

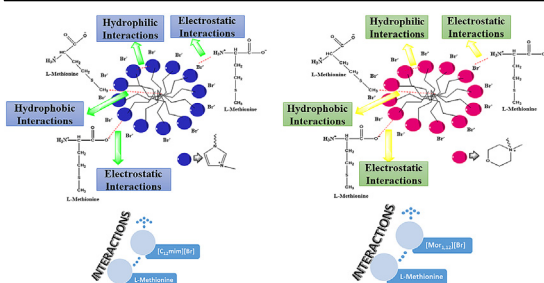


Research article

Effect of amino acid on the surface adsorption and micellar properties of surface active ILs varying in cationic head groups

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GRAPHICAL ABSTRACT



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ABSTRACT

The interfacial along with bulk characteristics of the aqueous solutions of ILs with dissimilar cationic head group viz. 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim][Br]$), and N-dodecyl-N-methylmorpholinium bromide ($[Mor_{1,12}][Br]$) in the absence and the presence of an amino acid L-Methionine as an external additive have been examined by electrical conductivity, UV-Visible, surface tension, and DLS measurements. The CMC values, and the lowest maximum surface excess concentration (Γ_{max}) achieved from all three techniques, and surface tension measurements respectively displayed more surface activity of the $[C_{12}mim][Br]$ than the $[Mor_{1,12}][Br]$. Also, the morpholinium head group is less hazardous than imidazolium, it can be utilised to design ILs that are greener, mainly in combination with polar, small, and non-toxic side chains and anions.

1. Introduction

In recent times, Ionic liquids (ILs) have received considerable interest as a unique category of surfactants. Ionic liquids are composed solely of ions which are usually in a liquid state at or near room temperature and are growing interest in many industrial applications by

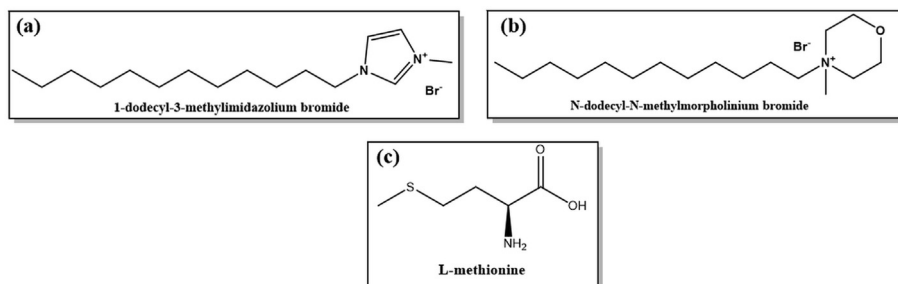
virtue of their exceptional physicochemical features, inclusive of high viscosity, nonvolatility, high ionic conductivity, high stability, broader liquid temperature range, and easy recyclability [1, 2, 3]. Over the last decade, research on ILs has taken a new direction that highlights the development of "task-specific" ILs [4], which involves designing the ILs' structure concerning the field of application. As a consequence,

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Scheme 1. Chemical structures of examined ionic liquids (a) $[C_{12}mim][Br]$ and (b) $[Mor_{1,12}][Br]$ along with amino acid (c) L-Methionine.

numerous ILs have been exposed to analyses of their structure-property relationships. These studies permit the physicochemical or thermodynamic properties to be predicted, as long as adequate combinations of cations and anions are examined and regular trends are understood [5]. This large number of probable ILs then requires the build-up of predictive models to recognize a particular IL for a specific application [6, 7]. As a result, a relatively large, systematic, and adequately precise dataset of properties is necessary for known, as well as new, ILs [8, 9, 10, 11, 12]. Even though a large amount of data have already been published on the physicochemical properties of ILs, systemic studies are still needed and should be further explored on this subject. So far, maximum studies have been dealing with ionic liquids that contain alkyl-imidazolium cations [12, 13, 14, 15, 16, 17]. These imidazolium-based ILs are observed to possess overall favorable features if compared with others, and their physical and electrochemical data is simply available. Still, for several industrial applications, most cation sources of ILs are upscale. The exploration of new ILs and their important properties are nevertheless quite a challenging task that aims to reduce costs and improve the properties of ILs. Therefore, the various studies which describe the physicochemical nature of ILs enlighten the synthesis of environmentally safe, biodegradable, and sustainable ILs. Numerous possible examples of "green" cations can be found in the literature. For instance, morpholinium-based cations are now identified as interesting substitutes to imidazolium-based cations. Morpholinium ILs possess fascinating features such as (a) simple synthetic procedures and shorter reaction times, (b) compared to imidazole, the low cost of 4-methyl morpholine lead to lower production rates, and (c) low toxicity and good ionic conductivity [18].

ILs comprising of longer alkyl chains are analogous to conventional surfactants which form aggregates in an aqueous medium [8, 19]. Nitrogen-containing surfactants (i.e., N-heterocycles) including imidazolium, pyrrolidinium, pyridinium, piperidinium, morpholinium, and piperazidinium based ILs, have been investigated by several researchers owing to their unique structures and exceptional surface properties, which makes them different from the traditional ionic surfactants and hence, their aggregation behavior have been investigated in an aqueous medium [15, 20, 21, 22, 23, 24, 25, 26, 27]. These aggregates are being

widely studied not only because of their fundamental importance but also for their practical applications in numerous fields such as the synthesis of nanoparticles, microemulsions, organic or bio-organic molecules, etc [28, 29, 30, 31, 32, 33, 34, 35, 36]. Furthermore, the physicochemical parameters of such ionic liquid surfactants could be modified by adding various external additives such as organic additives, salts, proteins, drugs, carbohydrates, traditional surfactants, etc [37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49]. Nowadays, Ionic liquids have been extensively employed as prominent media in the processes involving biomolecules [50, 51, 52]. However, the relative research is currently limited and most ILs utilized in these reports were the imidazolium-based ILs. The interaction of ionic liquids/surfactants with amino acids (as an external additive) has been widely studied, which basically reports the interaction studies for the imidazolium-based ionic liquids. However, no such investigation on the interaction of morpholinium-based ILs with amino acids is available in the literature. Further, the morpholinium based ILs are less toxic in comparison to imidazolium-based according to the cytotoxicity studies, therefore it can be utilised to design ILs that are greener, mainly in grouping with polar, small, and non-toxic side chains and anions [53]. The present studies of the amphiphilic nature of SAILs and the use of micellization involving amino acids may be helpful to other investigators in the medicinal and pharmaceutical fields.

The objective of this work is, therefore, to conduct a thorough investigation on the conductometric, UV-vis spectroscopic, tensiometric, and DLS measurements of ILs composed of dissimilar cation i.e., 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim][Br]$) and N-dodecyl-N-methylmorpholinium bromide in the absence and the presence of L-Methionine (Scheme 1) at four diverse temperatures ranging from 293.15 to 308.15 K. The obtained results were interpreted in terms of the effect of changing cation, temperature, and the presence of the external additive. Here, L-methionine has been primarily taken in comparison to other amino acids, since numerous studies have been conducted. on simple amino acids such as glycine, alanine, etc, [11, 48, 54, 55, 56, 57], and also several benefits associated with L-methionine makes it a primary choice for our study. L-Methionine is found to contain sulfur, which has a number of possible health benefits for the

Table 1. Sources, molecular formula and Grades of chemicals.

Chemicals	Provenance	Purification Method	Purity	CAS No.
1-methylimidazole	HiMedia Laboratories Pvt. Ltd., Mumbai, India	Used as such	≥0.99	616-47-7
1-Bromododecane	TCI Co. Ltd., Tokyo, Japan	Used as such	>0.98	143-15-7
4-methylmorpholine	Sigma-Aldrich	Used as such	≥0.99	109-02-4
L-Methionine	Spectrochem Pvt. Ltd Mumbai	Used as such	≥0.98	63-68-3
Acetonitrile	LOBA Chemie Pvt. Ltd Mumbai, India	Used as such	≥0.995	75-05-8
Hexane	TCI Co. Ltd., Tokyo, Japan	Used as such	>0.96	110-54-3
Toluene	TCI Co. Ltd., Tokyo, Japan	Used as such	>0.995	108-88-3
$[C_{12}mim][Br]$	Synthesized in the laboratory	Vacuum drying	>0.95**	61546-00-7
$[Mor_{1,12}][Br]$	Synthesized in the laboratory	Vacuum drying	>0.89**	-

*As stated by the supplier. **As per NMR investigation.

body, especially in the nourishment of hair, skin, and nails, as well as assists in the absorption of more nutrients (such as selenium and zinc). A low-methionine diet is advantageous in cancer treatment as limiting methionine-containing foods are useful for those who have certain types of cancer because it causes the cancer cells to die [58]. Consequently, it would certainly be beneficial by providing a set of data on the physicochemical characteristics of ILs containing small biomolecules such as amino acids to be able to realize the a number of interactions of ILs with biologically important macromolecules. Thus, this study will refine ionic liquid applications in industrial and biological systems.

2. Experimental

2.1. Materials

The complete description of the materials utilized in the present investigation has been specified in Table 1. Commercially available solvents i.e., Acetonitrile, Hexane, and Toluene were used as received from LOBA Chemie Pvt. Ltd Mumbai, India, and TCI Co. Ltd., Tokyo, Japan respectively. For the ILs synthesis used in the present work, starting reactants which include 1-methyl imidazole, 1-Bromododecane, 4-methyl morpholine have been bought from HiMedia Lab Pvt. Ltd., Mumbai, India, TCI Co. Ltd., Tokyo, Japan, Sigma-Aldrich respectively. Also, the additive amino acid L-methionine was procured from Spectrochem Pvt. Ltd Mumbai and was utilized without further purification. Both synthesized ILs were desiccated under vacuum for 48 h before usage. Stock solutions have been prepared using double-distilled water.

2.2. Synthetic procedures

The ionic liquids examined in the present work are 1-dodecyl-3-methylimidazolium bromide, and N-dodecyl-N-methylmorpholinium bromide, which differ in cation and are expressed as $[C_{12}mim][Br]$, $[Mor_{1,12}][Br]$, respectively.

2.2.1. Synthesis of $[C_{12}mim][Br]$

The halide-based imidazolium ionic liquid ($[C_{12}mim][Br]$) was synthesized in accordance with the standard methodology as reported in the literature [59, 60, 61]. 1-Methylimidazole along with an excess molar quantity of appropriate alkyl bromide (i.e., 1-bromododecane in the present case) were mixed in acetonitrile solvent and the whole mixture was put on refluxing accompanying stirring at 80 °C for 48–72h. The reaction progress was continuously monitored using the TLC technique and at the end of the reaction, a rotary evaporator was used to evaporate the remaining solvent under reduced pressure. The resultant ILs were repeatedly recrystallized in order to get the colorless solid.

2.2.2. Synthesis of $[Mor_{1,12}][Br]$

Utilizing the method described in the literature [62, 63], $[Mor_{1,12}][Br]$ has been synthesised in the laboratory. 4-methylmorpholine and 1-bromododecane in a 1:1.2 ratio were mixed in toluene solvent followed by a similar procedure as $[C_{12}mim][Br]$ i.e. refluxing accompanied by stirring at approximately 80–90 °C for 48h under nitrogen atmosphere. To obtain the desired product in its pure form, the reaction's leftover solvent was evaporated using a rotary evaporator after which the product was washed with ethyl acetate. 1H NMR spectrum of $[Mor_{1,12}][Br]$ was evaluated to confirm the IL obtained. The obtained ILs were then dried under vacuum for 3–4 days before its use and also the purity of the ILs was confirmed using 1H NMR spectrum for $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$ respectively.

$[C_{12}mim][Br]$: 0.88 (t, 3H); 1.25 (m, 18H); 1.94 (dd, 2H); 4.14 (s, 3H), 4.32 (t, 2H); 7.33 (d, 1H); 7.46 (d, 1H), 10.5 (s, 1H).

$[Mor_{1,12}][Br]$: 0.88 (t, 3H); 1.26 (dd, 18H); 1.7 (dd, 2H); 3.6 (t, 2H); 3.5 (s, 3H); 3.8 (dd, 2H), 3.86 (dd, 2H), 3.98 (dd, 2H), 4.20 (dd, 2H).

2.3. Experimental methods

2.3.1. Conductometric measurements

An electrical conductivity meter assembled with a dip-style conductivity cell of a unit cell constant was used to execute conductivity measurements (model 'Systronics 308'). Initially, standard KCl solutions were used to calibrate the conductivity metre ($[KCl] = 0.1M$, $\kappa = 12.97 \text{ mS cm}^{-1}$) at 298.15 K. The temperature was kept at $(298.15 \pm 0.1) \text{ K}$ using a constant temperature bath that was acquired from Macro Scientific Works Pvt. Ltd., in Delhi. In the course of the experiment, a sample cell containing 15 ml doubly distilled water was placed in a constant temperature water bath maintained at a particular temperature. The IL solution (having a concentration of 10–15 times the value of CMC) to the above sample cell was added in a specific amount by using a micropipette. The solution in the sample cell was agitated for 10 min after each titration to attain system equilibrium, and then the electrical conductivity of the solution was measured. The pH of the amino acid solutions has been taken at 7, therefore they are expected to be present in their zwitterionic forms. The change in pH may result in the ionization/protonation of their distinctive functional groups $-COOH$ and $-NH_2$ leading to different equilibrium forms of amino acids. Thus, the pH of amino acid solutions has been maintained at equal to 7. The conductivity measurements' reproducibility was within $\pm 0.2\%$.

2.3.2. Surface tension measurements

Tensiometer DCAT 15 has been employed in the deduction of CMC and various surface parameters of investigated ILs along with influence of an external additive. This has been purchased from Data Physics instruments, Germany, and offers an accuracy of about $\pm 0.01 \text{ mN m}^{-1}$. From the surface tension measurements, automated determination of the CMC value of an ionic liquid can be done using the DCAT 33 software for which Wilhelmy plate PT 11 is provided along with an automated unit of dosing LDU 25. All measurements were carried out at a temperature of 298.15 K which was maintained constant utilizing temperature controlling apparatus TV 70 accompanied by a highly accurate refrigerated circulated water thermostat. The Wilhelmy plate was adequately cleaned prior to each measurement by first cleaning it with acetone, and then drying it by burning red hot to remove the adsorbed solutes. The calibration of Tensiometer has been carried out by noting the surface tension value of water ($71.87 \text{ mN}\cdot\text{m}^{-1}$) at RT. A 40 mL sample of the solution is poured into the sample container and endorsed to equilibrate at RT for at least 20 min before being tested for surface tension. Then following the course of titrations, a specific volume of ionic liquid is added using LDU to obtain a plot of surface tension versus IL concentration. For each measurement, at least three readings were collected, and the average result has been reported with an uncertainty ranging from $(\pm 0.015 \text{ to } \pm 0.1) \text{ mN m}^{-1}$.

2.3.3. UV-visible measurements

In determination of CMC of IL, another important technique that has been employed is the probe less UV-Vis spectroscopy. The respective measurements have been recorded using a UV-Vis spectrophotometer (Agilent Technologies Carry 631), assembled with a quartz cuvette of unit path length in the wavelength range of 200–800 nm at 298.15 K. In this technique, the graph of absorbance at a fixed wavelength (λ) vs sample concentration is procured [64], where a point of crossing of two straight lines gives the value of CMC of IL.

2.3.4. DLS measurements

Knowledge concerning the hydrodynamic radius (D_h) i.e. micellar size of $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$ ILs in the existence of varying concentrations (0, 0.01, 0.05, and 0.10 mol kg $^{-1}$) of L-methionine was determined using DLS measurements. Zetasizer Nano ZS90 has been employed to perform DLS measurements. Each measurement was carried out at 90° scattering angle and at room temperature (298.15 K). A He-Ne laser with a power of 10mW was used as a light source operating at 633

nm. The solutions that are ten times concentrated than the corresponding CMC values of the IL-water/amino acid solutions were used in the DLS analysis. To eliminate interference from dust particles, the samples had been carefully filtered through 0.2 μm filters. DLS measurements were performed at least three times to ensure data accuracy.

3. Results and discussion

In this study, three techniques involving conductometric measurement at 293.15 K, 298.15 K, 303.15 K, and 308.15 K, UV-Visible, DLS, and tensiometric measurements at 298.15 K have been employed in the determination of micellization characteristics of two ILs differing in cation i.e., $[\text{C}_{12}\text{mim}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$ in the absence and existence of varying (0.01, 0.05, and 0.10 mol kg^{-1}) concentrations of L-methionine. The experimental values of conductivity, UV-visible, and surface tension are included in the manuscript's SI.

3.1. Conductance measurements

The conductivity behavior of two ILs which differ in their cation i.e., 1-dodecyl-3-methylimidazolium bromide $[\text{C}_{12}\text{mim}][\text{Br}]$, and N-dodecyl-N-methylmorpholinium bromide $[\text{Mor}_{1,12}][\text{Br}]$ has been explored in the aqueous and existence of varying concentrations (0.01, 0.05, and 0.10) mol kg^{-1} of L-methionine at four diverse (293.15, 298.15, 303.15 and 308.15) K temperatures in consideration to illuminate whether these investigated ionic liquids can form micelles and find applicability in several industrial and biological systems. The conductivity profiles where the specific conductivity (κ) values achieved for $[\text{C}_{12}\text{mim}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$ in the water and in the presence of L-methionine at varied concentrations and temperatures are plotted as a function of the IL concentration in Figures 1 and 2 respectively and the experimental value obtained has been reported in Table S1 and Table S2 for $[\text{C}_{12}\text{mim}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$ in the water and in the presence of L-methionine respectively in the supporting information. It is clearly visible from the obtained conductivity profiles that the value of κ escalates linearly with the rise in IL concentration, and the slope deviates steeply at a particular concentration. The sharp shift in the slope of κ value vs concentration of IL indicates that the micelles, or molecular aggregates, begin to form at the concentration corresponding to the breakpoint. Table 2 lists the values of the critical micelle concentrations (CMC) evaluated from the breakpoints in the κ vs concentration plot for the system of two ionic liquids $[\text{C}_{12}\text{mim}][\text{Br}]$ and $[\text{Mor}_{1,12}][\text{Br}]$ in the absence and existence of L-methionine at varied (0.01, 0.05, and 0.10) mol kg^{-1} concentrations and four (293.15, 298.15, 303.15, and 308.15) K temperatures. Table 2 also includes the CMC measurements for $[\text{C}_{12}\text{mim}][\text{Br}]$ and $[\text{Mor}_{1,12}][\text{Br}]$ in the water at 298.15 K as reported in the literature and it is clear that the obtained values in the current work are closely related to those that were published in the literature.

It can be observed from Table 2, that at any studied temperature, the values of CMC for the morpholinium based IL $[\text{Mor}_{1,12}][\text{Br}]$ in an aqueous solution of L-Methionine is decreasing with increasing molalities of the amino acid, which thereby indicate that the amino acid boosts the micellization of $[\text{Mor}_{1,12}][\text{Br}]$. However, in the case of $[\text{C}_{12}\text{mim}][\text{Br}]$, the higher value of CMC is achieved in presence of the amino acid L-Methionine. Although, on increasing the concentration of L-Methionine, the value of CMC of $[\text{C}_{12}\text{mim}][\text{Br}]$ decreases at a particular temperature. It can be attributed to the various interactions occurring between the IL and the amino acid, which include (1) the favorable interactions among the cation ($[\text{C}_{12}\text{mim}]^+$ of $[\text{C}_{12}\text{mim}][\text{Br}]$ and $[\text{Mor}_{1,12}]^+$ of $[\text{Mor}_{1,12}][\text{Br}]$) with the carboxyl group (COO^-) of amino acid which results in reduced electrostatic repulsions among the head groups of the ionic liquid and, hence enhances the micellization phenomena, (2) the attractive attraction between anion (Br^-) of IL and NH_3^+ of amino acid intensifies the solvation radius of the anions, and is generally followed by the rise in polarizability. High polarizability would also improve anions' binding to the micellar surface and reduce electrostatic repulsion among the IL's

charged head groups. As a consequence, the tendency of IL micellization upsurges [43]. Furthermore, an electronegative oxygen atom having lone pair of electrons is present in the morpholinium ionic liquid head group. These lone pairs of electrons may get involved in interactive interactions such as electrostatic and hydrogen bonding with the protons of other $[\text{Mor}_{1,12}]^+$ cations or H_2O molecules as well as repulsive interactions with negatively charged counter ions. As can be perceived from the reported CMC values in Table 2, the interactive interactions in $[\text{Mor}_{1,12}][\text{Br}]$ ionic liquid may be predicted to dominate in the presence of amino acid. These kind of interactions are absent in the case of imidazolium-based IL ($[\text{C}_{12}\text{mim}][\text{Br}]$), thus less reduction in the CMC values have been observed with the addition of amino acid L-Methionine than in the case of morpholinium-based IL ($[\text{Mor}_{1,12}][\text{Br}]$).

From Figure 3, one can clearly see that the fluctuation of the CMC for the two ILs $[\text{C}_{12}\text{mim}][\text{Br}]$ and $[\text{Mor}_{1,12}][\text{Br}]$ with temperature follows the standard ionic surfactant U-shaped curve. Generally, the influence of the temperature on the trend of CMC observed in the studied systems is a result of two contrasting factors [65, 66]. It can be expected that these ILs also behave analogously. In the beginning, when the temperature rises, the degree of hydration of the ionic imidazolium, and morpholinium head domain drops, which is then followed by an increase in the solute's hydrophobicity. As a consequence, the micellization process is favored, and it can take place at lower concentrations. Whereas, if the temperature rises, the structure of the water surrounding the hydrophobic domain may break down. This is detrimental to micelle formation since the structured water's low entropy is the primary driving force behind the self-association process. As a result, we suppose that the first impact is dominant at lower temperatures and that the second effect emerges after T_{min} is reached [67].

The degree of counter ion dissociation (α) has also been evaluated for the investigated systems by applying Eq. (1),

$$\alpha = S_2/S_1 \quad (1)$$

where S_1 and S_2 denote the slope in the pre and post-micellar regions respectively in the κ vs concentration plots. The values of α have also been enlisted in Table 2 for both the ILs $[\text{C}_{12}\text{mim}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$. It is clearly visible that the value of α decreases with the increasing molality of amino acid except in the case of the $[\text{C}_{12}\text{mim}][\text{Br}]$, wherein the presence of L-methionine, the value of alpha is more than that in an aqueous medium. Also, the U-shaped trend has been observed for α values similar to the CMC values, and the values of α increase with temperature enhancement (298.15 K–308.15 K) in the absence as well as the presence of the amino acid for both the ILs. In the view of penetration of an amino acid into the core of the micelle [55], the head groups of the ionic liquid molecule are fairly far apart. As a result of this, the charge density at the micellar surface reduces with counter ions bounded less strongly to the surface of the micelle. This leads to an upsurge in the value of α as temperature rises which ultimately promotes the ionization of IL.

The various thermodynamic parameters of micellization for $[\text{C}_{12}\text{mim}][\text{Br}]$ and $[\text{Mor}_{1,12}][\text{Br}]$ in an aqueous and in presence of varied concentrations of L-methionine at diverse temperatures can be calculated using the mass action model using Eqs. (2,3, and 4) below [59, 68].

$$\Delta G_m^0 = (2 - \alpha)RT(\ln X_{\text{CMC}}) \quad (2)$$

$$\Delta H_m^0 = -RT^2(2 - \alpha)[d(\ln X_{\text{CMC}}) / dT] \quad (3)$$

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (4)$$

where, ΔG_m^0 , ΔH_m^0 , and ΔS_m^0 are Gibb's free energy, the enthalpy, and the entropy of micellization, α is the degree of counterion dissociation, X_{CMC} is the value of CMC expressed in mole fraction, and T is the temperature in Kelvin.

Table 2 also summarises the thermodynamic parameters of micellization acquired using the above Eqs. (2), (3), and (4). The value of ΔG_m^0 ,

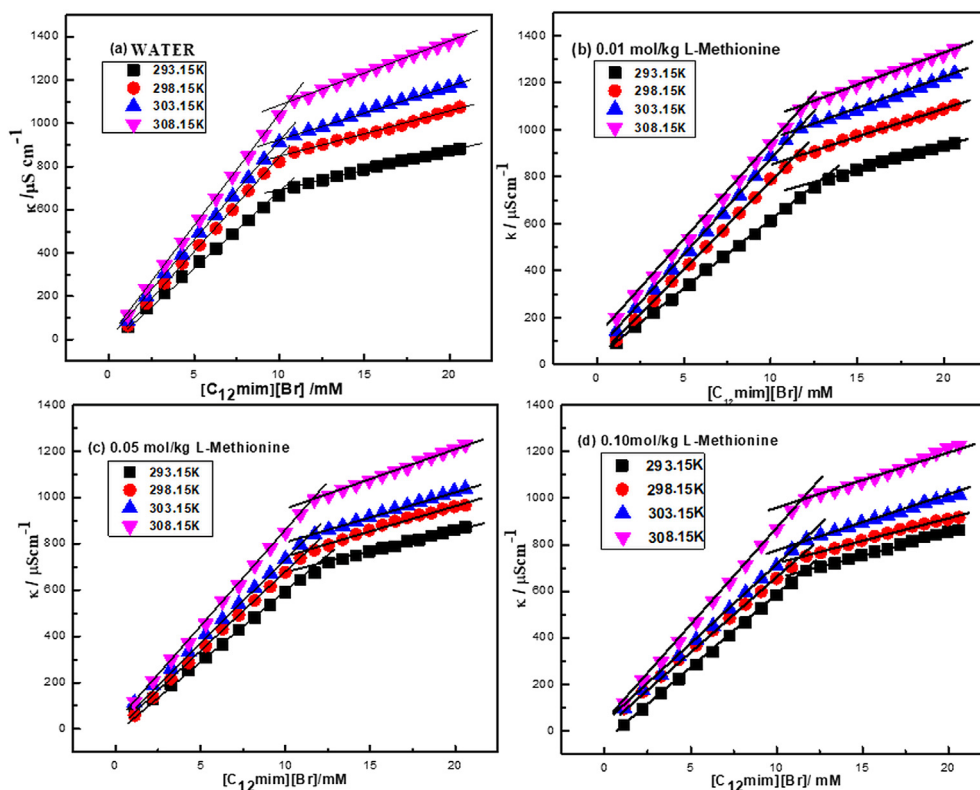


Figure 1. Variation of conductivity, (κ), as a function of IL (mM), for $[C_{12}mim][Br]$ in (a) aqueous and in presence of (b) 0.01 mol kg⁻¹, (c) 0.05 mol kg⁻¹ and (d) 0.10 mol kg⁻¹ aqueous solutions of amino acid L-methionine at (293.15–308.15)K.

Gibb's free energy of micellization is found to be negative in all cases, indicating the process of micellization to be thermodynamically favorable and spontaneous in nature. The value of ΔH_m^0 , in case of an aqueous solution of $[C_{12}mim][Br]$ is observed to be negative which indicates the exothermic nature of the micellization process. However, upon the addition of the amino acid, L-Methionine its value comes out to be positive in the case of $[C_{12}mim][Br]$, which shows the endothermic nature of the process. It means more energy is needed to break the structured water structure. In the case of $[Mor_{1,12}][Br]$, the ΔH_m^0 values are found to be negative in all cases, indicating the exothermic nature of micelle formation. Generally, the ΔH_m^0 values are influenced by various factors. The positive value of ΔH_m^0 may be due to the energy involved in the release of structured water from the hydration layer surrounding the hydrophilic domain. The release of water molecules from the water cage surrounding the IL's hydrophobic moiety also adds to the positive value contribution [69]. The transfer of the hydrocarbon chain into the micelle and the restoration of the hydrogen bonding structure of the water around the micelle is responsible for the negative contribution to the ΔH_m^0 value. Over the entire temperature range measured, the value of entropy of micellization is positive and decreases with temperature for both the ILs studied. Since, ΔG_m^0 , Gibb's free energy of micellization is negative and the value of enthalpy of micellization is positive, which thereby makes the entropy of micellization as a deciding factor. The highly organized water structure around the hydrophobic region of the ILs initiates micellization, and the value of entropy is the primary driving force behind it. Entropy contribution to the micellization lessens as temperature rises because water molecules around the hydrophobic region of the molecule become less structured at higher temperatures.

3.2. Surface tension measurements

Surface tension has long been regarded as one of the most common methods for defining and comprehending the surface and bulk charac-

teristics of a solution. In the present work, the surface tension of the aqueous solutions of two ionic liquids $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$ have been measured in the absence and existence of (0.01, 0.05, and 0.10) mol kg⁻¹ of amino acid L-methionine at 298.15 K in order to scrutinize the difference in the surface and micellization behavior of $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$, which vary in the cation part. The experimentally obtained data for the two investigated systems has been reported in Table S3 of supplementary data. Surface tension plots for aqueous solutions of $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$ in the absence and existence of L-methionine at 298.15 K are shown in Figure 4. As can be observed, the surface tension (γ) for all the systems under study decreased with increasing IL concentration, representing the adsorption of the IL molecules at the interface of air and water. As the concentration of IL is increased further, the γ approaches a plateau i.e., remains fairly constant which indicates the micelle formation. At the breakpoint, the value of CMC of IL has been determined and reported in Table 3 along with other surface parameters. The imidazolium-based IL $[C_{12}mim][Br]$ is observed to have less CMC value than the morpholinium-based IL $[Mor_{1,12}][Br]$ as can also be confirmed from the conductivity measurements. The presence of oxygen in the morpholinium-based IL in the form of cyclic ether linkage renders morpholinium surfactants/IL more hydrophilic (less surface-active), and soluble than other surfactants/IL with nitrogen-containing heterocycles, which explains the higher CMC values of $[Mor_{1,12}][Br]$ than $[C_{12}mim][Br]$, having the same hydrophobic carbon chain length. In Table 3, the value of γ_{cmc} has been presented, which is the measure of ionic liquid's ability to populate at the interface of air and water. It can be noticed that the γ_{cmc} values are lower for the $[C_{12}mim][Br]$ in aqueous solution than $[Mor_{1,12}][Br]$ which supports the higher surface activity of imidazolium-based ionic liquid than the morpholinium-based ionic liquid.

When an amino acid is added to water, it either causes water to be displaced from the surface adsorption layer (reduction in surface tension) or ionic liquid monomers to be displaced from the surface layer (raising the surface tension of the solution) [70, 71]. In the present case, the

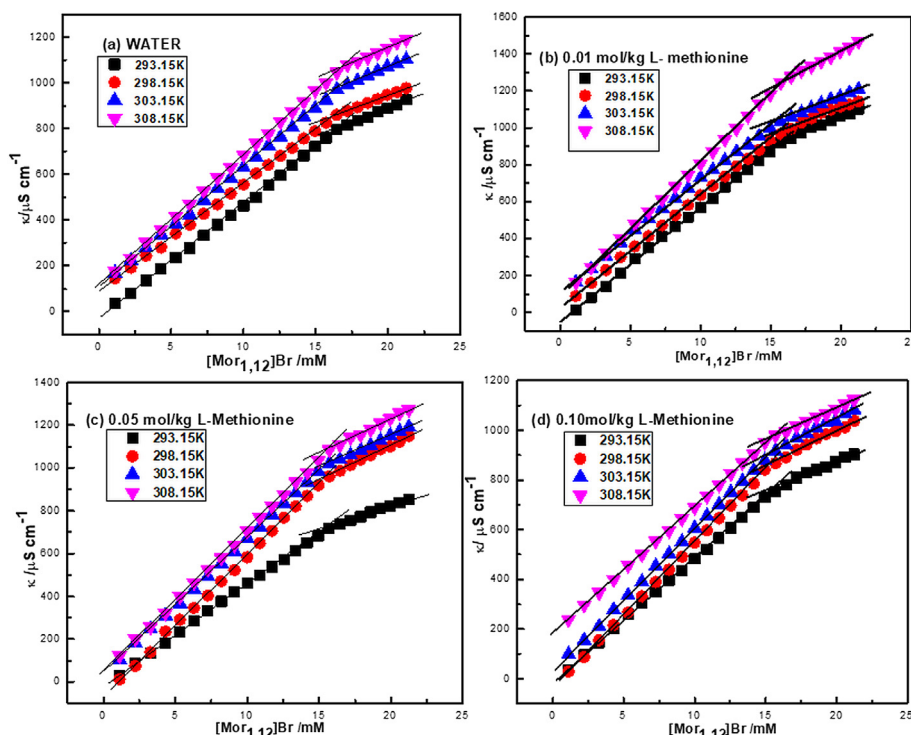


Figure 2. Variation of conductivity, (κ), as a function of IL (mM), for $[\text{Mor}_{1,12}]\text{Br}$ in (a) aqueous and in presence of (b) 0.01 mol kg^{-1} , (c) 0.05 mol kg^{-1} and (d) 0.10 mol kg^{-1} aqueous solutions of amino acid L-methionine at (293.15, 298.15, 303.15 and 308.15)K.

former effect is predominant which is confirmed by the decrease in the γ_{cmc} of both the ILs upon adding an amino acid. Moreover, amino-acids are suspected to limit water–water interactions, which also explains why γ_{cmc} has decreased. Another parameter, Π_{cmc} which measures the effectiveness of reduction in surface tension known as surface pressure at the saturated interface of air and solution has been achieved from the surface tension plots by applying the following Eq. (5):

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \quad (5)$$

where, γ_0 is the initial surface tension of the water/amino acid, and γ_{cmc} is the surface tension of ionic liquid after formation of micelles. From the values of Π_{cmc} which have been listed in Table 3, we can notice that the $[\text{C}_{12}\text{mim}]\text{Br}$ has a higher value of π_{cmc} than that of $[\text{Mor}_{1,12}]\text{Br}$ signifying more adsorption efficiency as well as a more effective tendency in surface tension reduction. We may, therefore, deduce that the surface activity of long-chained imidazolium ILs is slightly higher than that of morpholinium-based ILs (having the same hydrophobic chain length), which is consistent with the aforementioned discussion.

The surface tension is a versatile technique since it not only calculates CMC values but also offers important data regarding the adsorption properties of solutes at the interface of air and water. The maximum surface excess concentration (Γ_{max}), and the minimum area (A_{min}) occupied per ionic liquid/surfactant molecule at the air/water interface were investigated by applying Eqs. (6) and (7) respectively to better illustrate the properties of both the ILs' interfacial adsorption behaviour. Their values have been listed in Table 3, which have been acquired by using the Gibbs adsorption isotherm to the tensiometric profiles:

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial (\log C)} \right) \quad (6)$$

$$A_{min} = \frac{10^{18}}{N_A \Gamma_{max}} \quad (7)$$

where $\partial \gamma / \partial (\log C)$ gives the slope of the surface tension isotherm near the CMC, R is the gas constant (8.314 J $\text{mol}^{-1} \text{K}^{-1}$), n defines the no. of ionic species remaining in the solution after dissociating in water and C is the ionic liquid concentration. It can be observed from Eq. (7) that the greater the adsorption, the smaller the effective area occupied by the IL/surfactant molecule at the interface, i.e., A_{min} is inversely proportional to Γ_{max} . Thus, it may be concluded that a denser arrangement of IL/surfactant molecules at the air/solution interface is indicated by a higher value of Γ_{max} , or a lower value of A_{min} . Based on the values of Γ_{max} , and A_{min} , we can notice the higher values of A_{min} for $[\text{C}_{12}\text{mim}]\text{Br}$ in comparison to $[\text{Mor}_{1,12}]\text{Br}$, which is indicative of lesser packing density of imidazolium-based IL than morpholinium-based IL at the air/water interface [27]. Moreover, amino acid competes with the ionic liquids for their place at the interface of air and water and thereby lowers adsorption of IL molecules, which is the reason for the decrease in Γ_{max} , and increase in A_{min} .

In order to determine the shape of formed micelles, the packing parameter (p) has also been calculated by applying Eq. (8):

$$p = V_0 / l_c A_{min} \quad (8)$$

where l_c stands for the length of the hydrophobic core while V_0 denotes the volume occupied by the hydrophobic group in the micelle's core [72]. Values of l_c , V_0 can be calculated using Tanford's formulae (eqs. (9) and (10) respectively) [73]:

$$V_0 = [27.4 + 26.9(n_c - 1)] (A^0)^2 \quad (9)$$

$$l_c = [1.54 + 1.26(n_c - 1)] (A^0) \quad (10)$$

Here, n_c stands for the no. of carbons in the surfactant's hydrocarbon chain. From the packing parameter values listed in Table 3, it can be witnessed that in all studied cases the value comes out to be less than

Table 2. The values of CMC (mM) and various thermodynamic parameters of IL, [C₁₂mim][Br] and [Mor_{1,12}][Br] in the water and presence of three concentrations (0.01, 0.05 and 0.10)mol kg⁻¹ of amino acid L-Methionine at different temperatures (293.15, 298.15, 303.15 and 308.15)K.

T(K)	CMC/mM	α	ΔG_m^0 (kJ·mol ⁻¹)	ΔH_m^0 (kJ·mol ⁻¹)	ΔS_m^0 (J·mol ⁻¹ K ⁻¹)
[C₁₂mim][Br]					
Water					
293.15 K	10.19	0.267	-36.34	-2.84	114.27
298.15 K	10.07, 10.18 ^a ,10.50 ^b	0.249	-37.39	-2.97	115.48
303.15 K	10.14	0.274	-37.46	-3.02	113.58
308.15 K	10.56	0.288	-33.49	-3.10	111.94
0.01 mol kg ⁻¹ L-Methionine					
293.15 K	12.75	0.362	-33.46	4.40	129.14
298.15 K	11.41	0.315	-35.47	4.68	134.64
303.15 K	11.46	0.322	-35.89	4.81	134.27
308.15 K	11.96	0.330	-36.13	4.95	133.29
0.05 mol kg ⁻¹ L-Methionine					
293.15 K	11.93	0.327	-34.44	2.31	125.34
298.15 K	11.38	0.313	-35.52	2.41	127.21
303.15 K	11.42	0.320	-35.94	2.48	126.73
308.15 K	11.54	0.327	-36.36	2.55	126.26
0.10 mol kg ⁻¹ L-Methionine					
293.15 K	11.71	0.321	-34.63	1.72	124.00
298.15 K	11.28	0.309	-35.62	1.76	125.48
303.15 K	11.37	0.319	-35.99	1.84	124.77
308.15 K	11.41	0.320	-35.55	1.90	124.77
[Mor_{1,12}][Br]					
Water					
293.15 K	16.39	0.527	-29.18	-1.65	93.92
298.15 K	16.08, 16.11 ^c	0.521	-29.88	-1.71	94.48
303.15 K	16.41	0.528	-30.15	-1.76	93.65
308.15 K	16.71	0.535	-30.44	-1.81	92.91
0.01 mol kg ⁻¹ L-Methionine					
293.15 K	15.62	0.511	-29.68	-0.49	99.57
298.15 K	15.41	0.501	-30.43	-0.51	100.34
303.15 K	15.57	0.520	-30.51	-0.521	98.92
308.15 K	15.69	0.525	-30.88	-0.54	98.47
0.05 mol kg ⁻¹ L-Methionine					
293.15 K	15.41	0.509	-29.75	-0.70	99.10
298.15 K	15.40	0.501	-30.45	-0.73	99.67
303.15 K	15.46	0.511	-30.72	-0.75	98.87
308.15 K	15.56	0.519	-31.05	-0.77	98.25
0.10 mol kg ⁻¹ L-Methionine					
293.15 K	15.33	0.501	-29.96	-0.91	99.08
298.15 K	15.30	0.498	-30.52	-0.94	99.21
303.15 K	15.34	0.507	-30.83	-0.97	98.50
308.15 K	15.52	0.510	-31.24	-1.00	98.13

Standard uncertainties (u) are, u (CMC) = ± 0.01 mM, u (α) = ± 0.01, u (T) = ± 0.1 K, u (ΔG_m^0) = ± 0.025 kJ·mol⁻¹, u (ΔH_m^0) = ± 0.003 kJ·mol⁻¹, u (ΔS_m^0) = ± 0.02 J·mol⁻¹·K⁻¹.

^a Ref. [88].

^b Ref. [59].

^c Ref. [24].

0.33. This indicates that the formed micelles are spherical in shape. Also, the values of A_{min} and packing parameter (p) are inversely proportional to each other as indicated by Eq. (8) i.e. the values of A_{min} increases while that of the packing parameter decreases for both the ILs with the addition of more concentration of amino acid L-Methionine. Therefore, it demonstrates the looser packing of IL monomers in the existence of amino acid. Further, the value of aggregation number (N_{agg}) may be estimated using basic geometrical considerations since the packing parameter (p) value indicates that the produced micelles have a spherical shape [61, 73, 74, 75]. The volume and the area of the

entire spherical micelle have been calculated by applying Eqs. (11) and (12) respectively,

$$N = N_{agg} V_0 = 4\pi R^3 / 3 \quad (11)$$

$$A = N_{agg} A_{min} = 4\pi R^2 \quad (12)$$

where R stands for the spherical micelle's radius and N_{agg} stands for the aggregation number. Given that the micellar core is occupied and that the hydrophobic chain is not going to extend further than the hydrophobic

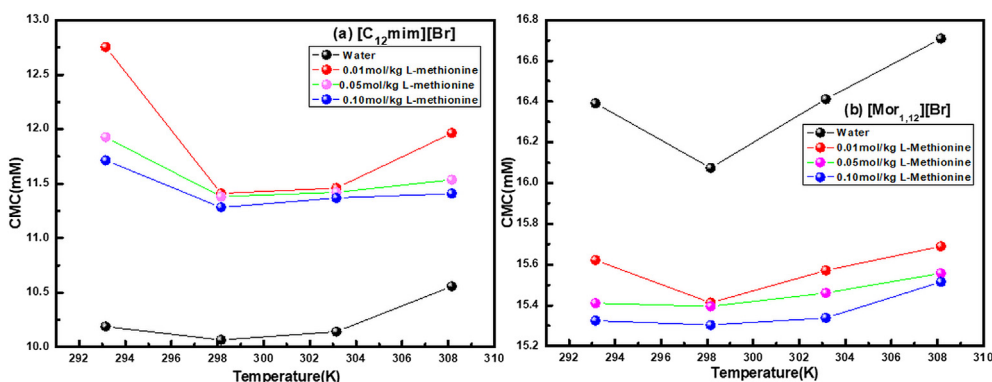


Figure 3. Variation of CMC (mM) of (a) [C₁₂mim][Br] and (b) [Mor_{1,12}][Br] in the aqueous and in presence of (0.01, 0.05 and 0.10) mol kg⁻¹ aqueous solutions of amino acid L-methionine wr.t. Temperature (K).

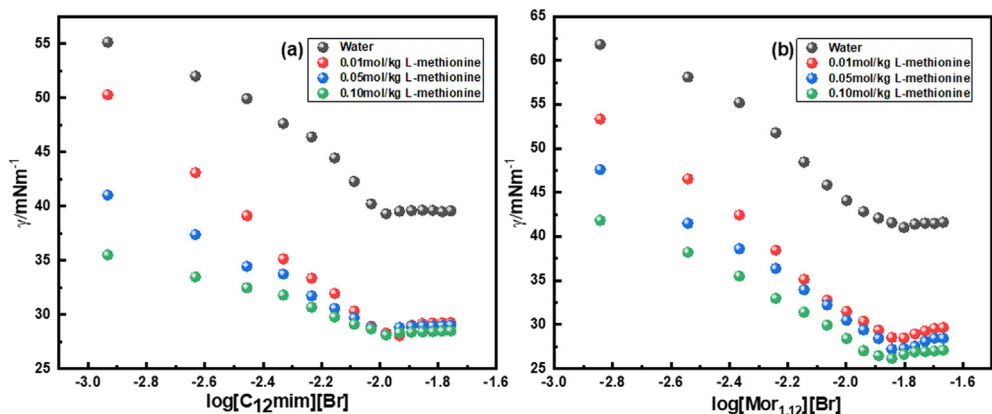


Figure 4. Graph of Surface tension (γ) vs log of the concentration of ILs (a) [C₁₂mim][Br], and (b) [Mor_{1,12}][Br] in water and in presence of L-Methionine at various concentrations (0.01, 0.05 and 0.10) mol kg⁻¹ and temperature 298.15K.

core's extended length l_c , the greatest aggregation number N_{max} for the given geometry is given by,

$$N_{max} = 4\pi l_c^3 / 3V_0 \tag{13}$$

Therefore, the value of the aggregation number (N_{agg}) can be determined by using Eqs. (11), (12), and (13) as follows:

$$N_{agg} = N_{max}(3V_0/A_{min}l_c)^3 \tag{14}$$

Table 3. Surface active parameters (critical micelle concentration, CMC, minimum area occupied by a single IL molecule at the air/solution interface, (A_{min}), maximum surface excess concentration (Γ_{max}), surface tensions at the CMC (γ_{cmc}), effectiveness of surface tension reduction (Π_{cmc}), and thermodynamic parameters of [C₁₂mim][Br], and [Mor_{1,12}][Br] in the aqueous and in presence of (0.01, 0.05 and 0.10) mol kg⁻¹ aqueous solutions of amino acid L-methionine at temperature 298.15 K.

Ionic Liquid (mM)	L-Methionine	CMC (mM)	γ_{cmc} (mN/m)	Π_{cmc} (mN/m)	$10^6 \Gamma_{max}$ (mol/m ²)	A_{min} (nm ²)	ΔG_m^0 (kJ mol ⁻¹)	ΔG_{ad}^0 (kJ mol ⁻¹)	G_{min}^s (kJ mol ⁻¹)	p	N_{agg}
[C ₁₂ mim][Br]	0	10.06, 10.60 ^d	39.29, 36.8 ^d	32.60	2.45, 3.03 ^d	0.67	-37.39	-50.68	13.28	0.310	38, 44 ^f
	0.01	11.41	29.04	42.51	1.68	0.99	-35.47	-60.77	25.29	0.212	12
	0.05	10.37	28.11	41.42	1.32	1.26	-35.52	-66.89	31.37	0.167	6
	0.10	10.28	28.09	39.97	0.93	1.78	-35.62	-70.98	35.36	0.118	2
[Mor _{1,12}][Br]	0	16.09, 16.11 ^c , 13.5 ^e	41.02, 42.98 ^e , 41.89 ^e	30.75	2.58, 2.51 ^c , 3.01 ^c	0.64	-29.88	-41.82	11.93	0.326	44
	0.01	15.42	28.47	42.01	2.10	0.79	-30.43	-50.39	19.97	0.266	24
	0.05	15.39	27.28	41.16	1.90	0.87	-30.45	-52.07	21.63	0.241	18
	0.10	15.30	26.61	39.15	1.59	1.05	-30.52	-55.18	24.66	0.201	10

Standard uncertainties u are u (T) = ±0.1 K, u (CMC) = ±0.01 mM, u (γ_{cmc}) = ±0.15 mN/m, u (Π_{cmc}) = ±0.10 mN/m, u (Γ_{max}) = ±0.01 μmol/m², u (A_{min}) = ±0.01 nm², u (ΔG_m^0) = ±0.25 kJ·mol⁻¹, u (ΔG_{ad}^0) = ±0.01 kJ·mol⁻¹, u (G_{min}^s) = ±0.02 kJ·mol⁻¹.

^c Ref. [24].

^d Ref. [89].

^e Ref. [27].

^f Ref [61].

The calculated values of N_{agg} by applying Eq. (14) have been reported in Table 3. With the addition of amino acid L-Methionine, it is found that the aggregation number of both ILs $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$ decreases.

Also, the standard Gibbs free energy of adsorption, ΔG_{ad}^0 , at the air/water interface is determined using the following Eq. (15),

$$\Delta G_{ad}^0 = \Delta G_m^0 - \frac{\Pi_{cmc}}{\Gamma_{max}} \quad (15)$$

The values of ΔG_{ad}^0 as can be seen from Table 3 are found to be negative for the complete system under investigation, which means that the spontaneous adsorption of both the ILs occurs at the interface of air and water in the absence and existence of amino acid. Additionally, more negative values of ΔG_{ad}^0 than their corresponding ΔG_m^0 (obtained from conductivity measurements) also suggests that when a micelle formation occurs, work has to be carried out to transfer the IL molecules (monomeric form) from the surface to the micellar region through an aqueous medium [76]. Hence, this predicts that adsorption is the primary route in contrast to micellization in the present work.

Further, the free energy of a surface at equilibrium (G_{min}^s), a thermodynamic parameter has also been calculated [77] and stated in Table 3.

$$G_{min}^s = A_{min} \gamma_{cmc} N_A \quad (16)$$

By applying Eq. (16), the value of free energy change which takes place during the transition from the solution's bulk phase to the solution's surface phase i.e., G_{min}^s has been calculated. A thermodynamically more stable surface or in other words, a surface with better surface activity is achieved, if the value of G_{min}^s is small. In this work, we can observe smaller values for G_{min}^s are obtained in all studied systems, which confirms that more thermodynamically stable surfaces are attained, and also favorable interactions are existing among the $[C_{12}mim][Br]$, and $[Mor_{1,12}][Br]$ with L-Methionine.

3.3. UV-vis spectroscopic measurements

The interaction of the two ionic liquids which differ in cation i.e., $[C_{12}mim][Br]$ and $[Mor_{1,12}][Br]$ with an important amino acid L-methionine has been explored by means of UV-Visible spectroscopy. Absorption measurements can be taken at a single wavelength or over a wide range of wavelengths in a direction to define the CMC of an IL. In the present study, the stock solutions of varying concentrations (0.01, 0.05, and 0.10) mol kg^{-1} of L-methionine were freshly prepared in aqueous media. The UV-vis measurements are carried out by stepwise adding a concentrated solution of $[C_{12}mim][Br]$ and $[Mor_{1,12}][Br]$ to the above-prepared stock solutions of amino acid utilizing an accurately calibrated pipette assured by proper mixing before every measurement. Table S4 and Table S5 show the absorbance values obtained for all of the systems examined. All measurements were taken at room temperature. A plot of absorbance at a fixed wavelength vs sample concentration (IL concentration) is obtained through these measurements which is then used to calculate the critical micelle concentration [64, 78]. As can be seen from all the UV plots which have been presented in Figures 5 and 6, the absorbance value begins to increase as the concentration of ionic liquid increases. However, the rising rate of absorbance value above CMC is slower compared to that below CMC which clearly marks a breakpoint between two straight lines [79, 80]. This breakpoint reflects the CMC of IL examined [81, 82]. The values of CMC derived from this technique were compared with those of conductance and surface tension measurements, and are noticeably quite similar to each other as presented in Table 4.

3.4. DLS measurements

DLS measurements were performed to acquire insight into the size distribution of IL micelles produced in various concentrations of amino acid. The intensity-weighted size distribution of micelles has been provided for $[C_{12}mim][Br]$ and $[Mor_{1,12}][Br]$ in the absence and existence of

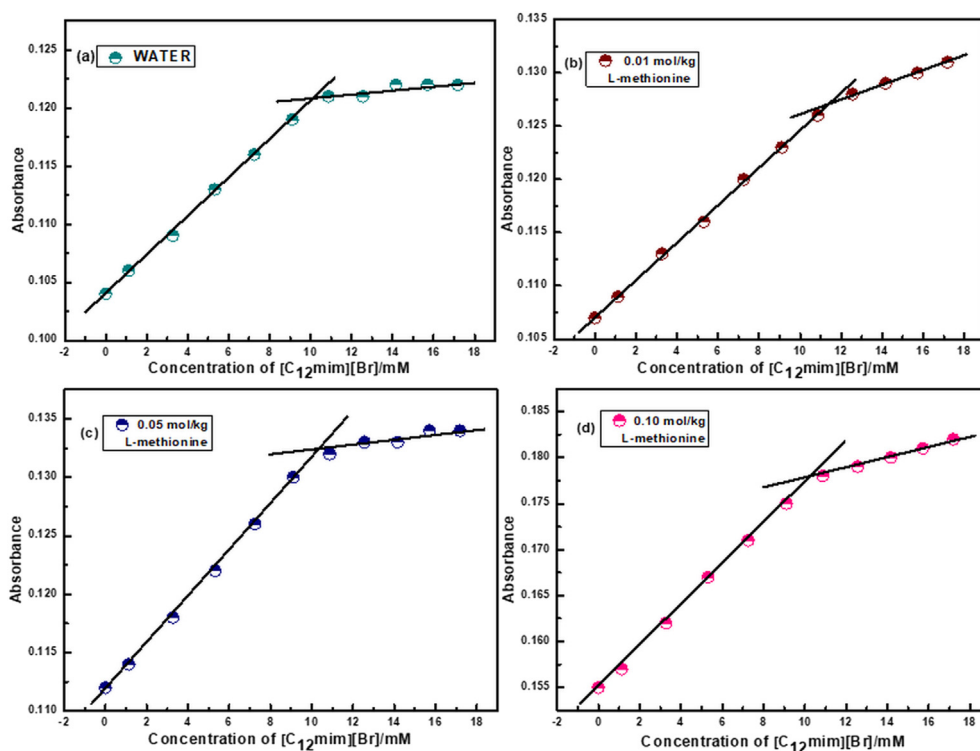


Figure 5. Graphs representing the absorbance variation of IL, $[C_{12}mim][Br]$ in the (a) water and in the presence of (b) 0.01 mol kg^{-1} , (c) 0.05 mol kg^{-1} and (d) 0.10 mol kg^{-1} of L-methionine in at 298.15 K.

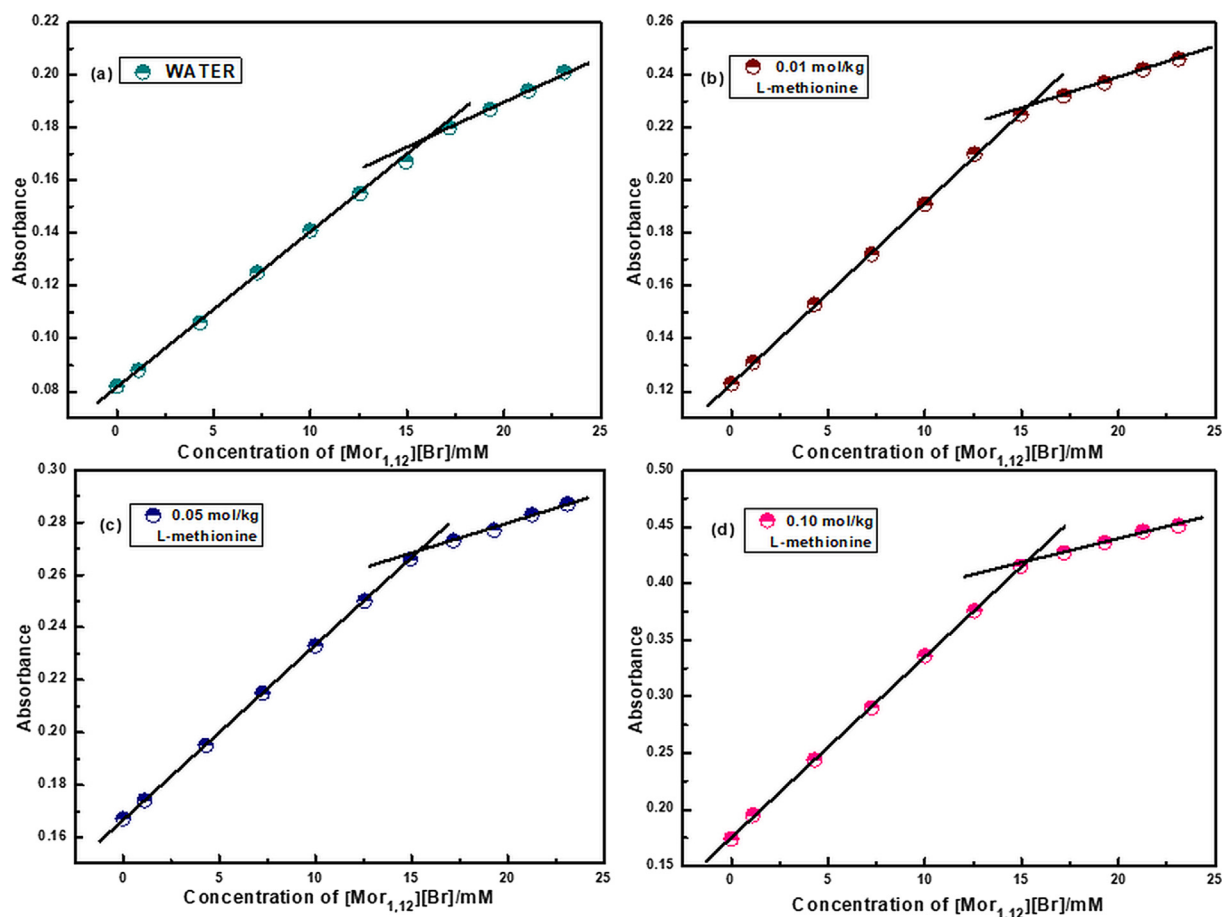


Figure 6. Graphs representing the absorbance variation of IL, $[\text{Mor}_{1,12}][\text{Br}]$ in the (a) water and in the presence of (b) 0.01 mol kg^{-1} , (c) 0.05 mol kg^{-1} and (d) 0.10 mol kg^{-1} of L-methionine in at 298.15 K.

various concentrations of amino acid as shown in the SI as Figures S1 and S2 respectively. The two ILs $[\text{C}_{12}\text{mim}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$ have been observed to form spherical micelles in the range of 1–2 nm. However, both the ILs in water/amino acid solutions also produce larger aggregates at higher concentrations [83, 84]. These two kinds of produced aggregates i.e. small and large can be described as primary and secondary micelles, respectively [85]. The size of micelles formed by $[\text{C}_{12}\text{mim}][\text{Br}]$ in water also agrees with the literature value [83]. The size (D_h) of the micelles reduces in the existence of amino acid in comparison to that in its absence. The size of micelles further reduces with an increase in the

concentration of amino acid as can be seen from the values of D_h reported in Table 5. However, $[\text{Mor}_{1,12}][\text{Br}]$ form larger micelles than the $[\text{C}_{12}\text{mim}][\text{Br}]$ in water/amino acid solution as observed from the reported D_h values. Based on the above findings, we can deduce that as amino acid concentration increases, an increase in the number of hydrophobic counterions results in stronger hydrophobic interactions. This may cause the greater size of the micelles to become unstable due to an increase in steric hindrance, causing the micelles to break up into smaller micelles. Besides, it can be observed that the hydrodynamic diameter (D_h) follows a similar trend to the aggregation number (N_{agg}) derived

Table 4. Comparison of CMC values of both ILs $[\text{C}_{12}\text{mim}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$ in water and in the presence of (0.01, 0.05 and 0.10) mol kg^{-1} of L-methionine at different temperatures, obtained from conductivity measurements, Surface tension, and UV-Visible spectroscopic measurements.

Ionic Liquid (mM)	L-Methionine (mol kg^{-1})	CMC (mM)					
		Conductivity measurements				Surface tension measurements	UV-Vis measurements
		293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	298.15 K
$[\text{C}_{12}\text{mim}][\text{Br}]$	0	10.19	10.07	10.14	10.56	10.06	10.09
	0.01	12.75	11.41	11.46	11.96	11.41	11.41
	0.05	11.93	11.38	11.42	11.54	10.37	10.37
	0.10	11.71	11.28	11.37	11.41	10.28	10.27
$[\text{Mor}_{1,12}][\text{Br}]$	0	16.39	16.08	16.41	16.71	16.09	16.06
	0.01	15.62	15.41	15.57	15.69	15.42	15.41
	0.05	15.41	15.40	15.46	15.56	15.39	15.39
	0.10	15.33	15.30	15.34	15.52	15.30	15.30

Standard uncertainties u are $u(\text{CMC}) = \pm 0.01 \text{ mM}$, and $u(T) = \pm 0.1 \text{ K}$.

Table 5. The micellar size (diameter) of aqueous [C₁₂mim][Br], and [Mor_{1,12}][Br] in the presence of (0, 0.01, 0.05 and 0.10) mol kg⁻¹ of L-methionine at ambient conditions.

Ionic Liquid	L-methionine (mol kg ⁻¹)	D _h (nm)
	0	1.44, 1.4 [83]
[C ₁₂ mim][Br]	0.01	1.34
	0.05	1.26
	0.10	1.14
[Mor _{1,12}][Br]	0	1.70
	0.01	1.59
	0.05	1.49
	0.10	1.38

Standard uncertainties u are $u(D_h) = \pm 0.02$ (nm).

from surface tension measurements (Table 3) where we have observed that with the addition of amino acid, the aggregation number of the IL decreases. From the conductance study (Table 2), the value of α for both the ILs decreases upon increasing the concentration of amino acid L-Methionine also indicates the formation of smaller-sized micelles [86]. Thus, these are all correlated in N_{agg} evaluated from surface tension, α from conductance study, and D_h observed from DLS study.

3.5. Comparison between micellization behaviour of [C₁₂mim][Br] and [Mor_{1,12}][Br]

In the present work, a comparative study of [C₁₂mim][Br] and [Mor_{1,12}][Br] ionic liquids is performed to study their micellization behavior. It is observed that with a similar hydrophobic chain length ($n = 12$), [Mor_{1,12}][Br] has the greatest CMC value, indicating the surface activity sequence as [C₁₂mim][Br] > [Mor_{1,12}][Br] which shows that morpholinium cations based ionic liquids have less surface activity as compared to imidazolium cation based ionic liquids. Micellization behavior or surface activity depends upon the interactions between ionic

liquid and additive, in the present case L-methionine, as the hydrophobic interactions will increase, the surface activity will also increase.

Various types of interactions such as hydrophobic, hydrophilic, and electrostatic interactions prevail in the system constituting L-methionine/[C₁₂mim][Br] and L-methionine/[Mor_{1,12}][Br] in the aqueous medium. In the case of [Mor_{1,12}][Br], the decrease in surface activity is because of an increase in hydrophilic interaction because of the presence of extra electronegative element oxygen 'O' in the heterocyclic ring which makes it more hydrophilic. So because of the increase in hydrophilic interactions micellization tendency decreases and CMC values increase [24]. Also, from the thermodynamic parameters of micellization (Table 2), this can be suggested that the micellization processes for both [C₁₂mim][Br] and [Mor_{1,12}][Br] are mainly entropy-driven, and enthalpy contributions are very small. So the hydrophobic interactions play a dominant role in both cases. The CMC value of our system with the similar alkyl chain length ($n = 12$, CMC = 16.075mM) was slightly higher than the reported CMC values of morpholinium-based amide-functionalized cationic surfactant [C_nAMorph][Br] investigated by Kang et al. in aqueous media (CMC = 3.1 mM for $n = 12$) [87]. Due to hydrogen bonding creation, the inclusion of an amide group was thought to generate a stronger connection between alkyl chains. Also, a Comparison of experimentally obtained and literature values of CMC for [C₁₂mim][Br], and surfactants having similar hydrophobic chain lengths in aqueous, and in presence of different amino acids using different techniques at 298.15 K has been presented in Table 6.

4. Conclusion

Since most of the ongoing research is focused on the long-chain imidazolium ILs, so in the present investigation, a comparison involving the Morpholinium-based IL, and imidazolium-based IL having the same hydrophobic alkyl chain length ($n = 12$), has been carried out in respect to their micellization behavior in the aqueous and in the presence of an amino acid L-Methionine by employing various techniques which included electrical conductivity, surface tension, UV-visible

Table 6. Comparison of experimentally obtained and literature values of CMC for [C₁₂mim][Br], and surfactants having similar hydrophobic chain length in aqueous, and in presence of different amino acids using different techniques at 298.15 K.

Ionic surfactant/IL	Additive	CMC ($\times 10^3$ mol L ⁻¹)
[C ₁₂ mim][Br]	Water	9.0 ^c [25], 9.19 ^c [90], 10.6 ^c [89], 11.21 ^c [91], 10.35 ^c [92], 9.6 ^d [93], 8.7 ^c [93], 10.06 (present work)
	0.01 mol kg ⁻¹ L-Methionine	11.41 (present work)
	0.05 mol kg ⁻¹ L-Methionine	11.38 (present work)
	0.10 mol kg ⁻¹ L-Methionine	11.28 (present work)
	0.7 mol kg ⁻¹ Glycine	7.4 ^d [93], 8.1 ^a [93], 8.0 ^c [93]
	0.7 mol kg ⁻¹ Alanine	8.1 ^d [93], 8.4 ^a [93], 7.5 ^c [93]
	0.7 mol kg ⁻¹ Proline	8.8 ^d [93], 9.8 ^a [93], 9.9 ^c [93]
SDS	Water	8.1 ^d [93], 8.1 ^a [54], 8.7 ^c [93]
	0.7 mol kg ⁻¹ Glycine	6.0 ^d [93], 6.0 ^a [93], 5.4 ^c [93]
	0.7 mol kg ⁻¹ Alanine	6.9 ^d [93], 6.1 ^a [93], 5.6 ^c [93]
	0.7 mol kg ⁻¹ Proline	10.8 ^d [93], 7.2 ^a [93], 6.4 ^c [93]
	0.10 mol kg ⁻¹ Glycine	7.6 ^a [54]
	0.10 mol kg ⁻¹ Alanine	6.5 ^a [54]
	0.10 mol kg ⁻¹ Glycyl Glycine	4.5 ^a [54]
SDBS	Water	1.29 ^c [94], 1.28 ^b [94]
	0.10 mol kg ⁻¹ Glutamine	1.33 ^c [94], 1.34 ^b [94]
	0.10 mol kg ⁻¹ Histidine	1.47 ^c [94], 1.47 ^b [94]
	0.10 mol kg ⁻¹ Methionine	1.24 ^c [94], 1.23 ^b [94]
DTAB	Water	15.3 ^c [94], 15.3 ^b [94]
	0.10 mol kg ⁻¹ Glutamine	15.1 ^c [94], 15.3 ^b [94]
	0.10 mol kg ⁻¹ Histidine	14.4 ^c [94], 14.5 ^b [94]
	0.10 mol kg ⁻¹ Methionine	14.8 ^c [94], 14.9 ^b [94]

a = conductivity, b = fluorescence, c = surface tension, d = apparent molar volume.

spectroscopic, and DLS measurements. On comparing, the surface activity of [C₁₂mim][Br] was found to be slightly higher than that of [Mor_{1,12}][Br]. This could be explained by the increased hydrophilicity of the head group of morpholinium IL as it consists of an oxygen atom, which thereby reduces its micellization ability and has a higher CMC value than [C₁₂mim][Br]. Furthermore, the CMC data availed by the three techniques are in complete agreement with each other as can be witnessed from Table 4. Furthermore, DLS measurements have been performed to deduce the micellar size, which indicated that the size of micelles decreases with amino acid addition in the case of both ILs. This supported the fact that hydrophobic interactions dominate at higher concentrations of amino acid. Also, the micellization behavior of both the ionic liquids was found to be improved with the addition of the amino acids, L-Methionine. Therefore, there are bigger chances of using such a combination in medical applications, especially in cancer treatment. Moreover, the non-toxicity of morpholinium ILs has led to their extensive use in fields of organic synthesis, thermodynamics, lubricants, and medicinal areas [5, 22, 63].

Declarations

Author contribution statement

Ramanjeet Kaur: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Harsh Kumar: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data. Barjesh Kumar: Performed the experiments; Analyzed and interpreted the data. Meenu Singla: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data. Vaneet Kumar, Ayman A. Ghfar, Sadanand Pandey: Analyzed and interpreted the data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interest statement

The authors declare no conflict of interest.

Additional information

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