Interfacial Activity and Micellar Morphology of a Imidizaolium Ring Containing Zwitterionic Surfactants

Hazrat Ali[a], Azim Khan[b], Tauqeer Ahmad[a], Athanasia Dervisi[c], Ian Fallis[c], Ibrahim O. Shoetan[c], Abbas Khan[d]*, Arshad Hussain[e] and Peter Griffiths[f]*

[a] Department of Chemistry, University of Mianwali, Mianwali-42200, Pakistan

[b] Institute of Chemical Sciences, Gomal University, Dera Ismail Khan, Pakistan

[c] School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, Wales, UK

[d] Department of Chemistry, Abdul Wali Khan University Mardan, 23200 Pakistan

[e] Department of Chemistry, University of Science and Technology Bannu, Pakistan

[f] Faculty of Engineering and Science, University of Greenwich, Medway Campus, Central Avenue, Chatham Maritime, Kent ME4 4TB, UK

Corresponding Authors:

1. Dr. Abbas Khan

Department of Chemistry,

Abdul Wali Khan University Mardan, 23200, Pakistan.

Telephone: +92-3408467885, Fax: +92-937-542188

E-mail: abbas053@gmail.com

2. Dr. Peter Griffiths

Department of Chemistry,

Faculty of Engineering and Science, University of Greenwich, Medway Campus, Central Avenue, Chatham Maritime, Kent ME4 4TB, UK

E-mail: P.Griffiths@greenwich.ac.uk

Abstract

Zwitterionic surfactants based on (3-(1-alkyl-3-imidazolio) propane-sulfonate [(ImS3-R) where R is octyl or dodecyl] are an emerging and important class of amphiphiles due to their useful applications in fields such as Nano reactors for the synthesis of metallic nanoparticles and acceleration acid hydrolysis. The physicochemical properties of such newly synthesized imidazolium ring containing zwitterionic surfactants have been characterized by surface tension and small-angle neutron scattering (SANS) techniques. Surface tension measurements were used to calculate several surface active, micellar and thermodynamic parameters over a range of concentrations and temperatures (298-313K). The results obtained showed a weak signature representing the critical micelle concentration (CMC) for ImS3-8, however, by increasing the alkyl length of the hydrophobic group to dodecyl *i.e.*, ImS3-8 to ImS3-12, the signature of the CMC was much more evident. As expected, the critical micelle concentration (CMC) for ImS3-12 shifted to a lower concentration. An increase in temperature increased the surface activity and decreased the CMC of both zwitterionic surfactants, although the change was small. As compared to classical surfactants *i.e.*, sodium dodecyl sulphate (SDS) and dodecyl trimethylammonium bromide (DTAB), the CMC of ImS3-12 is much lower. Small-angle neutron scattering modelling demonstrated that the morphology of the micelles formed by these amphiphiles may be described by the "classical" model, a central hydrophobic core, with a shell of hydrated headgroups. Due to the widespread applications in colloidal and interfacial science, it is essential to characterise the interfacial properties and micellar morphology of imidazolium based surface active ionic liquids (SAILs) (ImS3-R). The present study adds new insight to the fundamental understanding of these interesting molecules.

Keywords: Zwitterionic Surfactant, Imidazolium**,** Physicochemical, Surface-activity, Small-angle neutron scattering

Introduction

Surfactants are a well-known class of materials due to their beneficial amphipathic molecular structure, consisting of both a structural group known as the lyophobic group and a lyophilic group, which impart some interesting and useful interfacial and bulk properties (Moulik, SP, 1996). Properties of surfactants are structure dependent, and hence changing the molecular structure of the surfactants changes their properties and many hundreds of surfactants have been designed and evaluated (Kjellin et al., 2003; Stjerndahl et al., 2007; Zhu et al., 1990). Surfactants are often classified as neutral, ionic or zwitterionic based on the presence and character of any charged group. Zwitterionic surfactants have no net charge, but their micelles still have binding affinity for anions, and if suitable conditions are provided, they can also interact with cations (Tondo et al., 2010; Priebe et al., 2008; Iso and Okada, 2000; Marte et al., 2007; Tondo et al., 2007). Early investigations made on the molecular structure of ionic liquid disclosed inherent amphiphilicity *viz.* 1-methyl-3-alkylimidazlium salts with smaller counterions showed surfactant behavior comparable to cationic surfactant of short-chain. The amphiphilic nature of ionic liquids (ILs) was also confirmed from the study of N-methyl-N-alkyl pyrrolidines (Bowers et al., 2004; Baker et al., 2004). Recently, surface active ionic liquids (SAILs) have emerged as a new class of surfactants (Bowers et al., 2004; Inoue et al., 2007; Singh and A Kumar 2007; Shi et al., 2011; Wang et al., 2007; Kamboj et al., 2014a; Anouti et al., 2009; Kamboj et al., 2014b; Trivedi et al., 2011; Srinivasa et al., 2011; Brown et al., 2011; Seth et al., 2008; Chabba et al., 2016). It is obvious that low concentration aqueous solutions of SAILs lose many of the properties of ionic liquids (ILs). However, surface activity and structure of the self-assembly of SAILs can be controlled by appropriate choice of cation or anion which make them effective candidates to investigate and compared it to conventional ionic surfactants. Further the adjustable nature of SAILs in modulating hydrophilicity, hydrophobicity, size as well as polarizability of head-group proved them advanced of conventional ionic surfactants (Kamboj et al., 2014a).

Different classes of SAILs have been developed and their self-assembling behavior has been investigated. Effect of molecular structure *viz.* changing the head-group (Blesic et al., 2008; Wang et al., 2008; Tariq et al., 2011; Cornellas et al., 2011), changing the hydrophobicity (Liu et al., 2011; Shi L et al., 2011; Dong et al., 2010) and the effect of counter-ion (Wang et al., 2008), have been investigated and is found that the self-assembling properties of SAILs in aqueous media shows dependence on all these structural parameters (Singh and Kumar, 2007). Among the different classes of SAILs, cationic SAILs have shown better surface-activity

compared to the conventional surfactants having similar alkyl chain length. Substituents have specific effect on the aggregation properties and surface activity i.e., aggregation properties of imidazolium based cationic SAILs have been enhanced by hydroxyl substituent while better surface activity has been shown by larger hydrophobic substituent (Liu et al., 2011; Shi et al., 2011).

Amongst the different classes, zwitterionic surfactants are less investigated, although they are skin friendly, generally mild and ideal for in personal care products (Souza et al., 2015). Ionic liquid based, zwitterionic surfactant (3-(1-alkyl-imidazolio) propanesulfonate (ImS3-R) is synthesized which is different from sulfobetaines as the former contain imidazolium group instead of ammonium ion of the later (Tondo et al., 2010). Imidazolium based zwitterionic surfactants (ImS3-R) represent a versatile class of compounds, which form normal and reverse micelles without use of a co-surfactant, allows preparation of nanoparticles of palladium and gold in chloroform with small quantity of water, greener alternative to conventional surfactants in many applications etc., (Souza et al., 2015). It is therefore important to investigate the surface active, micellar and physicochemical properties of the emerging class of zwitterionic surfactants (3-(1-alkyl-imidazolio) propanesulfonate (ImS3-R).

Experimental

Synthesis and Spectral Summary of Surfactants

A simple and one-pot approach was employed for the syhthesis of the newly developed zwitterionic surfactants (3-(1-alkyl-3-imidazolio) propane-sulfonate [(ImS3-R) where R is octyl or dodecyl]. In a typical experiment to a solution of propanesulfonate (3.0 mmol) in acetone (4 mL), the corresponding alkyl imidazole (2.0 mmol) was added and the reaction solution was stirred overnight. As the product formed, it separated from the acetone solution either as a solid (C_{12} chains) or viscous liquid (C_8 chains). The product was isolated by separation from the supernatant acetone and was purified by further washings with acetone (2 x10 mL). The typical structure of the zwitterionic alkyl-imidazolyl propane sulfonate is shown in Fig. 1.
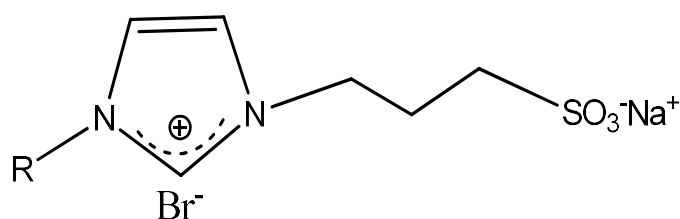
where, R = C_8H_{17} or R = $C_{12}H_{25}$

**Fig. 1:** Structure of zwitterionic alkyl-imidazolyl propane sulfonate where alkyl is octyl or dodecyl.

ImS3-8
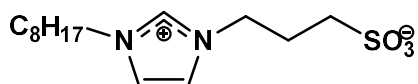
Yield: 91%; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.87 (t, J = 8, 3H), 1.24 – 1.38 (br, 10H), 1.86 (m, J = 8, 2H), 2.38 (m, J = 4, 8, 2H), 2.84 (t, J = 4, 8, 2H), 4.27 (t, ^{3}J = 4, 8, 2H), 4.55 (t, ^{3}J = 8, 2H), 7.32 (s, 1H), 7.69 (s, 1H), 9.52 (s, 1H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 14.09 (CH$_3$), 22.60 (CH$_2$), 26.30 (CH$_2$), 26.57 (CH$_2$), 28.99 (CH$_2$), 29.05 (CH$_2$), 30.22 (CH$_2$), 31.71 (CH$_2$), 47.49 (CH$_2$), 48.46 (CH$_2$), 50.02 (CH$_2$), 121.71 (CH), 122.99 (CH), 137.09 (NCHN). HRMS (ESI+) m/z: Found 303.1736 [(M+H$^+$)$^+$, (C$_{14}$H$_{27}$N$_2$O$_3$S$^+$), 100%], expected 303.1737.

ImS3-12
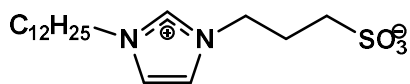
Yield: 89%; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.89 (t, J = 8, 3H), 1.24 – 1.38 (br, 18H), 1.89 (m, J = 8, 2H), 2.42 (m, J = 4, 8, 2H), 2.87 (t, J = 4, 8, 2H), 4.27 (t, J = 4, 8, 2H), 4.60 (t, J = 8, 2H), 7.22 (s, 1H), 7.57 (s, 1H), 9.72 (s, 1H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 14.15 (CH$_3$), 22.70 (CH$_2$), 26.31 (CH$_2$), 26.64 (CH$_2$), 29.03 (CH$_2$), 29.35 (CH$_2$), 29.39 (CH$_2$), 29.53 (CH$_2$), 29.61 (2C, CH$_2$), 30.26 (CH$_2$), 31.92 (CH$_2$), 47.35 (CH$_2$), 48.62 (CH$_2$), 50.14 (CH$_2$), 121.35 (CH), 122.64 (CH), 137.72 (NCHN). HRMS (ESI+) m/z: Found 359.2376 [(M+H)$^+$, (C$_{18}$H$_{35}$N$_2$O$_3$S$^+$), 100%], expected 359.2363.

Sample Preparation for Surface Activity and Micellar Studies

Aqueous stock solutions of all surfactants, 3-(1-alkyl-3-imidazolio) propanesulfonate [ImS3-R where, R is octyl or dodecyl (ImS3-8, ImS3-12)], were prepared by dissolving the required amount of the sample in the desired volume of de-ionized water. For the effect of salt, a 25mM of NaCl salt solution was also used. The concentration of stock solutions of both the surfactants was kept higher than the corresponding/expected values of their CMCs. All other solutions of lower concentrations were prepared by serial dilution of the stock solutions.

Surface Tension

Determination of the surface tension of aqueous solutions of ImS3-R was carried out using a maximum bubble pressure tensiometer (SITA online t60) with bubble lifetime 10s. Results presented here are an average of twenty discrete measurements per sample. The tensiometer was calibrated using the in-built software on ultrapure water and checked for linearity with water and ethanol mixtures. Temperature stability of $\pm$ 0.5 $^{\circ}$C was maintained through the use of a re-circulating water bath using the jacketed sample cell. All solutions were equilibrated for at least 30mins before measurement.

Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) experiments were performed on the fixed-geometry, time-of flight LOQ diffractometer at the ISIS Spallation Neutron Source, Rutherford Appleton Laboratory, Didcot, UK. This instrument spans a Q range ($Q = (4\pi/\lambda)\sin(\theta/2)$) 0.008 < Q < 0.25 Å^{-1} by using neutron wavelengths (λ) spanning 2.2 to 10 Å with a fixed sample-detector of 4.1m.Samples were contained in 2mm path length, UV-spectrophotometer grade, quartz cuvettes (Hellma, GmBh), mounted in aluminium holders on top of an enclosed, computer-controlled sample chamber. Sample volumes were kept around 0.6 cm^3. Temperature control was achieved by using a thermo-stated re-circulating bath pumping fluid through the base of the sample chamber, achieving a temperature stability of $\pm$ 0.2°C. Experimental measuring times were approximately 40 minutes per sample. All the scattering data were (a) normalized for the sample transmission, (b) background corrected using a quartz cell filled with D$_2$O, and (c) corrected for the linearity and efficiency of the detector response by using the instrument specific software package.

Results and Discussion

The newly synthesized zwitterionic surfactants *e.g.,* 3-(1-alkyl-imidazolio) propanesulfonate (ImS3-R) are proposed to have different physicochemical properties and micellization behavior compared to the classical surfactants and simple sulfobetaines due to the presence of the rigid unsymmetrical imidzolium ring attached with propylsulfonate in its structure. The difference of ImS3-R with sulfobetaines is that the former contains the imidazolium ion rather than an ammonium ion in its structure while alkyl sulfonate group make it different from simple alkyl imidazolium SAIL. To evaluate the physicochemical properties and micellar behavior of these

newly synthesized surfactants, surface tensiometry was extensively sued. The measured values of several interfacial parameters, the critical micelle concentration (CMC) and a number of thermodynamic derivatives are compared with others common surfactants.

Surface tension derived interfacial properties

Interfacial parameters *viz.* pC_{20}, Π_{CMC}, Γ_{max}, A_{min}, ΔG_{ads} are calculated from equations 1, 2, 3, 4 and 5 respectively (Souza et al., 2015; Dong et al., 2008), while CMC/C_{20} is calculated from the values of CMC and C_{20} obtained from Fig. 2, are listed in Table 1.

$$pC_{20} = - log\ C_{20} \tag{1}$$

$$\Pi_{CMC} = \gamma_o - \gamma_{CMC} \tag{2}$$

$$\Gamma_{max} = -1/RT\ [\partial\gamma/\ \partial\ lnC]_T \tag{3}$$

$$A_{min} = 1 \times 10^{18}/N_A\Gamma_{max} \tag{4}$$

$$\Delta G_{ads} = (\Delta G_{mic} - \Pi_{CMC})/\Gamma_{max} \tag{5}$$

where C_{20} is the concentration of the surfactant required to reduce the surface tension of the solvent by $20 mNm^{-1}$, surface pressure (Π_{CMC}), γ_o is the surface tension of the pure solvent and γ_{CMC} is the surface tension of the solution at the corresponding value of CMC, Γ_{max} is the maximum surface access concentration, T is the absolute temperature, R is gas constant, $\partial\gamma/\partial lnC$ is the slope of the linear line of surface tension curve just before CMC, A_{min} is the minimum area per molecule, ΔG_{ads} is the change in free energy of the interfacial adsorption and ΔG_{mic} is the change in free energy of micellization at CMC in the above equations.

The calculated data clearly indicates higher surface activity of ImS3-12 compared to ImS3-8, and the reason for this is the greater hydrophobicity of the former amphiphile. The values of interfacial parameters *viz.* Γ_{max} and A_{min} of ImS3-12 are lower while Π_{CMC} and Υ_{CMC} are approximately matching compare to conventional surfactants of the same alkyl chain length *i.e.*, sodium dodecyl sulphate (SDS) and dodecyl trimethylammonium bromide (DTAB) (Ananda et al., 1991; Penfold et al., 2009). Similarly, the surface activity of ImS3-12 is also greater than the newly synthesized N,N,N-tributyldodecane ammonium bromide (R12N4) and 1-dodecyl-1-methyl-imidazolium bromide (R12Im) (El-Dossoki et al., 2020).
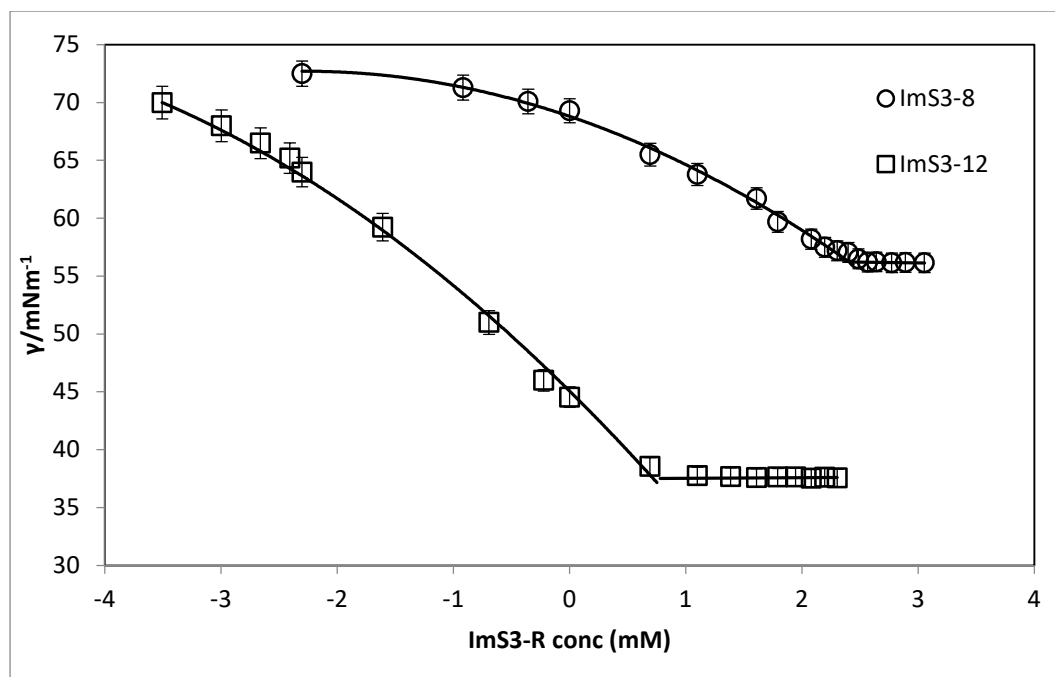
Fig. 2: Surface tension vs ln(concentration) of ImS3-8 and ImS3-12 at 298K.

Table 1 Effect of temperature over the interfacial, bulk and thermodynamic properties of the alkyl-imidazolium propylsulfonate surfactants

Surfactant	Temp[1]	CMC[2]	Υ_{CM}[3]	Π_{CM}[3]	pC_{20}[2]	$CMC/_{20}$[4]	Γ_{max}[5]	A_{min}[6]	ΔG_{mic}[7]	ΔH_{mic}[7]	$T\Delta S_{mic}$[7]	ΔG_{ads}[7]
ImS3-8	298	11.0	56.5	16.1	-----	-----	0.68	1.46	-41.5	-9.75	31.8	-55.6
	303	10.7	55.6	15.8	-----	-----	0.67	1.48	-42.4	------	32.6	-56.5
	308	10.5	55.0	15.7	-----	-----	0.65	1.51	-43.2	------	33.4	-57.4
	313	10.0	54.5	15.5	-----	-----	0.64	1.54	-44.2	------	34.4	-58.6
ImS3-12	298	2.22	38.1	34.4	3.35	4.94	0.98	1.01	-49.3	-5.90	43.4	-70.4
	303	2.12	37.2	34.3	3.37	4.92	1.00	0.99	-50.4	------	44.5	-71.0
	308	2.09	36.2	34.5	3.40	5.23	1.01	0.98	-51.3	------	45.4	-71.7

8

| 313 | 2.09 | 35.6 | 34.4 | 3.43 | 5.66 | 1.01 | 0.98 | -52.2 | ------ | 46.3 | -72.5 |

Units.[1]K, [2]mM, [3]mNm[-1], [4]no unit, [5]molecules/nm[2], [6]nm[2], [7]kJmol[-1]

Effect of temperature on the interfacial properties

The bulk of the available literature on the effect of temperature on interfacial properties of surfactants shows that an increase in temperature results in two competing phenomenon *i.e.*, reducing water of hydration of the head-group which result in decrease surface activity or breaks the structured water molecules surrounding the hydrophobic part of the surfactant thereby decreasing bulk concentration and increasing the interfacial adsorption respectively (Ananda et al., 1991; Penfold et al., 2009).

The effect of temperature on the interfacial parameters of ImS3-8 and ImS3-12, deduce from Figs. 3 and 4 and data are listed in Table 1. This data shows that an increase in temperature leads to a small increase in pC_{20}, A_{min} and a minor decrease in Γ_{max} and γ_{CMC} for both surfactants.
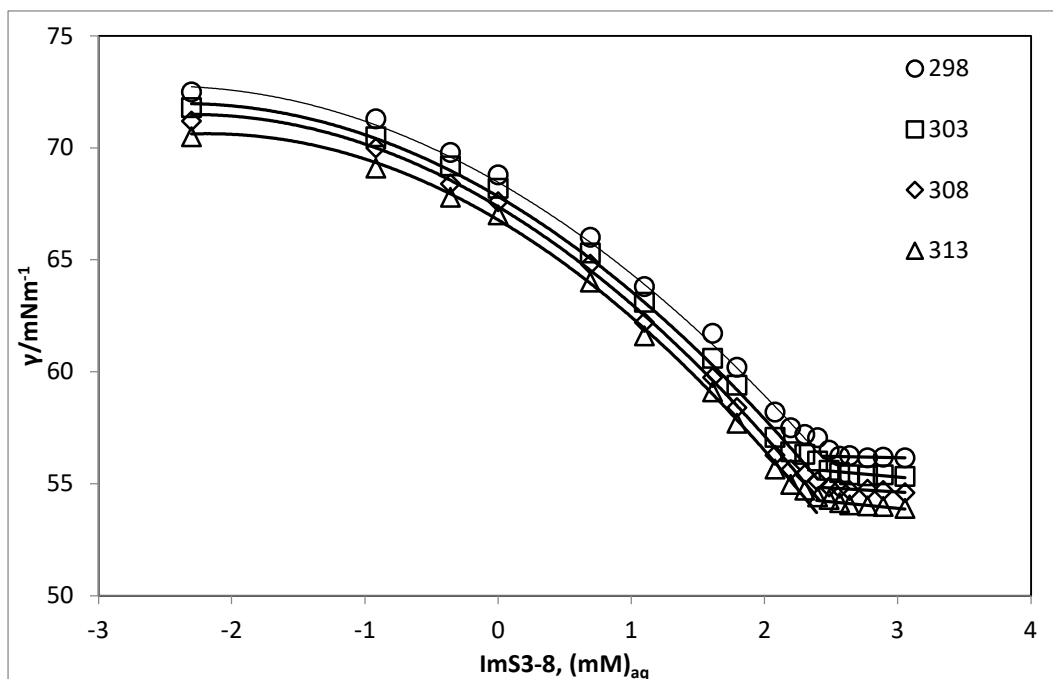

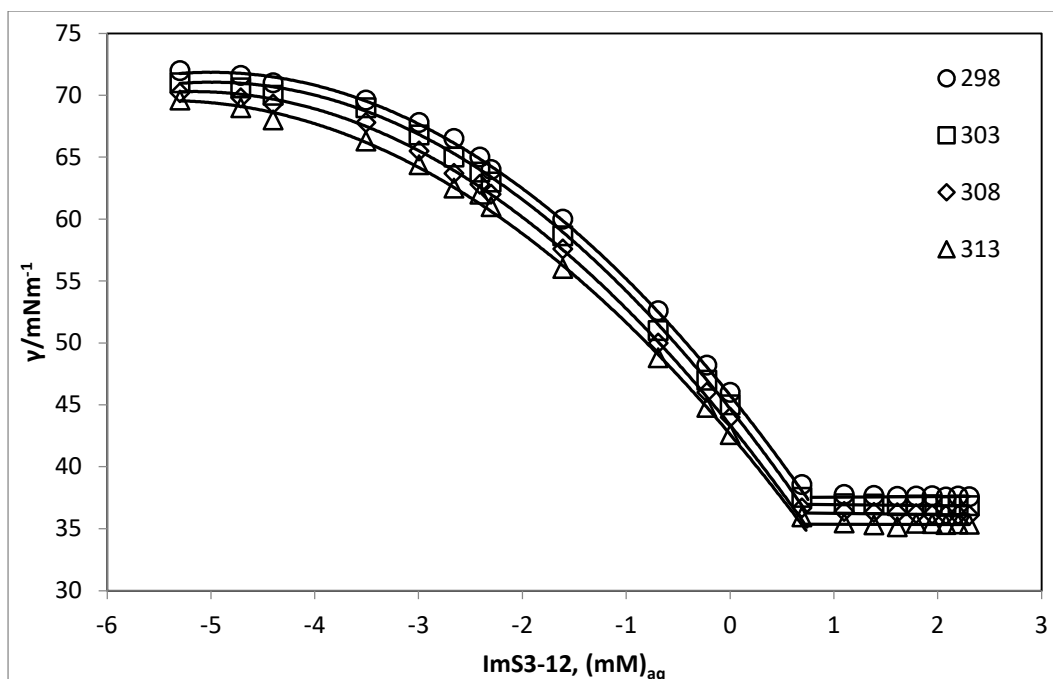**Fig. 3:** Surface tension vs ln (concentration) of ImS3-8$_{aq}$ at different temperatures.

Fig. 4: Surface tension vs ln(concentration) of ImS3-12$_{aq}$ at different temperatures.

Thermodynamic of Interfacial Adsorption and Effect of Temperature

Changes in the Gibbs free energy of adsorption (ΔG_{ads}) were used to evaluate the tendency of adsorption of surfactants at different interfaces, as it is the fundamental characteristic of surfactants. The value of ΔG_{ads} is determined by Eq. 5, listed in Table 1. The lower negative value of ΔG_{ads} of ImS3-8 shows reduced surface activity compared to ImS3-12. The values of ΔG_{ads} of ImS3-12 are more than two-fold smaller of the conventional surfactants such as SDS and DTAB (Ananda et al., 1991). The negative values of ΔG_{ads} of both selected SAILs increase as the temperature increases from 298 to 313K; this is showing enhancing spontaneity of the process.

Critical Micelle Concentration (CMC)

The concentration after which no obvious change in the surface tension occurs is assigned to be the critical micellization concentration (CMC) of the surfactants (Penfold et al., 2009). The CMC was determined from the interception of the decaying surface tension behavior at low concentrations and the limiting behavior at higher concentrations e.g. Fig. 2, with the CMCs therein obtained listed in Table 1. The values of CMC of ImS3-8 and ImS3-12 at room temperature are 11.2 and 2.2mM respectively, confirming the established fact of greater hydrophobicity, lesser CMC and vice versa. CMC of ImS3-12 is lower compared to conventional surfactants of the same alkyl chain length *i.e.,* (SDS) and (DTAB) (Ananda, K et

10

al., 1991), which can be explained by the greater hydrophobicity of the former in hydrophilic part due imidazolium propylsulfonate structure.

Temperature dependence of the Critical Micelle Concentration

The available literature on the effect of temperature on the CMC of aqueous solutions of surfactant does not always follow a linear dependence; often an increase in temperature decreases CMC of the surfactant to a minimum value and then subsequently increases. However, this broad trend is often surfactant specific. Interestingly, the effect of temperature in the range 6-60 ºC over CMC of aqueous solution of zwitterionic alkyl betaine has found a steady decrease in CMC (Marte et al., 2007).

The effect of temperature on the CMC over the range of 298 to 313K for ImS3-8 and ImS3-12, is shown in Figs. 3, 4 and 5. Table 1 shows the variation of CMC with an increase in temperature. Clearly, both surfactants show a decrease in the CMC with an increase in temperature. The effect of an increase in temperature from 298 to 313K over CMC of ImS3-12 compared to SDS follows the same decreasing trend in CMC while DTAB follow an opposite behavior compared to the former. These results suggest that increase in temperature decreases the hydrated radius of the hydrophilic groups of ImS3-R and SDS, while water of hydration of the hydrophobic part is reduced in case of DTAB (Ananda, K et al., 1991).
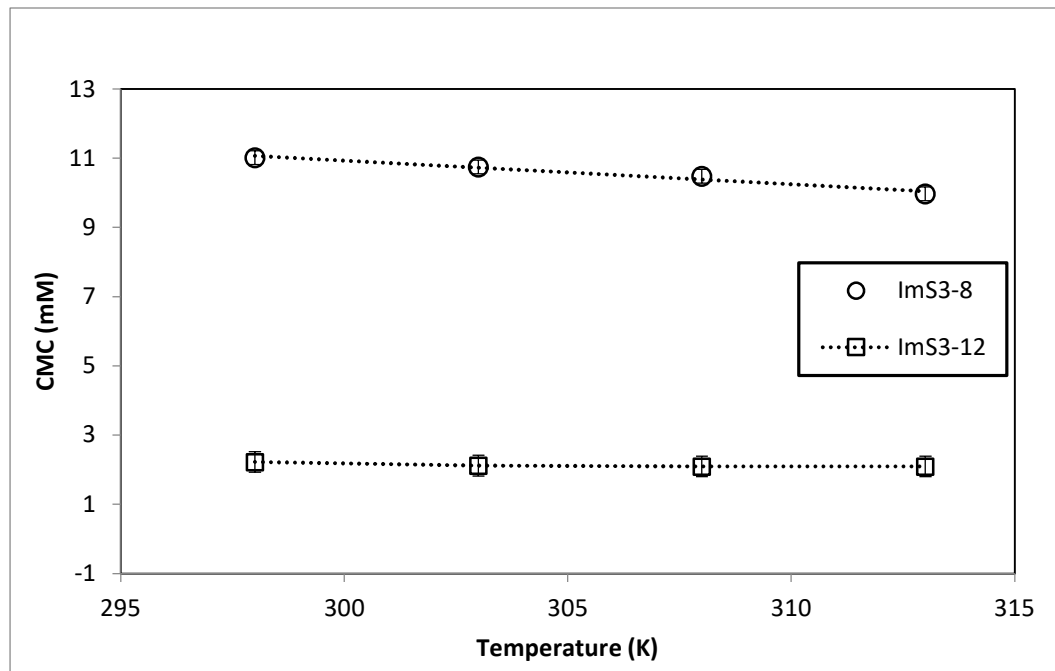

Fig. 5: Variation in CMC of ImS3-8 and ImS3-12 as a function of solution temperature.

Thermodynamic Parameters of Micellization

Thermodynamic parameters of micellization are important to understand the process of micellization which in turn helps to understand the structural factor's effect of the surfactant and environmental conditions over it. Change in free energy (ΔG_{mic}), enthalpy (ΔH_{mic}) and entropy (ΔS_{mic}) of micellization are the different thermodynamic parameters which have been determined for ImS3-R by using equations 6, 7 and 8, respectively (Abbas and Mohammad 2016; Tondo et al., 2007) and the calculated values are listed in Table 1.

$$\Delta G_{mic} = RT \ln X_{cmc} \tag{6}$$

$$\Delta H_{mic} = -2RT^2 (d\ln X_{cmc} / dT) \tag{7}$$

$$\Delta S_{mic} = (\Delta H_{mic} - \Delta G_{mic}) / T \tag{8}$$

Where, ΔG_{mic} is the Gibbs free energy change of micellization, R is gas constant, T is absolute temperature and X_{cmc} is the CMC in terms of mole fraction of the surfactant, ΔH_{mic} is enthalpy change of micellization, ΔS_{mic} is entropy change of micellization in the above equations.

The listed data show negative values of ΔG_{mic}, ΔH_{mic} and very small positive values of ΔS_{mic} of both ImS3-8 and ImS3-12, indicating that the process of micellization is enthalpically driven. It can be assumed that there is a low level of disruption of the water structure surrounding the hydrophobic group during the course of micellization making $\Delta S_{mic} > 0$, however, the overall process is spontaneous at room temperature. ImS3-12 has higher negative value of ΔG_{mic} than ImS3-8 indicating the greater spontaneity of micellization of the former. On inspection the thermodynamics data of ImS3-12 and the data in literature of sodium dodecyl benzene sulfonate (SDBS), DTAB, we found that negative ΔG_{mic} value of ImS3-12 is greater while negative value of ΔH_{mic} and value of ΔS_{mic} of ImS3-12 is lower compared to SDBS, DTAB (Ananda, K et al., 1991).

Effect of Temperature over Thermodynamic Parameters of Micellization

Effect of temperature on the thermodynamic parameters of the micellization has been studied and the results so obtained are presented in Fig. 6 and 7 and are also summarized in Table 1. The data show that the values of ΔG_{mic} are negative, ΔS_{mic} are positive and with a constant negative value of ΔH_{mic} of both ImS3-R throughout the temperature range (298-313K). Increase in temperature minutely increase ΔS_{mic} which is compensated by increase in negative values of ΔG_{mic} indicating that overall, the process of micellization has been favored by temperature. ImS3-R, when compare to classical surfactants such as SDBS and DTAB, the

trend of increase in thermodynamic parameters of micellization with increase in temperature are the same though, negative values of ΔG_{mic} of the former is greater while negative values of ΔH_{mic} and ΔS_{mic} of the later is greater at investigated temperature. This comparison suggests the process of micellization is enthalpically driven in both classes of surfactants, however, higher values of ΔS_{mic} of SDBS and DTAB compare to ImS3-12 indicate greater disruption occur due water structure surrounding the hydrophobic chain with transferring of the hydrophobic group to the interior of the micelle of the former (Ananda, K et al., 1991).
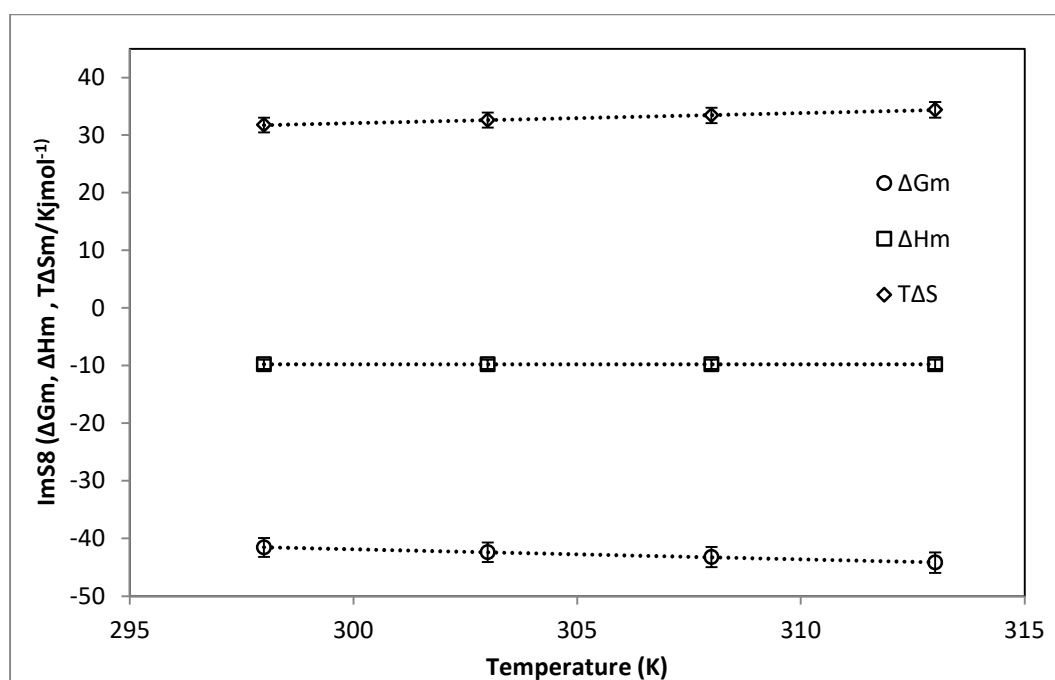

Fig. 6: Thermodynamic parameters of ImS3-8 micellization as a function of temperature.
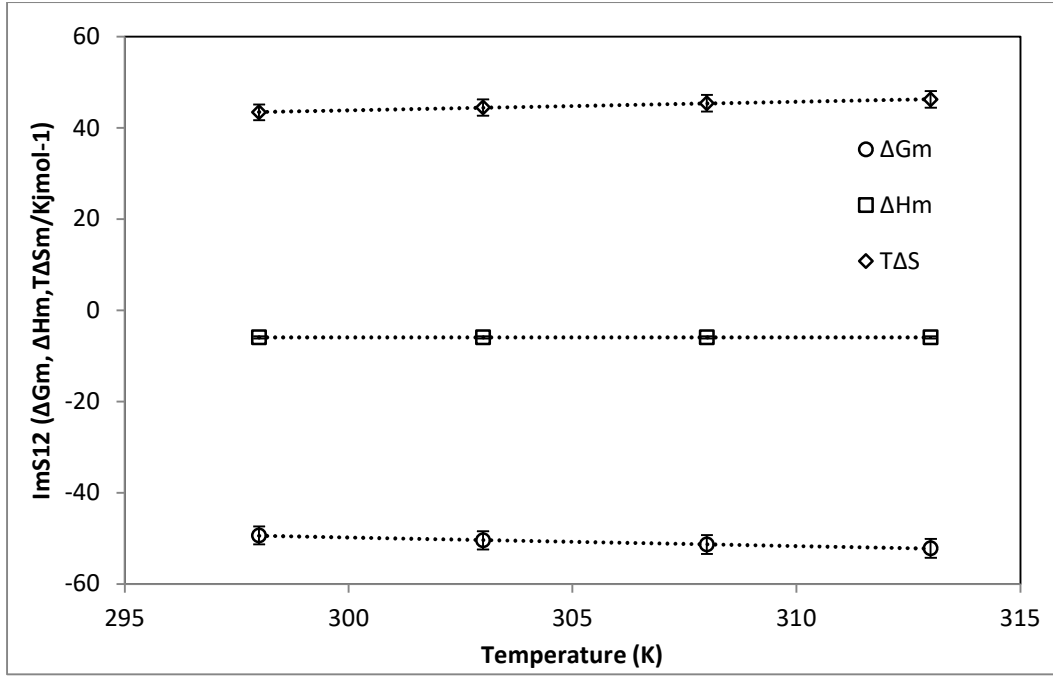
Fig. 7: Thermodynamic parameters of micellization as a function of temperature of ImS3-12 solution.

Characterization the morphology of the micelle of ImS3-R surfactants by SANS

Data analysis

The model adopted to analyse the SANS data describes the micelle structure as that of a charged particle, defined by the structure factor S(Q), with an elliptical core-shell morphology, defined by the shape related form factor P(Q). Models describing morphologies based on solid spheres or solid ellipsoids did not give satisfactory fits.

Therefore, a core-shell morphology has been adopted in which the intensity of scattered radiation, I(Q), as a function of the wave-vector, Q, is given by (Griffiths, PC et al., 2005).

$$I(Q) = n_m \left[S(Q)\{F(Q)\}^2 + \{|F(Q)|^2\} - \{F(Q)\}^2 \right] + B_{inc} \tag{9}$$

Where n_m is the number of micelles per unit volume, *S(Q)* is the structure factor and B_{inc} is the incoherent background. For an elliptical micelle, both F(Q) and F(Q)^2 require numerical integration over an angle γ between Q and the axis of the ellipsoid to account for the random distribution of orientations of the ellipse. For clarity, we omit this.

14

$$F(Q) = V_1 (\rho_1 - \rho_2)F_o (QR_1) + V_2 (\rho_2 - \rho_{solvent}) F_o (QR_2) \qquad (10)$$

The first term in Eq. (10) represents the scattering from the core with radius R (subscript 1) and the second, the polar shell (subscript 2). $V_i = \dfrac{4}{3}\pi R_i^3$ and $F_0(QR_i) = \dfrac{3 j_i (QR_i)}{QR_i}$ (j_i is the first-order spherical Bessel function of the first kind). The S(Q) represents the spatial arrangement of the micelles in solution and "n" the micelle number density. ρ is the neutron scattering length density of the micellar core (subscript 1), the polar shell (subscript 2) and the solvent (subscript 0). It is expedient here to limit the number of adjustable parameters within the core-shell fit and this is most conveniently undertaken by first delineating the head-group and tail regions, most simply by setting the alkyl group as the tail. The volume of the head-group and tail were calculated according to a molecular volume fragment summation approach and this ratio constrained in the fitting routine to define the micelle curvature (Zhao et al., 2003). For the dodecyl surfactant, this ratio is 0.77 whereas for the octyl 1.13. With this delineation, the scattering length densities (ρ) for the alkyl region and of the anhydrous surfactant head-groups may then be calculated, ρ = -0.38 (octyl), -0.27 (dodecyl) and 1.33 Å^{-2}. The scattering length density for the D$_2$O solvent was fixed at 6.33. The best fit for the amount of water associated with the head-group region was found through trial-and-error to be approximately 50%. Hence, the initial guess for the fit is constrained by the volumes of the molecular fragments and their molecular composition.

It is somewhat harder to constrain the parameters defining the structure factor, S(Q), as the ionic nature of these surfactants is not known. The electrostatic component is treated in terms of the Hayter-Penfold model, which requires knowledge (estimate) of the (effective) hard sphere radius, volume fraction of the scattering centres (which may be calculated from the mass concentration), the effective charge on the micelle and the screening length. Clearly, the last two parameters are coupled *via* the distribution of the various ions. Practically, an estimate (25%) of the counter ion dissociation is used to calculate the screening length, and the charge per micelle allowed to float. Once a fit is achieved, the screening length was systematically varied and the charge refitted. The "best" fit was taken as whichever combination of the values of charge and screening length led to the lowest residuals. Post-fitting, the absolute scattering intensity is compared with the known concentration of surfactant and its calculated composition, to validate the fit. The calculated and observed intensities should lie within ~20%.

Micelle morphology of ImS3-8 and ImS3-12

The morphology of the micelle of ImS3-R deduced from calculated intensities using ellipsoid core-shell model compared with the observed intensities shown in Fig. 8, are listed in Table 2. ImS3-8 with 50mM NaCl form almost spherical micelle with ellipticity x = 1 ± 0.5 and shell thickness is from 4-5 ± 0.5 Å while radius of the core is 11 ± 0.5 which shows no appreciable involvement of the carbon alkyl chain in the shell. The data show that ImS3-12 forms oblate micelles with ellipticity x= 0.8 ± 0.1. The radius of core of ImS3-12 is 16 ± 0.5 which indicates minimal involvement of the carbon alkyl chain to the shell thickness. The water percentage to the micelle shell remains around 60%.
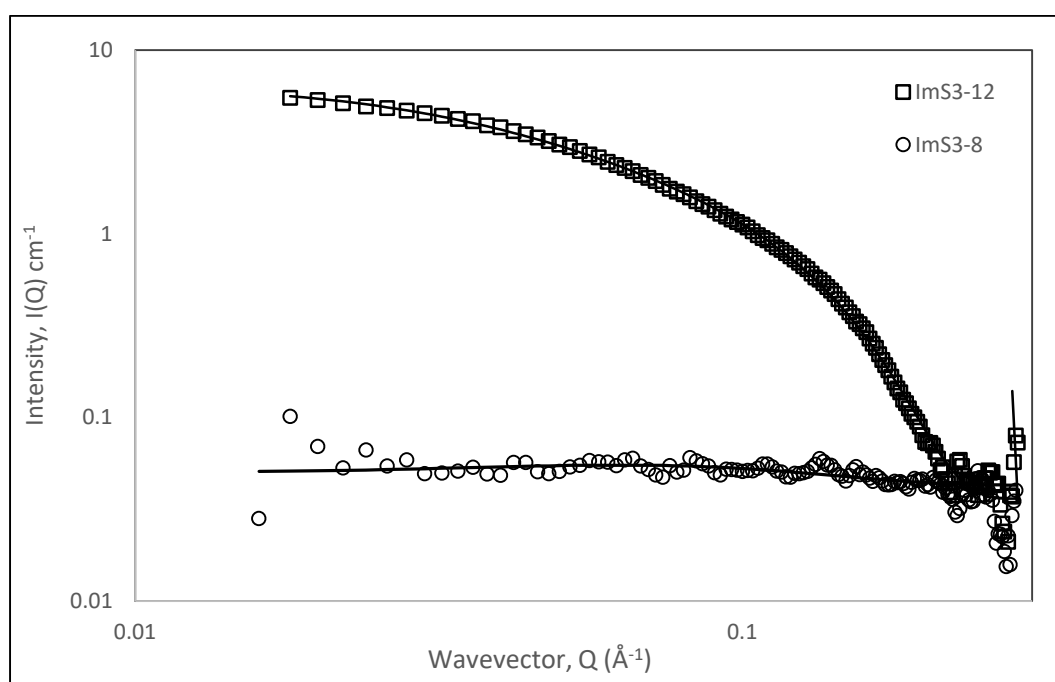

Fig. 8: Small angle neutron scattering from 25mM aqueous solution of ImS3-8 and ImS3-12

Table 2. Parameters describing the fit to the core-shell model used to describe the SANS data

Surfactant	Radius (Å)	Ellipticity (Å)	Shell thickness (Å)	Charge	Hard sphere radius
ImS8+Salt	11.4	1.1	5.1	3.1	16.8
ImS12+Salt	15.9	0.8	9.4	10.0	26.0

Conclusions

It is concluded that both the zwitterionic surfactants i.e., ImS3-8 and ImS3-12 show clear amphiphilic behavior, consistent with conventional surfactants. ImS3-8 showed weak indication of CMC while ImS3-12 is much more surface active and had an appreciably lower value for the CMC. The surface activities increase and CMC decrease of both the zwitterions with increase in temperature. The energetic changes of micellization *i.e.,* ΔG_{mic}, ΔH_{mic}, interfacial adsorption (ΔG_{ads}) have negative values while ΔS_{mic} has small positive values of ImS3-8 and ImS3-12. It has also been observed that ΔH_{mic} remains constant while ΔG_{mic}, ΔS_{mic} and ΔG_{ads} increase when temperature is increased from 298 to 313K. The micellization process of ImS-R is entropically controlled over the investigated temperature range. It is also concluded from the comparative study of ImS3-R and conventional surfactants such as SDS and DTAB (of same hydrophobic groups) that the former show greater surface activity and lower CMC than the later. SANS data interpretation showed spherical micelle of ImS3-8 while ImS3-12 form oblate micelle with ellipticity of 0.8 This change in shape of micelle from spherical to elliptical is attributed to the change in the hydrophobic block length. From the SANS results it can be further concluded that hydrophobic chain has not been involve in shell thickness of the micelle. The present results are interesting from academic as well as applied point of views.

Acknowledgements

References

Ananda, K., Yadav, O., & Singh, P. (1991) Studies on the surface and thermodynamic properties of some surfactants in aqueous and water+ 1, 4-dioxane solutions. *Colloids and Surfaces,* **55:**345-358.

Anouti, M., Jones, J., Boisset, A., Jacquemin, J., Caillon-Caravanier, M., & Lemordant, D. (2009) Aggregation behavior in water of new imidazolium and pyrrolidinium alkycarboxylates protic ionic liquids. *Journal of Colloid and Interface Science,* **340:**104-111.

Baker, G. A., Pandey, S., Pandey, S., & Baker, S. N. (2004) A new class of cationic surfactants inspired by N-alkyl-N-methyl pyrrolidinium ionic liquids. *Analyst,* **129:**890-892.

Blesic, M., Lopes, A., Melo, E., Petrovski, Z., Plechkova, N., Lopes, J.N.C., Seddon, K., & Rebelo, L.P.N. (2008) On the self-aggregation and fluorescence quenching aptitude of surfactant ionic liquids. *The Journal of Physical Chemistry B,* **112:**8645-8650.

Bowers, J., Butts, C. P., Martin, P. J., Vergara-Gutierrez, M. C., & Heenan, R. K. (2004) Aggregation behavior of aqueous solutions of ionic liquids. *Langmuir,* **20:**2191-2198.

Brown, P., Butts, C., Dyer, R., Eastoe, J., Grillo, I., Guittard, F., Rogers, S., & Heenan, R. (2011) Anionic surfactants and surfactant ionic liquids with quaternary ammonium counterions. *Langmuir,* **27:**4563-4571.

Chabba, S., Vashishat, R., Kang, T. S., & Mahajan, R. K. (2016) Self–Aggregation Behavior of Dialkyl Imidazolium Based Ionic Liquids in Aqueous Medium: Effect of Alkyl Chain Length. *ChemistrySelect, 1:*2458-2470.

Cornellas, A., Perez, L., Comelles, F., Ribosa, I., Manresa, A., & Garcia, M. T. (2011) Self-aggregation and antimicrobial activity of imidazolium and pyridinium based ionic liquids in aqueous solution. *Journal of Colloid and Interface Science, 355:*164-171.

Dong, B., Gao, Y., Su, Y., Zheng, L., Xu, J., & Inoue, T. (2010) Self-aggregation behavior of fluorescent carbazole-tailed imidazolium ionic liquids in aqueous solutions. *The Journal of Physical Chemistry B, 114:*340-348.

Dong, B., Zhao, X., Zheng, L., Zhang, J., Li, N., & Inoue, T. (2008) Aggregation behavior of long-chain imidazolium ionic liquids in aqueous solution: micellization and characterization of micelle microenvironment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 317:*666-672.

El-Dossoki, F. I., El-Maksoud, S. A., Migahed, M. A., & Gouda, M. M. (2020) Micellization and Solvation Properties of Newly Synthesized Imidazolium-and Aminium-Based Surfactants. *ACS Omega, 5:*9429-9441.

Griffiths, P. C., Paul, A., Khayat, Z., Heenan, R. K., Ranganathan, R., & Grillo, I. (2005) A small-angle neutron scattering study of biologically relevant mixed surfactant micelles comprising 1, 2-diheptanoyl-sn-phosphatidylcholine and sodium dodecyl sulfate or dodecyltrimethylammonium bromide. *Soft Matter, 1:*152-159.

Inoue, T., Ebina, H., Dong, B., & Zheng, L. (2007) Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. *Journal of Colloid and Interface Science, 314:*236-241.

Iso, K., & Okada, T. (2000) Evaluation of electrostatic potential induced by anion-dominated partition into zwitterionic micelles and origin of selectivity in anion uptake. *Langmuir, 16:*9199-9204.

Kamboj, R., Bharmoria, P., Chauhan, V., Singh, G., Kumar, A., Singh, S., & Kang, T. S. (2014a) Effect of cationic head group on micellization behavior of new amide-functionalized surface active ionic liquids. *Physical Chemistry Chemical Physics, 16:*26040-26050.

Kamboj, R., Bharmoria, P., Chauhan, V., Singh, S., Kumar, A., Mithu, V. S., & Kang, T. S. (2014b) Micellization behavior of morpholinium-based amide-functionalized ionic liquids in aqueous media. *Langmuir, 30:*9920-9930.

Khan, A., & Siddiq, M. (2016) Physicochemical investigation of the micellar behaviour of a diblock (PEO)62-b-(PBO)33 copolymer in water and its interaction with ionic surfactants. *Journal of Dispersion Science and Technology, 37*: 519-529.

Kjellin, U. R. M., Reimer, J., & Hansson, P. (2003) An investigation of dynamic surface tension, critical micelle concentration, and aggregation number of three nonionic surfactants using NMR, time-resolved fluorescence quenching, and maximum bubble pressure tensiometry. *Journal of Colloid and Interface Science, 262:*506-515.

Liu, X. f., Dong, L. I., & Fang, Y. (2011) Synthesis and self-aggregation of a hydroxyl-functionalized imidazolium-based ionic liquid surfactant in aqueous solution. *Journal of Surfactants and Detergents, 14*, 203-210

Marte, L., Beber, R. C., Farrukh, M. A., Micke, G. A., Costa, A. C., Gillitt, N. D., Bunton, C. A., Profio, P. D., Savelli, G., & Nome, F. (2007) Specific anion binding to sulfobetaine micelles and kinetics of nucleophilic reactions. *The Journal of Physical Chemistry B,* 111, 9762-9769.

Moulik, S. P. (1996) Micelles: self-organized surfactant assemblies. *Current Science-Bangalore-, 71:*368-375.

Penfold, J., Thomas, R., Zhang, X., & Taylor, D. (2009) Nature of Amine− Surfactant Interactions at the Air− Solution Interface. *Langmuir,* **25:**3972-3980.

Priebe, J. P., Satnami, M. L., Tondo, D. W., Souza, B. S., Priebe, J. M., Micke, G. A., Costa, A. C., Fiedler, H. D., Bunton, C. A., & Nome, F. (2008) The chameleon-like nature of zwitterionic micelles: the intrinsic relationship of anion and cation binding in sulfobetaine micelles. *The Journal of Physical Chemistry B,* **112:**14373-14378.

Seth, D., Sarkar, S., & Sarkar, N. (2008) Dynamics of solvent and rotational relaxation of Coumarin 153 in a room temperature ionic liquid, 1-butyl-3-methylimidazolium octyl sulfate, forming micellar structure. *Langmuir,* **24:**7085-7091.

Shi, L., Li, N., Yan, H., Gao, Y., & Zheng, L. (2011) Aggregation behavior of long-chain N-aryl imidazolium bromide in aqueous solution. *Langmuir,* **27:**1618-1625.

Singh, T., & Kumar, A. (2007) Aggregation behavior of ionic liquids in aqueous solutions: effect of alkyl chain length, cations, and anions. *The Journal of Physical Chemistry B,* **111:**7843-7851.

Souza, F. D., Souza, B. S., Tondo, D. W., Leopoldino, E. C., Fiedler, H. D., & Nome, F. (2015) Imidazolium-based zwitterionic surfactants: characterization of normal and reverse micelles and stabilization of nanoparticles. *Langmuir,* **31:**3587-3595.

Srinivasa, R. K., Singh, T., Trivedi, T. J., & Kumar, A. (2011) Aggregation behavior of amino acid ionic liquid surfactants in aqueous media. *The Journal of Physical Chemistry B,* **115:**13847-13853.

Stjerndahl, M., Lundberg, D., Zhang, H., & Menger, F. M. (2007) NMR studies of aggregation and hydration of surfactants containing amide bonds. *The Journal of Physical Chemistry B,* **111:**2008-2014.

Tariq, M., Podgoršek, A., Ferguson, J., Lopes, A., Gomes, M. C., Pádua, A., Rebelo, L., & Lopes, J. C. (2011) Characteristics of aggregation in aqueous solutions of dialkylpyrrolidinium bromides. *Journal of Colloid and Interface Science,* **360:**606-616.

Tondo D. W., Leopoldino, E. C., Souza, B. S., Micke, G. A., Costa, A. C., Fiedler, H. D., Bunton, C. A., & Nome, F. (2010) Synthesis of a new zwitterionic surfactant containing an imidazolium ring. Evaluating the chameleon-like behavior of zwitterionic micelles. *Langmuir,* **26:**15754-15760.

Tondo D. W., Priebe, J. M., Souza, B. S., Priebe, J. P., Bunton, C. A., & Nome, F. (2007) The chameleon-like nature of zwitterionic micelles. Control of anion and cation binding in sulfobetaine micelles. Effects on acid equilibria and rates. *The Journal of Physical Chemistry B,* **111:**11867-11869.

Trivedi, T. J., Rao, K. S., Singh, T., Mandal, S. K., Sutradhar, N., Panda, A. B., & Kumar, A. (2011) Task-specific, biodegradable amino acid ionic liquid surfactants. *ChemSusChem,* **4:**604-608

Wang, H., Wang, J., Zhang, S., & Xuan, X. (2008) Structural effects of anions and cations on the aggregation behavior of ionic liquids in aqueous solutions. *The Journal of Physical Chemistry B,* **112:**16682-16689.

Wang, J., Wang, H., Zhang, S., Zhang, H., & Zhao, Y., (2007) Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids [C4mim][BF4] and [C n mim] Br (n= 4, 6, 8, 10, 12) in aqueous solutions. *The Journal of Physical Chemistry B,* **111:**6181-6188.

Zhao, Y. H., Abraham, M. H., & Zissimos, A. M. (2003) Fast calculation of van der Waals volume as a sum of atomic and bond contributions and its application to drug compounds. *The Journal of organic chemistry,* **68:**7368-7373.

Zhu, Y. P., Masuyama, A., & Okahara, M. (1990) Preparation and surface active properties of amphipathic compounds with two sulfate groups and two lipophilic alkyl chains. *Journal of the American Oil Chemists' Society,* **67:**459-463.