A Review on Ionic Liquids and Their Interaction with Surfactants.

Nand Lal
Department of Chemistry, ABV GOVT. College Bangana, Distt Una, H.P.

***Abstract*—Improvement in the different processes such as, technologies related to water treatment, oil recovery, organic synthesis, extraction of biomass and carbon capture has been improved via the use of surface active molecules instead of using conventional surfactants. Self active ionic liquids are the ionic liquids having long alkyl chains. Use of ionic liquids and surface active ionic liquids improves the properties of conventional surfactants like, aggregation and surface activity. Surface active ionic liquids and ionic liquids provide an environment friendly alternative to the different organic catalysts and solvents with the properties like, self assembly, enhanced selectivity as well as higher activity. This review discuss about the ionic liquids, surface active ionic liquids, structure of ionic liquids and their characterization.**

***Index Terms*—ionic liquids, surface active ionic liquids, surfactants, selectivity, organic synthesis.**

I INTRODUCTION

Ionic liquids are the special category salts in molten state having inorganic/organic anions and organic cations with melting point lesser than 100°C. Ionic liquids can have head groups like, pyrrolidinium, imidazolium, pyridinium or morpholonium based cations and commonly used anions are bromide (Br)–, benzoate (Bz)–, octyl sulphate (C8SO4)–, chloride (Cl)–, fluorides (F)–, triflurومethanesulfonate (CF3SO3)–, hexaflurophosphate (PF6)– etc. Ions can be hydrophilic, hydrophobic or amphiphilic in nature. Major parts of the structure of ionic liquids are the head group and the side chains consisting of cation and anion. Representative organic cations which are nonsymmetrical are the aliphatic branches on the simple cations such as, sulfone, phosphonium, ammonium and guanidinium or on heterocyclic cations such as, piperdinium, pyridinium, pyrrolidinium and imidazolium coupled with various organic and inorganic anions which ranges from simple inorganic ions to the complex organic groups. Some examples of ionic liquid anions are like, phosphate, tetrafloroborate, sulphate, thiocynate, benzenesulfinic, sulfonate, borate, dicyanamide, bis(trifluoromethylsulfonyl) imide, halides and tricyanomethide. Figure 1a and 1 b shows a number of ionic liquid anions as well as cations.

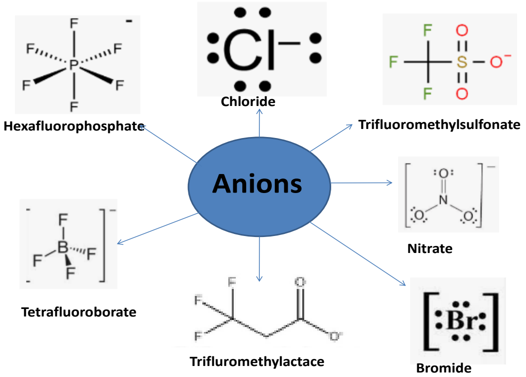

Figure 1 a. This figure is showing the number of anions, commonly used for the preparation of ionic liquids.

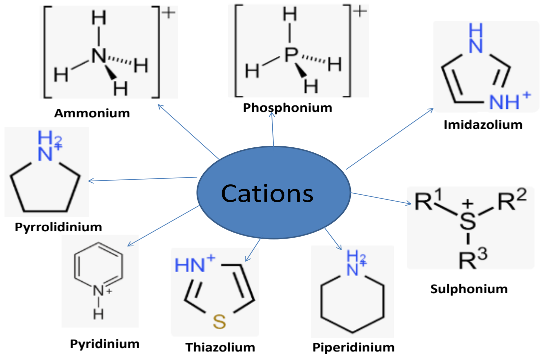

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Figure 1b. This figure is showing the number of cations commonly used for the preparation of ionic liquids.

Based on the unique biological properties of ionic liquids like, chemical, physical, biological and thermal properties like, ionic conductivity, basicity and acidity as well as miscibility of ionic liquids in organic and aqueous solvents and combinations of anion and cations, ionic liquids can be classified into several categories. These categories are task specific ionic liquids, supported ionic liquids, chiral ionic liquids, poly ionic liquids, bio ionic liquids, energetic ionic liquids and switchable polarity solvent ionic liquids (Singh and Savoy, 2018) table 1.

Table 1. Categories of ionic liquids based on cation and anion combinations as well as their biological, physical, chemical and thermal properties.

S.NO.	Category of ionic liquid	Example
1.	Task specific ionic liquids	3-sulphopropyl tri-phenyl phosphonium *p*-toluene sulphonate
2.	Chiral ionic liquids	The [N-(3'-oxobutyl)-N-methylimidazolium] [(+)-camphorsulfonate] C-IL
3.	Switchable polarity solvent ionic liquids	1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and alcohol
4.	Bio-ionic liquids	(2-hydroxyethyl)-ammonium lactates IL
5.	Poly-ionic liquids	pyrrolidinium-based polymeric ILs
6.	Energetic ionic liquids	N, N-dimethylhydrazinium hypergolic ILs
7.	Supported ionic liquids	N-(3-silicapropyl) imidazolium hydrogensulphate immobilized ILs
8.	Metallic ionic liquids	[(CH3)3C][Al2Br7] ILs

Ionic liquids are advantageous than other solvents in having higher thermal stability, negligible vapour pressure, easy dissolution, low volatility as well as non-flammability. Appropriate selection of anions and cations can alter the physicochemical properties.

Surface active ionic liquids (SAILs) are the ionic liquids with long chains of alkyl groups.

Surface active ionic liquids are a class of ionic liquids which are amphiphilic in nature. Surface active ionic liquids adsorption at the interface causes reduction in the interfacial reduction. Surface active ionic liquids are also found to make the miceller structures in bulk solutions.

Surface active ionic liquids properties can be controlled by the modification of anions and cations. Because of this property of modification, surface active ionic liquids are called as designer materials. It has been found that thermal stability and miscibility of surface-active ionic liquids depends on the anion whereas viscosity, density and interfacial reduction depends upon the molecular symmetry, shape and the alkyl chains.

Molecular aggregation of surface-active ionic liquids leads to the formation of micelles. Critical micelle concentration (CMC) is the concentration at which micelles are formed. There are few parameters on which the aggregation of surface-active ionic liquids depends such as, nature of solvent, additives, temperature and pH of the solution.

Surface active ionic liquids can undergo the formation of micelles. A charged head group and a longer hydrophobic tail is the part of cationic and anionic part of surface-active ionic liquids. These cationic and the anionic parts are responsible for the properties like surface activity and self-aggregation in surface active ionic liquids (Garcia et al., 2020; Alves et al., 2021). Surface active ionic liquids differ from traditional ionic surfactants in terms of surface activity, lower melting point and in their functionality. Surface active ionic liquids are highly beneficial than the conventional surfactants by having properties like, greater solubility in the aqueous medium, lower melting point, superior activity, tunable nature, lower critical miceller concentration and liquid nature etc. Surface active ionic liquids find applications as dispersants, emulsifiers and as foaming agents because of the similar amphiphilicity to the traditional surfactants. A large number of surfactant systems have been designed by the application of surface-active ionic liquids which are based on the self-assembled aggregates like, micelles, tubules, liquid crystalline phases, vesicles etc.

Out of these vesicles have been found to highly significant because they can mimic the biological membranes, transport nutrients, used in the colloid formulation, cell signaling, protection of DNA, material synthesis, act like a drug carrier as well as used in the targeted drug delivering system (Lépori et al., 2019; Kumar and Kaur, 2021; Garcia et al., 2020). Aggregates of surface-active ionic liquids served another purpose of miceller catalysis. Hydrophobic core of the surface-active ionic liquids act like an efficient micellar nano-reactor. A dramatic kinetic change of enhancing the yield of various chemical reactions has been observed in the rate of reaction while using surface active ionic liquids. Other applications of surface-active ionic liquids are like, antimicrobial, antifoaming and foaming agents, enhanced recovery of oil, drug solubilisation, demulsification of crude oil, electrophoretic as well as chromatographic separations, natural products extraction etc. (Shah et al., 2020; Kuddushi et al., 2019, 2020; Lee et al., 2020; Nandwani et al., 2020; El Seoud et al., 2021; Kumar and Kaur, 2021).

II SURFACTANTS

Surfactants consist of hydrophilic polar groups and hydrophobic alkyl chains. Polar groups of surfactants are found to enter the water while alkyl groups leave the water molecules, move in air and then arrange themselves on an interface in the aqueous medium.

Surface activity of the material increases with the increase in alkyl chains number in the surfactants. Amphiphilic nature of the surfactants is the excellent property of surfactants resulting in the formation of a variety of aggregates. Theses aggregates can be applied to the different fields such as, food preservation, soil rectification, organic compounds synthesis as well as exploitation of oil. Higher requirement of surfactants is due to enhancement in technology and nowadays monitoring has done on green and functional surfactants.

Micelles are formed when both SAILs and surfactants undergoes molecular aggregation. Micelles are formed at concentration called as critical micelle concentration (CMC). It is important to study interaction of SAILs/ Surfactants and understanding the mechanism of this interaction. Oppositively charged dye–SAILs/surfactants have been largely studied because it helps in understanding both electrostatic and hydrophobic interaction.

III CHARACTERIZATION OF IONIC LIQUIDS AND SURFACTANT INTERACTION

Spectroscopic studies

In physical and analytical chemistry, a variety of spectroscopic techniques are frequently employed to gather data on the detection, quantification, and identification of atoms and molecules. In order to determine a molecule's structure, proton nuclear magnetic resonance (^{1}H NMR) identifies the carbon-hydrogen framework of an organic complex. FTIR, mass spectroscopy and ^{1}H NMR provides comprehensive details about the chemical structure of the product and pinpoint the precise location of each molecule inside it.

UV-visible spectroscopy is a crucial method that might be used to establish the critical micelle concentration value of compounds that are surface-active. This technique is based on the observation that the behaviour of a solution during absorption changes when surface-active molecules aggregate.

A probe made of an organic dye with a distinctive UV-visible spectrum is used to determine the critical miceller concentration (CMC). The determination of the critical micelle concentration value may result from the change in that additive's absorption behaviour that was observed. However, adding these kinds of additions to a solution containing surface-active chemicals may change how they aggregate, leading to the estimate of apparent CMC value.

The stability of newly generated micelles may potentially be impacted by these chemical probes. The calculation of the critical micelle concentration using UV visible spectroscopic method does not require the inclusion of any organic probe in their solution because these SAILs can absorb in the entire UV-visible range (200-800 nm) (Rather et al., 2015; Adil et al., 2016; Kumar and Kaur 2021).

Farooq et al., (2017) studied the interaction of imidazolium based surface-active ionic liquid, namely 1-decyl-3-methylimidazolium chloride with cetrimide which is an cationic surfactant by spectroscopic method in pure water as well as in a binary mixture having diethylene glycol – water. Anionic dye, cresol red has been used as a probe for the UV – visible spectrum of mixed and pure systems and it has been observed that mixed micellization process is supported by the surface-active ionic liquids (Farooq et al., 2017).

Ionic liquids are one of the emerging catalyst and solvents in industries. Baghersaei et al., (2023) studied the interaction of three ionic liquids, having sterate, oleate and cinnamate as anions and tetrabutylammonium as cation and use them as asphaltene dispersants in the petroleum industry. Spectroscopy technique has been used for testing the efficiency of the synthesized ionic liquids on the stability of the aggregates of asphaltene. Tetrabutylammonium oleate and tetrabutylammonium cinnamate was found highly efficient as compared to the tetrabutylammonium stearate.

Anions like, oleate, cinnamate and stearate have one, four and no carbon–carbon π bonds, respectively. It is the presence of π bonds in these anions by which they are interacting with the π bonds of asphaltene molecules which is an important factor for stabilizing the asphaltene molecules by these ionic compounds in the petroleum industry. It has been further observed that higher net negative charge on the anions provides greater ability to the anions for the stabilization of asphaltene aggregates (Baghersaei et al., 2023). Jafari-Chashmi et al., (2018) observed stronger synergistic interactions between anionic surfactant, *N*-lauryl sarcosine sodium and surface active ionic liquid, 1-dodecyl-3-methylimidazolium bromide in the mixed micelle.

Anionic surfactant, dioctyl sodium sulfosuccinate on aggregation with the surface-active ionic compounds such as, 1-dodecyl-3-methylimidazolium bromide and 1-nonyl-3-methylimidazolium bromide has been studied in the aqueous medium via different techniques like, UV–Visible spectroscopy, conductivity measurement and FT-IR spectroscopy. Surface active ionic liquids, 1-dodecyl-3-methylimidazolium bromide and 1-nonyl-3-methylimidazolium bromide are found in very good agreement with the surfactant, dioctyl sodium sulfosuccinate (Kumar et al., 2021).

IV VOLUMETRIC ANALYSIS

Interaction among the solutions can be well understood via the volumetric analysis. Parameters like, limiting apparent molar volumes, hydration number, transfer volumes from the aqueous to mixed aqueous solutions of solvents with infinite solute dilutions, apparent molar volumes etc. can be determined for a range of temperature conditions.

V LIMITING APPARENT MOLAR VOLUME

Information about the interaction among the solute and the co-solute has been provided via the limiting thermodynamic properties. This is because the interactions among the solute molecules become negligible at the infinite dilutions. Therefore the limiting apparent molar volume which is represented by V^0_φ provides highly valuable data about the interaction of solute and co-solutes at infinite dilution. Following equation can be used for the determination of apparent molar volume by using accurate density data.

$V^0_\varphi = (M/\rho) - [(\rho - \rho o)/ m\rho\rho o]$

Where, M represents the molar mass of the solute (kg mol−1), ρ and ρo represents the densities of solution and solvent and m represents the molality of the solute (mol kg−1).

Cases in which, themolality dependence of $V\varphi$ was found to have no definite pattern or trend or found negligible then the partial molar volume or the limiting apparent molar volume can be determined by taking an average.

The following relation can be used for the calculation of the limiting value of the apparent molar volume via the least square fitting of the apparent molar volume:

$V\varphi = V^0\varphi + S_v m$

Where, $V^0\varphi$ represents the partial molar volume or the limiting apparent molar volume at infinite dilution and S_v represents the experimental slope considered as a pairwise interaction, volumetric virial coefficient. Nature of solute – solute interactions in indicated by the sign, S_v. Whereas $V^0\varphi$ shows the presence of solute solvent interactions.

VI LIMITING APPARENT MOLAR VOLUME OF TRANSFER

Information about the solute and co-solute has been provided by the limiting t hermodynamic transfer properties. The limiting apparent molar volume of transfer is represented by $\Delta tr\ V^o\varphi$ and provides valuable information about the interactions between solute and solvent and is found free from the solute – solute interactions.

Calculation of transfer volume ($\Delta tr\ V^o\varphi$) of amino acids from the water to the aqeous solutions at infinite dilutions can be done by the following equation:

$\Delta tr\ V^o\varphi = V^0\varphi$ (in aqeous drug) – $V^0\varphi$ (in water)

Where $V^0\ \varphi$ (in water), is representing the limiting values of the apparent molar volume of the amino acids in the aqeous solution.

VII TEMPERATURE DEPENDENT LIMITING APPARENT MOLAR VOLUME

The general polynomial equation given below expressed the variations of apparent molar volume at infinite dilution with a range of temperature conditions.

$V^0\ \varphi = a + b\ (T - T_{ref}) + c\ (T - T_{ref})^2$

Where T represents the temperature in Kelvin; a, b and c represent the empirical constants. The limiting apparent molar expansivity can be evaluated as follows:

$E^0\ \varphi = (a\ V^0\ \varphi / a\ T)\ P = b + 2c\ (T - T_{ref})$

A general thermodynamic expression has been developed to show whether a particular solute behave like a structure maker or structure breaker in the mixed solvent system.

$(a\ E^{0\ \varphi}/aT)P = (a^2 V^0\ \varphi / a\ T^2)\ P = 2c$

Kaur and chauhan (2020) measured the speed and density of sound of the anionic surfactant, sodium dodecylsulphate and cationic surfactant, dodecyltrimethyl ammonium bromide in the aqueous solution of tetraalkyl ammonium- based ionic liquid in different temperature conditions ranging from 293.15−318.15 kelvin.

Apparent molar volume has been evaluated using volumetric analysis along with other parameters which provides qualitative information about the surfactants self-assembly behaviour in the ternary system of surfactant – water and ionic liquid. This information is very important for the clarification of the nature of molecular interactions present between the solvent and surfactant.

VIII CONDUCTIVITY MEASUREMENT

Conductivity data is important data for measurement of interaction between solute and solvent. From the specific conductivity data critical micelle concentration (CMC), degree of ionisation can be used to obtain the thermodynamic parameters of micellization. such as the standard free energy of micellization ΔG^0_m, the standard entropy of micellization ΔS^0_m and the standard enthalpy of micellization ΔH^0_m.

Conductometrically, it is possible to estimate the degree of ionization via using the slopes obtained from two linear segments above and below crtitical micelle concentration of specific conductivity verses the concentration of surfactant. $\alpha = 1 - \beta$ is representing the degree of counter ion association. It has been reported that this is a simple and satisfactory method for the estimation of β.

It has been found that the degree of counter ion association α and counter ion dissociation β are experimental technique dependent like critical micelle concentration. Thermodynamic parameters of the micellization were calculated via using the values of critical micelle concentration. ΔG^o_m which is representing the standard free energy of micelle formation per mole of the monomer was determined via mass action model.

$\Delta G^o_m = (2 - \beta)RT\ln X_{CMC}$

Where T is representing temperature in Kelvin, X_{CMC} is the value of critical micelle concentration in terms of mole fractions and R is gas constant.

Then, the Gibbs–Helmholtz relation has been used for the calculation of enthalpy of micellization:

$\Delta H^0 m = - (2- \beta)\ RT^2\ (\partial \ln X_{cmc} / \partial T)$

The values of entropy of micellization, ΔS^o m, can be estimated from the calculated enthalpy and free energy values, as:

$\Delta S^o\ m = \Delta H\ ^o m - \Delta G\ ^o\ m / T$

The conductivity measurement technique is used for ion surfactant micellization and for non-ion surfactant cloud point measurement (Rahim et al., 2021).

Cationic surfactants namely, alkane-bis (tetradecyltrimethylammonium bromide), tetradecyltrimethylammonium bromide and dimethylditetradecylammonium bromide interaction with the surface-active ionic compound 1-tetradecyl-3-methylimidazolium bromide has been studied by Sharma et al., (2013).

Conductivity measurements have been used to study the interaction of the surfactants (alkane-bis (tetradecyltrimethylammonium bromide), tetradecyltrimethylammonium bromide and dimethylditetradecylammonium bromide) with the ionic liquid 1-tetradecyl-3-methylimidazolium bromide. Surfactant tetradecyltrimethylammonium bromide and ionic liquid 1-tetradecyl-3-methylimidazolium interaction was studied and it has been observed that both are antagonistic and non – ideal. It has been observed that on the replacement of single chain surfactant with the double chain surfactant, the interaction becomes synergistic. Interaction of binary mixture of dimethylditetradecylammonium bromide with ionic liquid has been found to promote the micellization more easily as compared to the binary mixture of ionic liquid with alkane-bis (tetradecyltrimethylammonium bromide) (Sharma et al., 2013).

Kaur et al., (2023) studied the interaction of cationic surfactant, tetradecyltrimethylammonium bromide, morpholinium-based ionic liquid, *N*-pentadecyl-*N*-methylmorpholinium bromide and imidazolium-based surface-active ionic liquid, 1-tetradecyl-3-methylimidazolium bromide in the aqueous medium. The critical micelle concentration values have been determined which has been further used for the determination of surface-active parameters as well as the thermodynamic properties of micellization. These interactions between the ionic liquid and surfactant are highly useful in various industrial applications such as, emulsions, surface coatings, suspensions, froths and foams for enhancing the performance as well as the quality (Kaur et al., 2023).

IX CONCLUSION

This review introduced the surface-active ionic liquids and their interaction with different surfactants. This is highly needed as the demand of time, our safety as well as the environmental safety. Surface active ionic liquids form micelles by self-aggregation in the aqueous solution as well as form mixed micelles by aggregation of other surface-active molecules (surfactants). Interaction of surfactants with ionic liquids form mixed micelles, which are highly applicable in various chemical reactions with greater stability as compared to the ordinary micelles. One of the very interesting features of these mixed systems is that they can be modified according to our requirement just by altering the composition of surface active monomers. Surface active ionic liquid´s ultimate value lies in the potential functionalization as well as the variability that can be harnessed directly from the pool of ionic liquids. With the interaction of different surfactants with the ionic liquids, a distinct chemistry has been represented via each new interaction.

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