increased from –0.50 to –0.57 e. Structures of [MIM]+ cations and \([\text{C}_m\text{H}_n\text{COO}]^-\) anions form multiple H bonds with water molecules (Figs. 6, 7, and 8). The [MIM]+ cations form H bond via C–H···O and the fatty acid \([\text{C}_m\text{H}_n\text{COO}]^-\) anions form H bond via O–H···O interactions with the water molecules. It was found that the water molecules prefer to bind with the fatty acid anions rather than the [MIM]+ cations [32, 64].
Vibrational frequency analysis

The strength of interaction between cation and anions in ILs can be identified by infrared (IR) spectra analysis. The frequency analysis of X–H···Y H bond is important to characterize their nature, whether the X–H bonds are proper or improper i.e. red-shifted or blue-shifted. The H bond formation leads to increase in the X–H bond length because

![Image of optimized structures of ILs][MIM]⁺–[C₉H₁₈COO]⁻ (where m=1–6; n=3–13) at M06-2X/6-311++G** level of theory (site-1)

**Fig. 5** The optimized structures of ILs [MIM]⁺–[C₉H₁₈COO]⁻ (where m=1–6; n=3–13) at M06-2X/6-311++G** level of theory (site-1)

| ILs                  | Bond type   | Bond length (Å) | Bond angle (°) | ρ(r) (a.u.) | ∇²ρ(r) (a.u.) | H_{BCP}   |
|----------------------|-------------|-----------------|----------------|-------------|---------------|-----------|
| [MIM]⁺–[C₅H₁₀COO]⁻   | N–H–O       | 1.693           | 174.83         | 0.05295     | 0.10516       | −0.01190  |
|                      | C–H–O       | 2.310           | 122.14         | 0.01347     | 0.04995       | 0.00187   |
| [MIM]⁺–[C₆H₁₃COO]⁻   | N–H–O       | 1.692           | 174.96         | 0.05301     | 0.10511       | −0.01195  |
|                      | C–H–O       | 2.303           | 122.47         | 0.01365     | 0.05065       | 0.00189   |
| [MIM]⁺–[C₇H₁₄COO]⁻   | N–H–O       | 1.696           | 174.84         | 0.05252     | 0.10516       | −0.01164  |
|                      | C–H–O       | 2.300           | 122.59         | 0.01373     | 0.05099       | 0.00191   |
| [MIM]⁺–[C₈H₁₅COO]⁻   | N–H–O       | 1.700           | 174.67         | 0.05196     | 0.10539       | −0.01098  |
|                      | C–H–O       | 2.300           | 122.54         | 0.01369     | 0.05102       | 0.00192   |
| [MIM]⁺–[C₉H₁₇COO]⁻   | N–H–O       | 1.704           | 174.63         | 0.05151     | 0.10532       | −0.01098  |
|                      | C–H–O       | 2.293           | 122.74         | 0.01388     | 0.05188       | 0.00195   |
| [MIM]⁺–[C₁₀H₁₉COO]⁻  | N–H–O       | 1.699           | 174.92         | 0.05216     | 0.10558       | −0.01138  |
|                      | C–H–O       | 2.310           | 122.50         | 0.01344     | 0.04978       | 0.00186   |

**Fig. 6** The optimized structures of ILs [MIM]⁺–[C₉H₁₈COO]⁻ (where m=1–6; n=3–13) with one water molecule (H₂O) at M06-2X/6-311++G** level of theory
of the proton donor (X), as a result of red-shift observed in the X–H stretching frequencies. On the other hand, the contraction of X–H bond length will give blue-shift H bonds. The N–H bond stretching frequency in the isolated $[\text{MIM}]^+$ cation is calculated as 3636 cm$^{-1}$ which is in agreement with the experimental value of 3518 cm$^{-1}$ [65]. During the $[\text{MIM}]^+$–water interaction, the addition of water molecules (H$_2$O)$_{1–3}$ leads to red-shift in N–H bond stretching frequencies in the $[\text{MIM}]^+$ cation from 393 to 434 cm$^{-1}$. This is due to the presence of water molecules produces higher flexibility to the $[\text{MIM}]^+$ cation ring [66]. Similarly, the fatty acid anion–water interactions leads to increase in the bond length of C–O in the $[\text{C}_m\text{H}_n\text{COO}]^-$ ($m = 1–6; n = 3–13$) anions which corresponds to the red-shift H bonds. In the case of $[\text{MIM}]^+$– $[\text{C}_m\text{H}_n\text{COO}]^-$ interactions, there are two types of H bonds found (i.e. N–H···O and C–H···O). The N–H bond in $[\text{MIM}]^+$ cation is red-shifted by 634–659 cm$^{-1}$ during the $[\text{MIM}]^+$–$[\text{C}_m\text{H}_n\text{COO}]^-$ interactions. The C–H bond stretching frequency in the isolated $[\text{MIM}]^+$ cation is calculated as 3293 cm$^{-1}$ which is in agreement with the experimental value 3160 cm$^{-1}$ [65]. The C–H bond in $[\text{MIM}]^+$ cation is also red-shifted by 13–47 cm$^{-1}$ during the $[\text{MIM}]^+$–$[\text{C}_m\text{H}_n\text{COO}]^-$ interactions. Further, the nature of H bond is investigated for the interactions of $[\text{MIM}]^+[\text{C}_m\text{H}_n\text{COO}]^-$–water molecules. The addition of water molecules (i.e. (H$_2$O)$_{1–3}$) causes the N–H bond of $[\text{MIM}]^+$ cation to blue-shift by 10–335 cm$^{-1}$. On the other hand, the red-shift nature of C–H bond in $[\text{MIM}]^+$ cation is maintained same during the interactions with water molecule (H$_2$O)$_{1–3}$. This may be due to that the addition of water molecules (i.e. (H$_2$O)$_{1–3}$) occupies
the interstitial space between cation and anion and makes the change in its H bonding nature which is responsible for the above results.

Interaction energy

One of the advantages of theoretical methods is that the calculation of interaction energy of ILs which plays a vital role in understanding the structure–energetic properties of ILs. The basis set superposition error (BSSE)-corrected interaction energy using the counterpoise method of Boys and Bernardi [68] can be calculated as the difference between the energy of a total system $E_{AB}$ (example, Cation–Anion of ILs and ILs–Water) and the energy of isolated systems $E_A$ and $E_B$ (example, cation, anion, water).

$$E_{int} = [E_{AB} - \{E_A + nE_B\}] + \text{BSSE}$$

In this study, the BSSE-corrected interaction energy between cation–water, anion–water, cation–anion and ILs–water are calculated and shown in Figs. 9–11. The total interaction energy ranges from $-1$ to $-140$ kcal/mol for the systems considered in this study. In the case of cation–water and anion–water interactions, the total interaction energy is increased by the addition of 1 to 3 water molecules. Especially, the total interaction energy is large in the anion–water interaction than the cation–water interaction which infers that the water molecules prefer to interact with the anion systems (i.e. $[C_mH_nCOO]$ ($m = 1–6; n = 3–13$)) (Fig. 9).

In general, the fatty acid anion with carboxyl functional group (COO$^-$) is preferred interaction site for the water molecules. The increase in the chain length of the fatty acid anions does not influence much in the interaction energy value since the interaction mainly depends on the carboxyl functional group (COO$^-$). In the case of $[\text{MIM}]^+[C_mH_nCOO]$ interactions, the calculated interaction energy value show that among the studied systems the $[\text{MIM}]^+[C_1H_3COO]$ has the maximum interaction energy value of $-130.76$ kcal/mol. Similarly, the $[\text{MIM}]^+[C_1H_3COO]$ has the maximum interaction energy value of $-139.56$ kcal/mol in the water phase (dielectric constant $= 78.35$) (Fig. 10).

The continuum solvation models are used to study the solvent effects on molecular structure and energetics of ILs. In this study, the calculated solvation energy ($\Delta G_{sol}$) of $[\text{MIM}]^+[C_mH_nCOO]$ ($m = 1–6; n = 3–13$) is listed in Table 2. For ILs–Water cluster interactions, the calculated total interaction energy values are ranges from $-1.14$ to $-8.63$ kcal/mol. The calculated interaction energy value shows that the ILs with two water molecules (i.e. dimer of $H_2O$) have the strong interaction than the other (i.e. $1H_2O$ (monomer of $H_2O$) and $3H_2O$ (trimer of $H_2O$)) (Fig. 11). The reason for the dimer of $H_2O$ has more interaction with ILs than monomer and trimer of $H_2O$ is due to its coordination number and H bond distance values. The coordination numbers for the $[\text{MIM}]^+[C_mH_nCOO]$ ($m = 1–6; n = 3–13$) ILs with $1H_2O, 2H_2O$ and $3H_2O$ are 3, 7 and 7 respectively. Even though dimer and trimer of $H_2O$ have the same coordination numbers, the average H bond distance value of ILs with dimer of $H_2O$ are equal or even shorter in few cases than the trimer of $H_2O$ molecules. The above results lead to more interaction between ILs with dimer of $H_2O$ than the monomer and trimer of $H_2O$. The thermodynamic properties such as changes in enthalpy ($\Delta H$) and changes in Gibbs’ free energies ($\Delta G$) related to the ILs–Water cluster interaction are calculated and listed in Table 2. From Table 2, it is found that the changes in enthalpy corresponds to ILs–Water interaction are negative (i.e. $\Delta H < 0$) which indicates the above interaction is an exothermic in nature. The changes in Gibbs’ free energies corresponding to the interactions of $[\text{MIM}]^+[C_mH_nCOO]$ ($m = 1–6; n = 3–13$) ILs with water clusters ($H_2O$)$_{1–3}$ are positive. It indicates that the formation of $[\text{MIM}]^+[C_mH_nCOO]$ ($m = 1–6; n = 3–13$) ILs with water clusters ($H_2O$)$_{1–3}$ are not a spontaneous process [69]. Also, it indicates that the $[\text{MIM}]^+[C_mH_nCOO]$ ($m = 1–6; n = 3–13$)
ILs in water clusters prefer to be as solvated ions instead of ion pairs solvated by water [62].

**AIM analysis**

To investigate about the nature of H bond in the selected ILs, we employ the electron density-based topological parameter within the framework of Bader’s quantum theory of atoms in molecule (QTAIM) using MORPHY 98 program [56, 57]. The QTAIM method examines the topology of electron density $\rho(r)$ (in a.u.), Laplacian of electron density $\nabla^2 \rho(r)$ (in a.u.) at bond critical point (BCP) and Hessian ($H_{BCP} = G_{BCP} + V_{BCP}$) values and based on the above values the strength of the H bond can be identified. In general, if the both $\nabla^2 \rho(r)$ and $H_{BCP}$ values are positive then the H bond is weak interaction and if $\nabla^2 \rho(r)$ is positive and $H_{BCP}$ is negative then the H bond is strong. Also, the $H_{BCP} > 0$ indicates the electrostatic interaction and the

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**Fig. 9** The BSSE-corrected interaction energy values of $[\text{MIM}]^+$ cation and $[\text{C}_n\text{H}_2\text{COO}]^-$ ($n=3-13$) anions with water clusters $(\text{H}_2\text{O})_{1-3}$, (1 W, 2 W, 3 W denotes $(\text{H}_2\text{O})_1$, $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_3$ respectively)

**Fig. 10** The BSSE-corrected interaction energy values for the interaction between $[\text{MIM}]^+$ cation and $[\text{C}_n\text{H}_2\text{COO}]^-$ ($m=1-6; n=3-13$) anions of ILs in gas phase and water phase
$H_{BCP} < 0$ indicates the covalent interaction. In this study, the calculated electron density $\rho(r)$, Laplacian of electron density $\nabla^2 \rho(r)$ and $H_{BCP}$ values are listed in Table 1. From Table 1, we can found that the H bond interaction between $[\text{MIM}]^+–[\text{C}_m\text{H}_n\text{COO}]^− (m = 1–6; n = 3–13)$ ILs consists of one strong and one weak H bond. In our studied $[\text{MIM}]^+$ and $[\text{C}_m\text{H}_n\text{COO}]^− (m = 1–6; n = 3–13)$ ILs, there are two types of bonds found (i.e. N–H···O and C–H···O). Among the two H bond interactions, the N–H···O interactions correspond to strong one and the C–H···O interactions correspond to weaker one. The calculated $\rho(r)$ values ranges from 0.013 to 0.053 a.u. and the $\nabla^2 \rho(r)$ value range of 0.050–0.105 a.u is observed. Also, the $H_{BCP}$ value is negative for N–H···O interactions and it is positive for C–H···O interactions. The above values suggests that there is one strong H bond (N–H···O) and one weak H bond (C–H···O) found between $[\text{MIM}]^+–[\text{C}_m\text{H}_n\text{COO}]^− (m = 1–6; n = 3–13)$ ILs. The result from AIM analysis is in correlation with the H bond distance between $[\text{MIM}]^+–[\text{C}_m\text{H}_n\text{COO}]^− (m = 1–6; n = 3–13)$ ILs. That is, strong H bond corresponds to N–H···O interactions (1.70 Å) and the weak H bond corresponds to C–H···O interactions (2.31 Å).

**Table 2** The solvation energy ($\Delta G_{solv}$) and thermodynamic properties such as change in enthalpy and change in Gibbs free energies corresponding the interactions of $[\text{MIM}]^+–[\text{C}_m\text{H}_n\text{COO}]^− (m = 1–6; n = 3–13)$ ionic liquids with water clusters ($\text{H}_2\text{O})_{1–3}$.

| ILs        | $\Delta G_{solv}$ | $\Delta G_{1(\text{H}_2\text{O})}$ | $\Delta G_{2(\text{H}_2\text{O})}$ | $\Delta G_{3(\text{H}_2\text{O})}$ |
|------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $[\text{MIM}]^+–[\text{C}_1\text{H}_3\text{COO}]^−$ | $−9.31$           | $−2.64$                           | $5.64$                            | $−9.90$                           |
| $[\text{MIM}]^+–[\text{C}_2\text{H}_5\text{COO}]^−$ | $−9.60$           | $−2.90$                           | $6.72$                            | $−9.83$                           |
| $[\text{MIM}]^+–[\text{C}_3\text{H}_7\text{COO}]^−$ | $−9.78$           | $−3.37$                           | $5.26$                            | $−10.27$                          |
| $[\text{MIM}]^+–[\text{C}_4\text{H}_9\text{COO}]^−$ | $−7.61$           | $−2.71$                           | $7.10$                            | $−10.07$                          |
| $[\text{MIM}]^+–[\text{C}_5\text{H}_{11}\text{COO}]^−$ | $−7.71$           | $−3.54$                           | $7.45$                            | $−10.44$                          |
| $[\text{MIM}]^+–[\text{C}_6\text{H}_{13}\text{COO}]^−$ | $−8.76$           | $−2.86$                           | $6.29$                            | $−10.70$                          |

**NBO analysis**

The H bond formation is associate with certain amount of charge is transferred from the proton acceptor to the proton donor molecule [48]. The NBO analysis is used to understand the charge transfer corresponds to the H bond formation. In a system with X–H···Y H bond interaction, the charge transfer takes place between the lone pair of proton acceptor/electron donor (Y) to the anti-bonding orbital $\sigma^*(X–H)$ of proton donor/ electron acceptor. The stabilization energy $E^{(2)}$ corresponds to Y(LP) $\sigma^*(X–H)$ H bond can calculated by $E^{(2)} = \rho(r) F(i, j) E_i / (E_i - E_j)$, where $F(i, j)$ is the off-diagonal or coupling NBO fock matrix element, and $E_i$ and $E_j$ are the diagonal elements. In this study, the calculated occupation number of donor and acceptor of ions and...
the stabilization energy values are listed in Table 3. Here, the [MIM]⁺–[C₄H₇COO]⁻ (m = 1–6; n = 3–13) interactions lead to the charge transfer from the fatty acid anion to cation is 0.41 e/a.u.. The calculated occupancy values show that the occupancies of proton acceptor N (σ*(X–H)) and (C–H···O) units, the stabilization energy corresponding to the H bond formed between [MIM]⁺ and [C₄H₇COO]⁻ (m = 1–6; n = 3–13) ionic liquids and the changes in the fatty acid anionic charge (Δq) during ILs formation are optimized in both gas phase and water phase. The optimized structures show that the [MIM]⁺–[C₄H₇COO]⁻ (m = 1–6; n = 3–13) ILs has one strong (N–H···O) and one weak (C–H···O) H bond interactions. During the ion pair formation, the proton transfer process is observed from ‘N’ atom of [MIM]⁺ cation to the ‘O’ atom of fatty acid anions [C₄H₇COO]⁻ (m = 1–6; n = 3–13). From the vibrational frequency analysis, it is evident that the red-shifted H bond is found between [MIM]⁺–[C₄H₇COO]⁻ (m = 1–6; n = 3–13) ionic liquids. From the interaction energy calculations, it is found that the water molecules (i.e. (H₂O)₁–₃) preferentially interact with fatty acid-based anions rather than methyl-imidazolium cation. Further, the ILs–water molecule interactions show that the addition of water molecule reduces the interaction between methyl-imidazolium cation and fatty acid-based anions of ILs. The AIM and NBO analysis also confirms the presence of one strong (N–H···O) and one weak (C–H···O) H bond interactions between methyl-imidazolium cation and fatty acid-based anions of ILs. The stabilization energy corresponding to the proton transfer process (i.e. N–H···O interaction) is calculated as 36.98–38.51 kcal/mol.

**Table 3** The electron occupancy in H bond electron donor N(Y) and electron acceptor σ*(X–H) units, the stabilization energy corresponds to the H bond formed between [MIM]⁺ and [C₄H₇COO]⁻ (m = 1–6; n = 3–13) ionic liquids and the changes in the fatty acid anionic charge (Δq) during ILs formation

| ILs Bond type          | Donor N(Y) | Acceptor | E[(2)] | Δq on anion |
|------------------------|------------|----------|--------|-------------|
| Complex Monomer        | Monomer    |          |        |             |
| [MIM]⁺–[C₄H₇COO]⁻      | N–H···O    | C–H···O  | 1.9701 | 0.0792      | 0.0108      | 38.51 | −0.5888 |
| [MIM]⁺–[C₄H₇COO]⁻      | C–H···O    |          | 1.9764 | 0.0200      | 0.0094      | 1.02  |
| [MIM]⁺–[C₅H₁₁COO]⁻     | N–H···O    | C–H···O  | 1.9699 | 0.0786      | 0.0108      | 37.96 | −0.5882 |
| [MIM]⁺–[C₅H₁₁COO]⁻     | C–H···O    |          | 1.9765 | 0.0201      | 0.0094      | 1.07  |
| [MIM]⁺–[C₆H₁₃COO]⁻     | N–H···O    | C–H···O  | 1.9695 | 0.0769      | 0.0108      | 36.98 | −0.5863 |
| [MIM]⁺–[C₆H₁₃COO]⁻     | C–H···O    |          | 1.9765 | 0.0202      | 0.0094      | 1.10  |
| [MIM]⁺–[C₆H₁₃COO]⁻     | N–H···O    | C–H···O  | 1.9695 | 0.0778      | 0.0108      | 37.60 | −0.5869 |
| [MIM]⁺–[C₆H₁₃COO]⁻     | C–H···O    |          | 1.9766 | 0.0201      | 0.0094      | 1.03  |

### Conclusion

Herein, we employed the DFT calculations for the studies on water aggregation behaviour of methyl-imidazolium cation [MIM]⁺ with fatty acid anions [C₄H₇COO]⁻ (m = 1–6; n = 3–13) of ILs. The selected ILs are optimized in both gas phase and water phase. The optimized structures show that the [MIM]⁺–[C₄H₇COO]⁻ (m = 1–6; n = 3–13) ILs has one strong (N–H···O) and one weak (C–H···O) H bond interactions. During the ion pair formation, the proton transfer process is observed from ‘N’ atom of [MIM]⁺ cation to the ‘O’ atom of fatty acid anions [C₄H₇COO]⁻ (m = 1–6; n = 3–13). From the vibrational frequency analysis, it is evident that the red-shifted H bond is found between [MIM]⁺–[C₄H₇COO]⁻ (m = 1–6; n = 3–13) ionic liquids. From the interaction energy calculations, it is found that the water molecules (i.e. (H₂O)₁–₃) preferentially interact with fatty acid-based anions rather than methyl-imidazolium cation. Further, the ILs–water molecule interactions show that the addition of water molecule reduces the interaction between methyl-imidazolium cation and fatty acid-based anions of ILs. The AIM and NBO analysis also confirms the presence of one strong (N–H···O) and one weak (C–H···O) H bond interactions between methyl-imidazolium cation and fatty acid-based anions of ILs. The stabilization energy corresponding to the proton transfer process (i.e. N–H···O interaction) is calculated as 36.98–38.51 kcal/mol.

### Supplementary information

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### Author contribution

The authors Suresh Sampathkumar and Vijayakumar Subramaniam have contributed to the development of this manuscript and the associated research work and deserve authorship.

### Data availability

The manuscript has no associated data to be deposited.

### Declarations

#### Ethics approval

The authors declare that the manuscript satisfy the ethical standards required for publication.

#### Consent to participate

The authors listed are aware and have approved the submission of the article.

#### Consent for publication

The authors agree on the publication of the article on acceptance of the submission.

#### Conflict of interest

The authors declare no competing interests.
References

1. Gabriel S, Weiner J (1888) On some derivatives of propylamines. Ber Dtsch Chem Ges 21:2669–2679
2. Welton T (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev 99(8):2071–2084
3. Holbrey JD, Seddon KR (1999) Ionic liquids. Clean Prod Process 1(4):223–236
4. Dupont J, de Souza RF, Suarez PAZ (2002) Ionic liquid (molten salt) phase organometallic catalysis. Chem Rev 102(10):3667–3692
5. Baudequin C, Baudoux J, Levillain J, Cahard D, Gaumont AC, Plaquenst JC (2003) Ionic liquids and chirality: Opportunities and challenges. Tetrahedron: Asymmetry 14(20):3081–3093
6. Bao W, Wang Z, Li Y (2003) Synthesis of chiral ionic liquids from natural amino acids. J Org Chem 68(2):591–593
7. Wasserscheid P, Welton T (2008) Ionic liquids in synthesis. John Wiley & Sons
8. Weingärtner H (2008) Understanding ionic liquids at the molecular level: Facts, problems, and controversies. Angew Chem Int Ed 47(4):656–670
9. Zhou Y (2005) Recent advances in ionic liquids for synthesis of inorganic nanomaterials. Curr Nanosci 1(1):35–42
10. Nockemann P, Binnekins K, Driesen K (2005) Purification of imidazolium ionic liquids for spectroscopic applications. Chem Phys Lett 415(1–3):131–136
11. Párvulescu VI, Hardacre C (2007) Catalysis in ionic liquids. Chem Rev 107(6):2615–2665
12. Dyson PJ, Geldbach TJ (2007) Applications of ionic liquids in synthesis and catalysis. Interface-Electroch Soc 161(1):50–53
13. Harjani JR, Singer RD, Garcia MT, Scammells PJ (2009) Biodegradable pyridinium ionic liquids: Design, synthesis and evaluation. Green Chem 11(1):83–90
14. Atefi F, Garcia MT, Singer RD, Scammells PJ (2009) Phosphonium ionic liquids: Design, synthesis and evaluation of biodegradability. Green Chem 11(10):1595–1604
15. Aparicio S, Atilhan M, Karadas F (2010) Thermophysical properties of pure ionic liquids: Review of present situation. Ind Eng Chem Res 49(20):9580–9595
16. Hallett JP, Welton T (2011) Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. Chem Rev 111(5):3508–3576
17. Dong K, Zhang S (2012) Hydrogen bonds: a structural insight into ionic liquids. Chem Eur J 18(10):2748–2761
18. Yang Q, Xu D, Zhang J, Zhu Y, Zhang Z, Qian C, Ren Q, Xing H (2015) Long-chain fatty acid-based phosphonium ionic liquids with strong hydrogen-bond basicity and good lipophilicity: Synthesis, characterization, and application in extraction. ACS Sustain Chem Eng 3(2):309–316
19. Rocha MAA, van den Bruinhorst A, Schröer W, Rathke B, Kroon MC (2016) Physicochemical properties of fatty acid based ionic liquids. J Chem Thermodyn 100:156–164
20. Wasserscheid P, Keim W (2000) Ionic liquids—new solutions for transient metal catalysis. Angew Chem Int Ed 39(21):3772–3789
21. Wang P, Zakeeruddin SM, Moser JE, Nazeeruddin MK, Sekiguchi T, Grätzel M (2003) A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitiser and polymer gel electrolyte. Nat Mater 2(6):402–407
22. Song CE (2004) Enantioselective chemo- and bio-catalysis in ionic liquids. Chem Commun 9:1033–1043
23. Buzzo MC, Evans RG, Compton RG (2004) Non-haloaluminate room-temperature ionic liquids in electrochemistry—a review. ChemPhysChem 5(8):1106–1120
24. Ni X, Xing H, Yang Q, Wang J, Su B, Bao Z, Yang Y, Ren Q (2012) Selective liquid–liquid extraction of natural phenolic compounds using amino acid ionic liquids: a case of α-tocopherol and methyl linoleate separation. Ind Eng Chem Res 51(18):6480–6488
25. Chen X, Li F, Asumana C, Yu G (2013) Extraction of soluble dyes from aqueous solutions with quaternary ammonium-based ionic liquids. Sep Purif Technol 106:105–109
26. Vander Hoogerstraete T, Binnekins K (2014) Highly efficient separation of rare earths from nickel and cobalt by solvent extraction with the ionic liquid trihexyl (tetradeceyl) phosphonium nitrate: a process relevant to the recycling of rare earths from permanent magnets and nickel metal hydride batteries. Green Chem 16(3):1594–1606
27. Fukumoto K, Yoshizawa M, Ohno H (2005) Room temperature ionic liquids from 20 natural amino acids. J Am Chem Soc 127(8):2398–2399
28. Manojkumar K, Sivaramakrishna A, Vijayakrishna K (2016) A short review on stable metal nanoparticles using ionic liquids, supported ionic liquids, and poly (ionic liquids). J Nanopart Res 18(4):103
29. Qian W, Texter J, Yan F (2017) Frontiers in poly (ionic liquid)s: Syntheses and applications. Chem Soc Rev 46(4):1124–1159
30. Tao GH, He L, Liu WS, Xu L, Xiong W, Wang T, Kou Y (2006) Preparation, characterization and application of amino acid-based green ionic liquids. Green Chem 8(7):639–646
31. Li T, Yang Q, Ding H, Li J, Peng C, Liu H (2015) Ammonium acid based ionic liquids as additives for the separation of an acetonitrile and water azetotropic mixture: COSMO-RS prediction and experimental verification. Ind Eng Chem Res 54(48):12143–12149
32. Shyma M, Lakshmipathi S (2020) Water confined (H2O)n=1–10 amino acid-based ionic liquids—a DFT study on the bonding, energetics and IR spectra. J Mol Liq 304:112720
33. Giernoith R (2010) Task-specific ionic liquids. Angew Chem Int Ed 49(16):2834–2839
34. Yuvaraj SVJ, Zhdanov RK, Belosludov RV, Belosludov VR, Subbotin OS, Kanie K, Funaki K, Muramatsu A, Nakamura T, Kawazoe Y (2015) Solvation mechanism of task-specific ionic liquids in water: a combined investigation using classical molecular dynamics and density functional theory. J Phys Chem B 119(40):12894–12904
35. Bera A, Belhaj H (2016) Ionic liquids as alternatives of surfactants in enhanced oil recovery—a state-of-the-art review. J Mol Liq 224:177–188
36. Šarac B, Medoš Ž, Cognigni A, Bica K, Chen LJ, Bešter-Rogač M (2017) Thermodynamic study for micellization of imidazolium based surface active ionic liquids in water: Effect of alkyl chain length and anions. Colloids Surf A 532:609–617
37. Čobanov I, Šarac B, Medoš Ž, Vaněš M, Gadjuzič S, Zec N, Bešter-Rogač M (2018) Effect of cationic structure of surface active ionic liquids on their micellization: a thermodynamic study. J Mol Liq 271:437–442
38. Mezzetta A, Łuczak J, Woch J, Chiappe C, Nowicki J, Guazzelli L (2019) Surface active fatty acid ILs: Influence of the hydrophobic tail and/or the imidazolium hydroxyl functionalization on aggregates formation. J Mol Liq 289:111155
39. Qin M, Zhong F, Sun Y, Tan X, Hu K, Zhang H, Kong M, Wang G, Zhuang L (2020) Effect of cation substituent of dodecanesulfonate-based anionic surface active ionic liquids on micellization: Experimental and theoretical studies. J Mol Liq 303:112695
40. Brown P, Butts CP, Eastoe J, Fermin D, Grillo I, Lee HC, Parker D, Plana D, Richardson RM (2012) Anionic Surfactant ionic liquids with 1-butyl-3-methyl-imidazolium cations: Characterization and application. Langmuir 28(5):2502–2509
41. Trush MM, Semenyuta IV, Vdovenko SI, Rogalsky SP, Lobko EO, Meteytsia LO (2017) Synthesis, spectroscopic and molecular docking studies of imidazolium and pyridinium based ionic fluids.
Research on the aggregation behavior of imidazolium-based ionic liquids with and without a small amount of water. J Phys Chem 121(14):3121–3129

59. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Li X, Caricato M, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Jr., Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg J, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox, DJ (2009) Gaussian 09, Revision A.02, Wallingford CT

60. Hunt PA, Kirchner B, Welton T (2006) Characterising the electronic structure of ionic liquids: an examination of the 1-butyl-3-methylimidazolium chloride ion pair. Chem Eur J 12(26):6762–6775

61. Xu W, Wang T, Cheng N, Hu Q, Bi Y, Gong Y, Yu L (2015) Experimental and DFT studies on the aggregation behavior of imidazolium-based surface-active ionic liquids with aromatic counterions in aqueous solution. Langmuir 31(4):1272–1282

62. Roohi H, Khyrkah S (2015) Quantum chemical studies on nanostructures of the hydrated methylimidazolium-based ionic liquids. J Mol Model 21(1):1

63. Ali MK, Moshikar RM, Wakabayashi R, Tahara Y, Moniruzzaman M, Kamiya N, Goto M (2019) Synthesis and characterization of choline–fatty-acid-based ionic liquids: a new biocompatible surfactant. J Colloid Interface Sci 551:72–80

64. Yamada T, Tominari Y, Tanaka S, Mizuno M (2017) Infrared spectroscopy of ionic liquids consisting of imidazolium cations with different alkyl chain lengths and various halogen or molecular anions with and without a small amount of water. J Phys Chem B 121(14):3121–3129

65. Belloqc AM, Perchard C, Novak A, Josien ML (1965) Spectres de vibration de l’imidazole, de l’imidazole (D)-1, de l’imidazole (D3)-2, 4, 5 et de l’imidazole (D4)-Partie I: Région entre 4000 et 1700 cm⁻¹. J Chim Phys 62:1334–1343

66. Voss JM, Marsh BM, Zhou J, Garand E (2016) Interaction between ionic liquid cation and water: infrared predissociation study of [bmim]+·(H₂O)₄ clusters. Phys Chem Chem Phys 18(28):18905–18913.

67. Van Duijneveldt FB, van Duijneveldt-van de Rijdt JGCVM, van Lenthe JH (1994) State of the art in counterpoise theory. Chem Rev 94(7):1873–1885

68. Boys S, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol Phys 19(4):553–566

69. Roohi H, Khyrkah S (2013) Ion-pairs formed in [Mim]+·[N(CN)₂]⁻ ionic liquid: structures, binding energies, NMR SSCCs, volumetric, thermodynamic and topological properties. J Mol Liq 177:119–128

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