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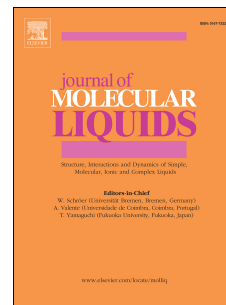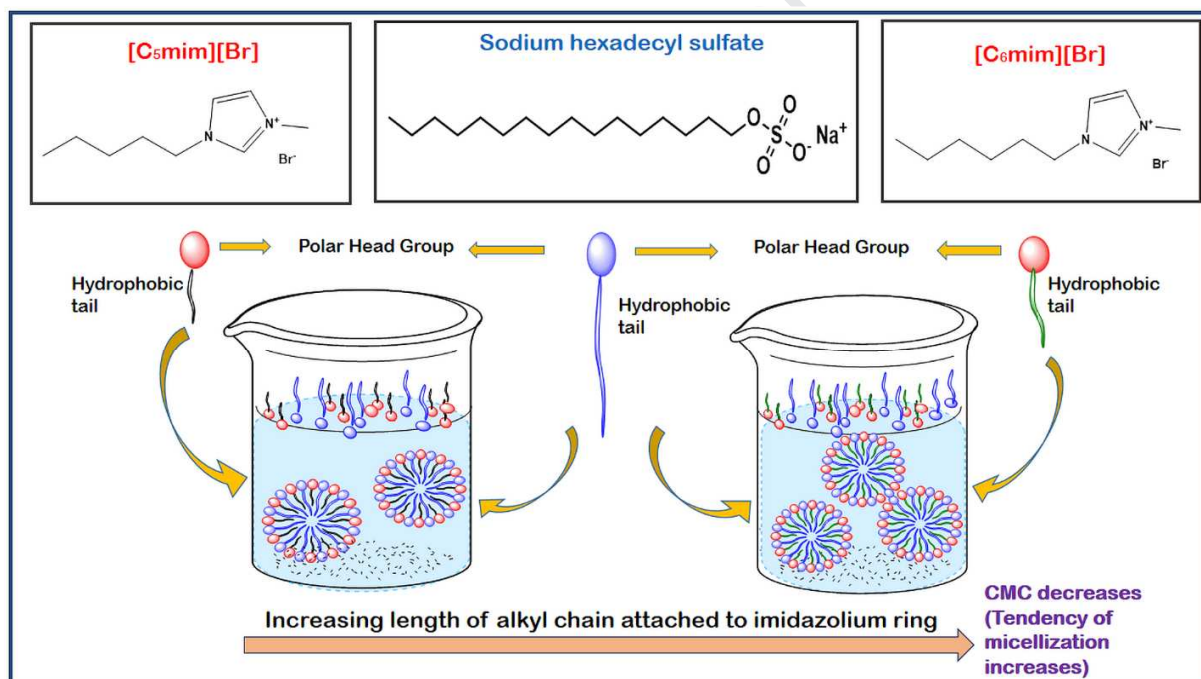
GRAPHICAL ABSTRACT

Deciphering aggregation behavior and thermodynamic properties of anionic surfactant sodium hexadecyl sulfate in aqueous solutions of ionic liquids [C$_5$mim][Br] and [C$_6$mim][Br]

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Deciphering aggregation behavior and thermodynamic properties of anionic surfactant sodium hexadecyl sulfate in aqueous solutions of ionic liquids [C₅mim][Br] and [C₆mim][Br]

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ABSTRACT

The present work aims to study the interactions of cationic imidazolium based ionic liquids i.e. 1-alkyl-3-methylimidazolium bromide ([C$_n$mim][Br], where n=5 &6) with anionic surfactant sodium hexadecyl sulfate (SHS) in aqueous media employing the various techniques such as conductivity measurement, fluorescence spectroscopy, UV-visible spectroscopy and FT-IR spectroscopy. The temperature dependence of critical micelle concentration (CMC) determined using conductivity measurements at temperatures (298.15, 303.15 and 308.15) K at different concentrations (0.02, 0.05 and 0.1) wt. %, of ionic liquids (ILs) in aqueous medium was used to calculate the various thermodynamic parameters of micellization such as, standard free energy of micellization (ΔG_m^0), standard enthalpy of micellization (ΔH_m^0), and standard entropy of micellization (ΔS_m^0). Further, fluorescence and UV-Visible spectroscopy have been utilized to confirm the CMC values obtained from conductivity measurements, which were found to be in good agreement. A continuous increment in CMC value was observed with the increase in concentration of ILs as well as in temperature. Further FT-IR Spectroscopic studies have been done to demonstrate the structural alterations occurring in the respective mixtures.

Keywords: 1-alkyl-3-methylimidazolium bromide [C$_n$mim][Br]; sodium hexadecyl sulfate (SHS); Fluorescence; UV-visible; Micellization; FT-IR

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INTRODUCTION

The use of surfactants have been the focus of significant research interest due to their applications in numerous fields such as biotechnology [1], solubilizing and emulsifying agents [2], personal care and laundry products [3], pharmaceuticals [4], nano-reactors for enzymatic reactions [5] This is due to their capability to form spontaneous self-assembled structures in different solvents [6]. On the other hand, ionic liquids are of significant interest due to their useful properties such as non-flammability, negligible volatility, high ion conductivity, thermal and chemical stability. Also they are known to be safe and sustainable substitutes to various organic solvents for their use in many applications [7, 8]. They can alter the surface and thermodynamic properties of various surfactants [9–18], which help to understand various types of interactions between ionic surfactants and ionic liquids [19]. The magnitude of change in properties of surfactant on using IL as an additive depends upon the composition of IL as well as various interactions of IL with the surfactant [20, 21].

Micelle is an aggregate of surfactant molecules formed above a particular concentration. Critical micelle concentration (CMC) is the concentration above which the monomers of surfactant aggregate and micelle formation takes place [22-24]. The formation of micelle occur when there is balance between hydrophobic and hydrophilic forces. This governs the aggregation properties of surfactant solutions in the presence of different additives. The aggregation properties show variations by the change in temperature and concentration of surfactant solutions. The hydrophobic interactions between the hydrophobic chains is the driving force for micelle formation. This corresponds to favorable contribution towards free energy of micellization. But electrostatic repulsions between surfactant head groups at the surface of micelle contribute to positive free energy, which is unfavorable for micelle formation. This type of micelle destabilizing interactions can be reduced by the adsorption of counterions at the surface of micelle. Thus the degree of counterion binding (α) governs the stability of micelles [25]. The inclusion of additive into an associates of an amphiphiles will affect their physicochemical characteristics for instance the degree of ionization, reaction rates and clouding or phase separation [26-29].

Armstrong's group [30] was first to explore the aggregation behavior of different surfactants in ILs 1-butyl-3-methylimidazolium chloride [C$_4$mim][Cl] and 1-butyl-3-methylimidazolium

hexafluorophosphate [C$_4$mim][PF$_6$]. The observed CMCs were found to be higher than the CMCs of same surfactants in aqueous solution [30]. Reddy's group investigated the aggregation properties of aqueous sodium dodecyl sulfate (SDS) with the variation in alkyl chains of ILs [31]. Javadian et al. studied the micellization behavior of cetyltrimethyl ammonium bromide (CTAB) in various ILs in aqueous media [21]. Bermudez and Chen uses 1-ethyl-3-methylimidazolium ethyl sulfate [C$_2$mim][C$_2$OSO$_3$] as the solvent to study the aggregation and interfacial behavior of anionic and cationic surfactants [18]. Pandey et al. observed the aggregation behavior of SDS in the presence of hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF$_6$] and a hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF$_4$] [32-35].

In this paper, we report the aggregation behavior of anionic surfactant sodium hexadecyl sulfate (SHS) in the presence of imidazolium based ILs such as 1-pentyl-3-methylimidazolium bromide [C$_5$mim][Br] and 1-hexyl-3-methylimidazolium bromide [C$_6$mim][Br]. Conductivity measurements have been performed to evaluate the CMC as well as various thermodynamic parameters of micellization for the aggregation of sodium hexadecyl sulfate (SHS) in the presence both the ILs at different concentrations i.e. (0.02, 0.05 and 0.10) wt. % and at different temperatures i.e. (298.15, 303.15 and 308.15) K. Further fluorescence spectroscopy and UV-visible spectroscopic techniques have been employed to validate the CMC values obtained using conductivity measurement at 298.15 K. These investigations provide the better insight for the types of interactions existing in hydrophobic and hydrophilic parts of surfactant and ILs.

2. EXPERIMENTAL

2.1 Chemicals

1-methylimidazole (purity >99.0%) purchased from HIMEDIA Laboratories Pvt. Ltd. is used to synthesize the ionic liquid [C$_5$mim][Br] and [C$_6$mim][Br]. The alkyl halides i.e. 1-bromopentane (purity >98.0%) and 1-bromohexane (purity 99.0%) used for this purpose are obtained from TCI Pvt. Ltd. and HIMEDIA Laboratories Pvt. Ltd. respectively. Acetonitrile (purity >99.5%), which was used as a solvent was procured from LOBA Chemie Pvt. Ltd. The anionic surfactant Sodium hexadecyl sulfate (SHS) used in this study was procured from TCI Pvt. Ltd. Before the use of SHS, it was dried under vacuum and then stored over P$_2$O$_5$ in vacuum desiccators for at least

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48h. All the chemicals used during the experimental work along with their details have been enlisted in Table 1.

2.2 Synthesis of ionic liquids

1-Bromopentane was added drop wise into a vigorously stirred solution of 1-methylimidazole and acetonitrile in the ratio 1:1.2 in 500ml round bottom flask. The solution was refluxed at around 80°C for 48 h. To monitor the progress of reaction thin layer chromatography is used. Then the reaction mixture was cooled to room temperature. Rota evaporator was used to remove the excess of acetonitrile present in the reaction mixture. The obtained ionic liquid, 1-pentyl-3-methylimidazolium bromide $[C_5mim][Br]$, was then washed several times using hexane. To synthesize 1-hexyl-3-methylimidazolium bromide $[C_6mim][Br]$, the same procedure is repeated with 1-bromohexane instead of 1-bromopentane. The synthesized ionic liquid is dried under vacuum for few days before its use. The structure of both the ILs is confirmed by using ^{1}H NMR (Bruker 400 MHz) and FT-IR (Agilent Carry 630) spectroscopic studies. The ^{1}H NMR and FT-IR spectroscopic studies of $[C_5mim][Br]$ have been reported as Figure S1 and that for $[C_6mim][Br]$ have been shown as Figure S2 in supporting information. The results obtained for both the ionic liquids are found to be in good agreement with the literature data [36].

2.3 Instruments and methods

Doubly distilled deionized water from Millipore, Milli-Q Academic water purification system having conductance < 5 μS cm^{-1} had been used for sample preparation. To prepare the stock solutions, the required amount of ILs was accurately weighed using Sartorius CPA 225 D with a precision of ±0.00001g. Microsoft Excel and OriginPro 8 software were used to analyze the data as per the model/equations given in the different sections and used in the present study.

2.3.1 Conductivity measurements

The measurements of electrical conductivities for all mixtures had been performed at different temperatures (298.15, 303.15, 308.15) K using a digital conductivity meter (Systronics 308) in a water jacketed flow dilution cell. The solution was maintained at specific temperatures using refrigerated circulated water thermostat provided by Macro Scientific Works Pvt. Ltd. Delhi which controlled temperature with accuracy of ±0.1 K as already mentioned our previous study [37]. The calibration of conductivity meter had been done before the measurements using the

aqueous KCl solutions in the concentration range of 0.01-1.0 mol kg^{-1}. The value of conductivity is noted after adding the required amount of homogeneous solution of surfactant followed by the proper stirring of solution.

2.3.2 Fluorescence measurements

The fluorescence measurements had been done on a RF 5301 PC spectrophotometer purchased from Shimadzu in the range 350–600 nm at an excitation wavelength of 320 nm. TCC 240A thermoelectrically temperature controlled cell holder was used to maintain a constant temperature within ±1 °C. Pyrene was utilized as fluorescence probe, whose stock solution had been prepared in methanol at a very low concentration i.e. 1 μM, to prevent excimer formation. Doubly distilled de-ionized degassed water had been used to prepare the solutions of [C$_5$mim][Br] + SHS and [C$_6$mim][Br] + SHS at different concentrations. The ratio 'I_I / I_{III}' of the fluorescence intensities of the first and third vibronic peaks was then calculated, as it gives a measure of the polarity of the microenvironment of pyrene in the micelles.

2.3.3 UV-visible spectroscopy

Agilent Technologies Cary series UV-Vis spectrophotometer using a quartz cuvette having path length of 1 cm was employed to record the UV spectra. The stock solution of SHS was added using micro syringe to the aqueous solutions of IL taken in the cuvette. A number of spectra were recorded after addition of particular amount of SHS in the cuvette. The absorbance behavior of IL was monitored in the UV-visible range (200-800 nm) by varying the concentration of SHS in the aqueous solutions of both the ILs.

2.3.4 FT-IR spectroscopic study

Agilent technologies Carry 630 FT-IR Spectrophotometer was utilized to carry out FT-IR spectral studies in the wave number region from 4000 cm^{-1} to 400 cm^{-1}. The FT-IR spectra were recorded for different concentrations (0.02, 0.05and 0.10 wt. %) of both the ILs as well as SHS/IL mixtures when the concentration of SHS in respective IL correspond to concentration at CMC, below CMC and above CMC.

3. RESULT AND DISCUSSIONS

Aggregation behavior of sodium hexadecyl sulfate (SHS) has been investigated in the absence and presence of ionic liquids in aqueous media using conductivity measurement, fluorescence spectroscopy, UV-Visible spectroscopy and FT-IR spectroscopy.

3.1 Conductivity measurements

3.1.1 Critical micelle concentration (CMC) and degree of counterion dissociation (α)

Specific conductivity is the important property to study the aggregation behavior of surfactants. Electrical conductivity measurements are made to study the aggregation behavior of anionic surfactant sodium hexadecyl sulfate (SHS) in the absence and presence of ionic liquids [C_5mim][Br] and [C_6mim][Br] in aqueous medium. The measurements were taken for different IL/SHS mixtures at different concentrations of both the ionic liquids i.e. (0.02, 0.05 and 0.1) wt. % of ionic liquids and at various temperatures (298.15, 303.15 and 308.15) K. The measured values of specific conductivity have been shown in Table 2 and Table 3. The variation of specific conductivity, κ with the change in concentration of sodium hexadecyl sulfate (SHS) is plotted at different concentrations of both the ionic liquids at various temperatures. The respective plots have been shown in Figure 1 and Figure 2. The specific conductivity varies linearly with the change in concentration of anionic surfactant but the slope in the premicellar region is always greater than the postmicellar region [38, 39].The point of intersection of the two line segments corresponding to premicellar and postmicellar region was termed as critical micelle concentration (CMC). The ratio of slope in the postmicellar to the premicellar region give rise to the degree of counterion dissociation (α). The value of CMC obtained for aqueous SHS in the absence of IL is in good agreement with literature [40]. The value of CMC as well as α have been reported in Table 4 for IL/SHS mixtures at various concentrations of [C_5mim][Br] at various temperatures. Similarly these values at various concentrations of [C_6mim][Br] and at various temperatures have been reported in Table 5.

The value of critical micelle concentration (CMC) as well as degree of counterion dissociation (α) increases with the increase in concentration of both the ionic liquids. The process of micellization is mainly dependent upon two types of interactions i.e. electrostatic interactions occurring between the charged head groups as well as hydrophobic interactions occurring in the hydrophobic tails of different components. These two types of interactions have opposite effects. This is because electrostatic interactions can lower the CMC of mixture thereby favoring the

micellization by reducing the repulsions among the charged head groups. On the other hand hydrophobic interactions can lead to increase in CMC of mixture by stabilizing the surfactant monomers thereby delaying the micellization [41]. The hydrophobic interactions dominates over the electrostatic interactions due to the insertion of ionic liquid into inter-cluster space of water which in turn lead to increase in CMC of mixture. Here $[C_5mim]^+$ and $[C_6mim]^+$ of ionic liquid interacts with the anion of SHS through hydrophobic interactions which leads to increase in CMC upon addition of both the ionic liquids.

At a particular concentration of ionic liquid, the value of CMC increases with the increase in temperature. On increasing temperature, the degree of hydration of hydrophilic parts decreases, thereby reducing the CMC. But increasing temperature can also lead to disruption of water structure, which can delay the tendency of micellization. Thus these two opposite effects prevail in the mixture on increasing the temperature. As the CMC increases with increase in temperature, hence latter effect dominates.

But the micellization of SHS takes place rapidly in case of $[C_6mim][Br]$ in comparison to $[C_5mim][Br]$ as the value of CMC in case of $[C_6mim][Br]$ is always less than that of $[C_5mim][Br]$ at all the concentrations of IL as well as at all the studied temperatures. This is because the hexyl chain in $[C_6mim][Br]$ is more flexible as compared to the pentyl chain in $[C_5mim][Br]$, which leads to increase in the value of change in entropy of system, thereby increasing the tendency of micellization in case of $[C_6mim][Br]$ as compared to $[C_5mim][Br]$.

3.1.2 Thermodynamics of micellization

The conductivity measurement of the studied IL/SHS mixtures at various temperatures can also lead to evaluation of various thermodynamic parameters of micellization such as the standard Gibbs' free energy change of micellization, ΔG_m^0, the standard enthalpy change of micellization, ΔH_m^0 and the standard entropy change of micellization, ΔS_m^0 by using the equations (1)-(3).

$$\Delta G_m^0 = (2-\alpha)\,RT\,(lnX_{CMC}) \tag{1}$$

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

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)\,/\,T \tag{3}$$

, where R is gas constant, T is temperature and α is degree of counter ion dissociation, X_{CMC} is the value of CMC in the mole fraction unit [42]. After evaluating ΔG_m^0 and ΔH_m^0, from equation (1) and (2), the value of ΔS_m^0 can be calculated by equation (3). The values of all these thermodynamic parameters of micellization have been enlisted in Table 4 for SHS in presence of different wt. % of [C$_5$mim][Br] in aqueous medium. Similarly these values for SHS in presence of different wt. % of [C$_6$mim][Br] in aqueous medium have been shown in Table 5. The values of these thermodynamic parameters helps in understanding the driving force of micellization. The variation of ΔG_m^0, ΔH_m^0 and ΔS_m^0 with the change in temperature and concentration of both the ionic liquids has been shown in Figure 3 and 4. It can be observed that the value of ΔG_m^0 and ΔH_m^0 is negative for all the studied mixtures which indicates the process of micellization is spontaneous and exothermic in nature. The value of ΔG_m^0 becomes less negative with the addition of different wt. % of ionic liquids at a particular temperature indicating the decrease in tendency of micellization upon addition of both the ionic liquids. The value of ΔG_m^0 is dependent upon two terms, entropic ($-T\Delta S_m^0$) and enthalpic (ΔH_m^0) contribution. From the values of ΔS_m^0 and ΔH_m^0, it can be seen that the process of micellization is entropy driven for both the studied mixtures.

3.2 Fluorescence probe behavior

Pyrene is used as a fluorescent probe showing the significant vibrational bands in their fluorescence spectra. The ratio of first to third vibrational peaks of pyrene is widely used for the determination of the CMC of micellar systems [43-51]. Pyrene I_I / I_{III} versus the concentration of SHS in the presence of different wt. % of both the ILs has been given as Table S1 and S2. These values have also been shown graphically in Figures 5 and 6. The curves obtained in all the plots shows a sigmoidal decrease, which fit well to Boltzmann type equation [49]. The I_I / I_{III} remains constant up to a particular concentration and then decreases rapidly on the onset of micellization. This is because this ratio is very sensitive to solvent polarity. Initially before the micellization, this ratio is high in polar medium, but as the concentration of SHS increases, the micellization of SHS takes place. This decreases the polarity of medium, which in turn is responsible for the abrupt decrease in value of I_I / I_{III} upon micellization as the non-polar pyrene goes into

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hydrophobic micellar phase. The midpoint of the curves obtained corresponds to CMC of IL/SHS mixtures. The values of CMC obtained using fluorescence spectroscopy for SHS in presence of different concentrations of both the ionic liquids at 298.15 K have been reported in Table 6. The values of CMC obtained using Fluorescence spectroscopy are quite close to that obtained using conductivity measurements.

3.3 UV-visible spectroscopy

In the present study, the absorbance behavior of ionic liquid is monitored in UV–visible range (200–800 nm) on the addition of SHS. This method of analyzing absorbance versus concentration of SHS can be regarded as simplest and quickest method for the determination of CMC. In case of imidazolium based ionic liquids, there is inherent structural feature that makes them to absorb in the entire UV-region [52-54]. The presence of imidazolium ring in these type of ionic liquids negate the requirement of any probe for the determination of CMC [55]. The absorbance versus concentration of SHS is plotted to determine the CMC of SHS in presence of imidazolium based ionic liquid. But this method cannot help to evaluate CMC in the absence of imidazolium based ionic liquid in aqueous media, because water itself does not absorb in UV-region. The absorbance varies linearly with concentration of SHS up to a certain concentration of SHS, but after the micellization of SHS begins, the rate of the increase is different from the rate before. Then the point of intersection of two lines in the plot corresponds to the point of CMC [56]. The plots of absorbance versus concentration of SHS in the presence of different wt. % of [C$_5$mim][Br] and [C$_6$mim][Br] in aqueous medium have been shown in Figures 7 and 8, respectively. The absorbance values for the same are reported in Tables S3 and S4. The CMC of SHS in presence of different wt. % of both the ionic liquids at 298.15 K is compared with that obtained through conductivity and fluorescence spectroscopy. The same is listed in Table 6. It can be observed from the table that the value of CMC of obtained using these three methods are very close to each other.

3.4 FT-IR spectroscopic study

The variation of local polarity and conformation of alkyl chains with temperature is indicator of micellization, which can be ascertained using FT-IR spectroscopic technique [57-59]. The various molecular scale interactions occurring in the mixtures can be monitored using FT-IR spectroscopic technique, which is remarkable tool for obtaining such information. The mixture

constituting surfactant and ionic liquid show various structural alterations upon micellization. In this study, FT-IR spectra of SHS in presence of different concentrations of both the ionic liquids have been recorded for concentration of SHS below CMC, at CMC and above CMC. The spectrum is unique for different IL/SHS mixture. The obtained spectra are shown in as Figures S3 and S4 of supplementary data. FT-IR spectra of SHS in (0.02, 0.05, and 0.10) wt. % of [C$_5$mim][Br] and [C$_6$mim][Br] in the wavenumber range 3000-3600 cm^{-1} at different concentrations of SHS have been shown in Figures 9 and 10. The spectra shows two major peaks. The one peak, which is appearing in the wavenumber 3200-3300cm^{-1} may be due to N-H stretching whereas the other that appearing in the 1600-1690cm^{-1} wavenumber range may be due to N-H bending and C=C stretching. There is a shift in the wavenumber which is contained in Table 7 that indicate interactions prevailing in the mixture of SHS in presence of ionic liquid [60]. This specifies that, the SHS interacts with both the imidazolium based ionic liquids giving rise to various structural alterations within the mixture.

4. CONCLUSION

Aggregation behavior of conventional anionic surfactant SHS have been examined in the presence of imidazolium based ionic liquids in aqueous media at different temperatures by utilizing various techniques. An increase in CMC is obtained for SHS in presence of different wt. % of both the ionic liquids, which may be due to hydrophobic interactions that stabilize the surfactant monomers, which in turn is responsible for delay in tendency of micellization. On the other hand, the value of CMC of SHS in presence of both the ionic liquids increases with the increase in temperature, indicating the delay in micellization on increasing temperature from 298.15 K to 308.15 K. The value of CMC in presence of [C$_6$mim][Br] is always less than that in presence of [C$_5$mim][Br] at a particular temperature and concentration of ionic liquid. This shows the tendency of micellization of SHS is more in presence of [C$_6$mim][Br] as compared to [C$_5$mim][Br]. Further, the large negative value of ΔG_m^0 for both the studied mixtures indicates the process of micellization is spontaneous in nature. The negative ΔH_m^0 values indicate the exothermic nature of micellization. The large positive values of ΔS_m^0 reveals that the process of micellization is entropy driven, where the hydrophobic interactions between the alkyl chains plays prominent role. The CMC values determined for both the mixtures from all methods are found to be in good agreement with each other. Also, the FT-IR spectra shows the various shifts

in the wavenumber in for the mixtures constituting SHS in presence of different wt. % of both the ionic liquids.

Acknowledgements

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Table 1: Specification of chemicals

Chemicals	Source	CAS No	Purification Method	Mass Fraction Purity[#]
1-methylimadazole	HIMEDIA Laboratories Pvt. Ltd	616-47-7	No further purification	>99.0%
1-bromopentane	TCI Pvt. Ltd	110-53-2	No further purification	>98.0%
1-bromohexane	HIMEDIA Laboratories Pvt. Ltd	111-25-1	No further purification	99.0%
Acetonitrile	LOBA Chemie Pvt. Ltd Mumbai	75-05-8	No further purification	>99.5%
Sodium Hexadecyl Sulfate	TCI Pvt. Ltd	1120-01-0	Vacuum drying	>95.0%
Pyrene	SIGMA ALDRICH Pvt. Ltd.	129-00-0	No further purification	98.0%

[#]As declared by supplier

Table 2: Conductance κ (µS) of SHS in (0.02, 0.05, 0.10) wt. % of [C$_5$mim] [Br] at different temperatures (298.15, 303.15 and 308.15) K

Conc. (mM)	0.02 wt.% [C$_5$mim] [Br]			0.05 wt.% [C$_5$mim] [Br]			0.10 wt.% [C$_5$mim] [Br]		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
	κ (µS)			κ (µS)			κ (µS)		
0.00746	180.3	201.1	207.8	283.8	309.3	338.6	494.8	540.1	577.6
0.01141	180.8	201.6	208.4	284.1	309.6	338.9	495.3	540.2	578.1
0.01632	181.3	202.2	208.7	284.4	309.9	339.1	495.5	540.4	578.0
0.02217	181.8	202.7	209.2	285.5	310.1	339.6	495.8	540.7	578.5
0.02893	182.3	202.9	210.1	285.9	310.5	339.9	496.1	540.9	578.7
0.03659	182.9	203.0	210.5	286.6	310.9	340.4	496.4	541.0	578.9
0.04510	183.5	203.9	211.0	287.1	311.5	340.9	496.8	541.1	579.2
0.05445	184.1	204.4	212.0	287.3	311.7	341.3	497.1	541.4	579.4
0.07279	185.1	205.1	212.8	288.4	312.7	341.8	497.7	541.8	579.8
0.09944	186.3	206.3	214.1	289.8	313.7	343.1	498.7	542.4	580.2
0.13346	188.4	207.7	216.8	291.5	315.6	344.9	500.5	543.4	581.6
0.17374	190.3	208.9	218.8	293.7	317.5	346.7	502.2	544.5	582.6
0.21904	191.9	210.5	221.6	296.3	319.4	348.7	504.1	545.6	583.8
0.26814	194.0	212.7	224.9	299.1	322.1	350.9	506.3	546.8	585.1
0.31983	195.6	214.3	228.1	301.6	323.9	353.1	508.4	548.1	586.3
0.37303	197.4	215.4	229.8	303.6	325.8	354.5	509.9	549.1	587.8
0.42678	199.2	216.9	231.9	305.8	327.3	356.1	511.3	549.9	588.7
0.49844	201.9	218.8	234.7	308.3	329.7	357.9	513.2	551.1	590.1
0.58032	204.8	220.9	238.5	311.1	332.0	360.7	515.3	552.3	591.4
0.66559	207.3	223.5	241.4	314.0	334.6	363.0	517.6	553.6	592.8
0.74912	210.2	225.6	244.9	316.7	336.9	365.2	519.9	555.1	594.4
0.83755	212.9	227.5	248.6	319.9	339.6	368.1	522.3	556.5	595.8

Standard uncertainties s are s (T) = ±0.1 K, s (κ) = ±0.1 µS

Table 3: Conductance κ (μS) of SHS in (0.02, 0.05, 0.10) wt. % of [C_6mim] [Br] at different temperatures (298.15, 303.15 and 308.15) K

Conc. (mM)	0.02 wt.% [C_6mim] [Br]			0.05 wt.% [C_6mim] [Br]			0.10 wt.% [C_6mim] [Br]		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
	κ (μS)			κ (μS)			κ (μS)		
0.00746	157	170.7	183.9	270.4	295.6	324.6	438.6	476.6	518
0.01141	158.2	170.9	184.1	270.8	295.9	324.9	438.8	476.9	518.5
0.01632	158.4	171.2	185.1	271.1	296.4	325.3	439	477.1	518.8
0.02217	158.7	172.3	186.2	271.5	296.9	325.8	439.5	477.4	519.1
0.02893	159.3	172.8	187.1	272.1	297.2	326.4	439.9	477.7	519.7
0.03659	160.3	173.3	187.4	272.3	297.9	327.1	440.1	478.1	520.1
0.04510	161.2	174.1	188.6	272.8	298.3	327.7	440.8	478.4	520.5
0.05445	162.1	174.7	189.3	273.3	298.5	328.1	441.1	478.7	521.1
0.07279	163.5	175.9	190.1	273.9	299.4	329.2	441.9	479.3	522.1
0.09944	165.3	177.7	192.1	275.3	300.5	330.5	443.1	480.2	523.7
0.13346	167	179.9	194.9	276.9	302.6	332.4	444.9	481.5	525.6
0.17374	170.2	183.1	199.1	279.2	304.8	334.9	446.7	482.8	527.8
0.21904	173.1	185.9	202.2	281.3	306.9	337.8	448.4	484.4	530.6
0.26814	176.5	189.6	206.3	283.9	309.4	340.4	450.7	486.1	533.5
0.31983	178.7	191.5	210.2	285.8	311.8	343.3	452.9	487.8	536.6
0.37303	180.5	194.2	212.2	287.4	313.7	345.5	454.4	489.2	538.7
0.42678	183.8	196.8	215.5	289.1	315.6	347.8	456.1	490.4	540.7
0.49844	187.1	199.8	219.8	291.3	317.8	350.4	458.1	492.1	543.5
0.58032	190.6	203.8	223.4	293.9	320.9	353.7	460.5	493.9	546.6
0.66559	195.1	207.6	228.9	296.5	323.3	356.9	463.1	495.8	549.6
0.74912	198.2	211.5	232.6	299.2	326.1	360.1	465.3	497.7	552.7
0.83755	202.5	215.1	237.6	302.1	329.0	363.2	468.1	499.8	556.4

Standard uncertainties s are s (T) = ±0.1 K, s (κ) = ±0.1 μS

Table 4: Critical micelle concentration (CMC), degree of counter ion binding (α), free energy of micellization (ΔG^0_m), enthalpy of micellization (ΔH^0_m), and entropy of micellization (ΔS^0_m) of SHS in (0.02, 0.05, 0.10) wt.% of [C$_5$mim] [Br] at different temperatures (298.15, 303.15 and 308.15) K.

[C$_5$mim] [Br] (wt.%)	CMC (mM)	α	ΔG^0_m (kJ·mol^{-1})	ΔH^0_m (kJ·mol^{-1})	ΔS^0_m (J·mol^{-1}·K^{-1})
T = 298.15 K					
0.00	0.2173	0.612	-42.84	-20.28	75.67
0.02	0.2568	0.614	-42.22	-17.83	81.81
0.05	0.2849	0.618	-41.72	-14.42	91.57
0.10	0.3247	0.624	-41.11	-10.92	101.25
T = 303.15 K					
0.00	0.2435	0.620	-42.91	-20.84	72.79
0.02	0.2879	0.621	-42.29	-18.33	79.05
0.05	0.3098	0.624	-41.94	-14.84	89.40
0.10	0.3499	0.627	-41.43	-11.26	99.52
T = 308.15 K					
0.00	0.2648	0.628	-43.08	-21.42	70.31
0.02	0.3056	0.630	-42.52	-18.82	76.90
0.05	0.3281	0.632	-42.21	-15.25	87.48
0.10	0.3615	0.636	-41.75	-11.56	97.94

Standard uncertainties *s* are *s* (T) = ±0.1 K, *s* (CMC) = ± 0.0001 mM, *s* (ΔG^0_m) = ±0.03 kJ·mol^{-1}, *s* (ΔH^0_m) = ±0.02 kJ·mol^{-1}, s (ΔS^0_m) = ±0.02 J·mol^{-1}·K^{-1}

Table 5: : Critical micelle concentration (CMC), degree of counter ion binding (α), free energy of micellization (ΔG^0_m), enthalpy of micellization (ΔH^0_m), and entropy of micellization (ΔS^0_m) of SHS in (0.02, 0.05, 0.10) wt.% of [C$_6$mim] [Br] at different temperatures (298.15, 303.15 and 308.15) K.

[C$_6$mim] [Br] (wt.%)	CMC (mM)	α	ΔG^0_m (kJ·mol^{-1})	ΔH^0_m (kJ·mol^{-1})	ΔS^0_m (J·mol^{-1}·K^{-1})
T = 298.15 K					
0.00	0.2173	0.612	-42.84	-20.28	75.67
0.02	0.2378	0.625	-42.14	-17.54	82.50
0.05	0.2669	0.629	-41.62	-13.75	93.46
0.10	0.3069	0.632	-41.06	-10.62	102.08
T = 303.15 K					
0.00	0.2435	0.620	-42.91	-20.84	72.79
0.02	0.2619	0.635	-42.19	-18.00	79.79
0.05	0.2871	0.638	-41.78	-14.12	91.23
0.10	0.3219	0.643	-41.23	-10.89	100.09
T = 308.15 K					
0	0.2648	0.628	-43.08	-21.42	70.31
0.02	0.2826	0.641	-42.45	-18.52	77.65
0.05	0.3057	0.644	-42.08	-14.53	89.40
0.10	0.3409	0.646	-41.64	-11.23	98.67

Standard uncertainties *s* are *s* (T) = ±0.1 K, *s* (CMC) = ± 0.0001 mM, *s* (ΔG^0_m) = ±0.03 kJ·mol^{-1}, *s* (ΔH^0_m) = ±0.02 kJ·mol^{-1}, s (ΔS^0_m) = ±0.02 J·mol^{-1}·K^{-1}

Table 6: Critical micelle concentration (mM) of SHS in (0.02, 0.05, 0.10) wt.% of [C$_5$mim] [Br]

	CMC (mM)		
	Conductivity measurement	**Fluorescence spectroscopy**	**UV-visible spectroscopy**
[C$_5$mim] [Br] (wt.%)			
0.00	0.2173	0.2154	-
0.02	0.2568	0.2521	0.2575
0.05	0.2849	0.2789	0.2844
0.1	0.3247	0.3146	0.3112
[C$_6$mim] [Br] (wt.%)			
0.00	0.2173	0.2154	-
0.02	0.2378	0.2292	0.2388
0.05	0.2669	0.2661	0.2671
0.10	0.3069	0.3095	0.3131

and [C$_6$mim] [Br] using different techniques at 298.15K

Standard uncertainties *s* in *s* (CMC) = ± 0.0001 mM

Table 7: Wavenumber obtained from FT-IR spectra recorded for (0.02, 0.05, 0.10) wt. % of ILs [C$_5$mim][Br] and [C$_6$mim][Br] in the absence and presence of sodium hexadecyl sulfate (SHS)

	wt.% of IL	SHS / (mM)	Wavenumber (cm^{-1})
[C$_5$mim] [Br]			
	0.02	0	3257
		0.12832	3272
		0.25663	3275
		0.38495	3269
	0.05	0	3269
		0.14197	3256
		0.28393	3268
		0.42590	3272
	0.10	0	3254
		0.15987	3273
		0.31973	3278
		0.47960	3269
[C$_6$mim][Br]			
	0.02	0	3272
		0.11823	3277
		0.23647	3262
		0.35470	3278
	0.05	0	3271
		0.13357	3269
		0.26713	3270
		0.40070	3272
	0.10	0	3285
		0.15402	3272
		0.30803	3271
		0.46205	3278

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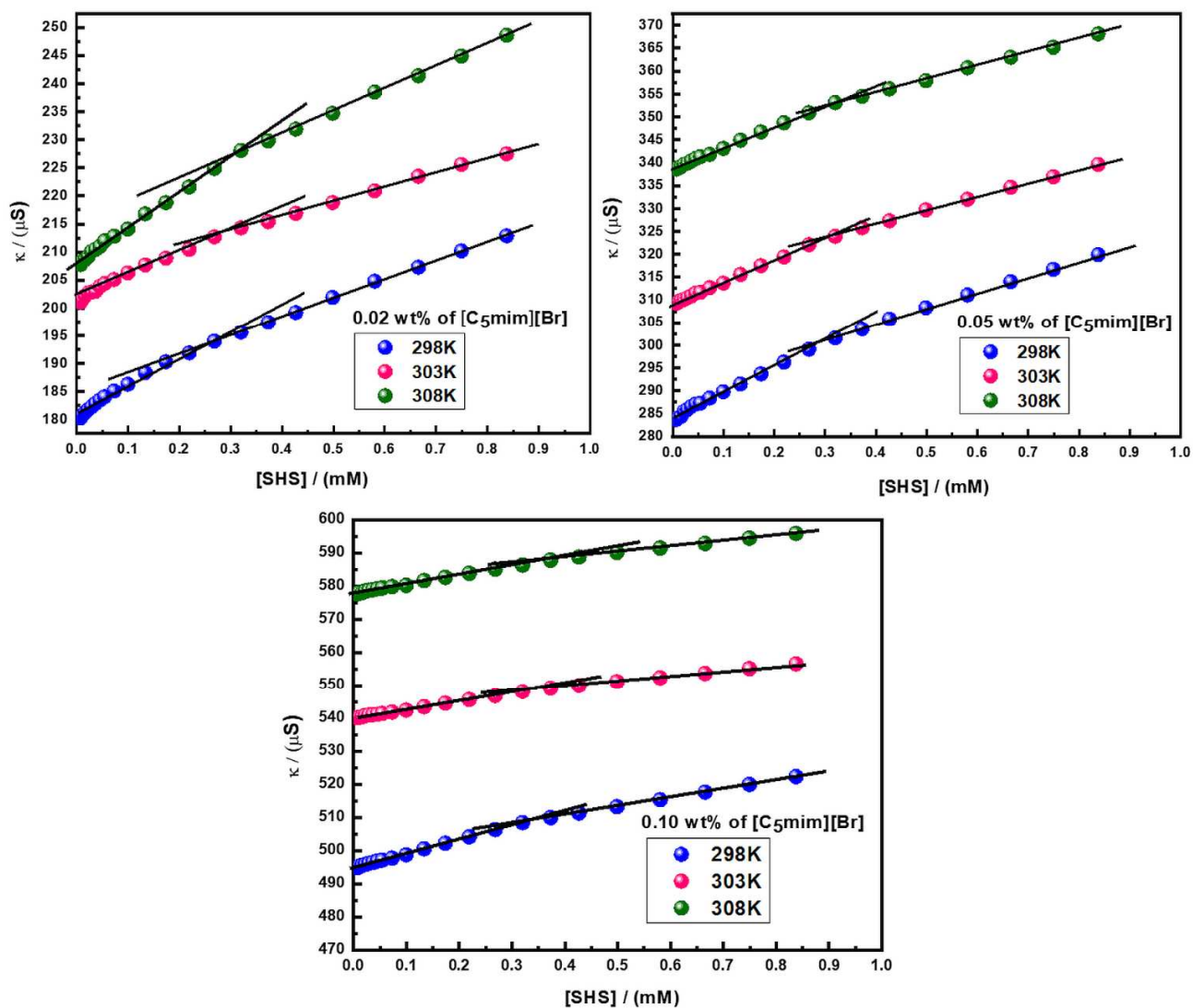
Figure 1 Specific conductance (κ) versus concentrations of SHS in (0.02, 0.05 and 0.10) wt. % of aqueous [C$_5$mim][Br] solutions at temperatures (298.15, 303.15 and 308.15) K
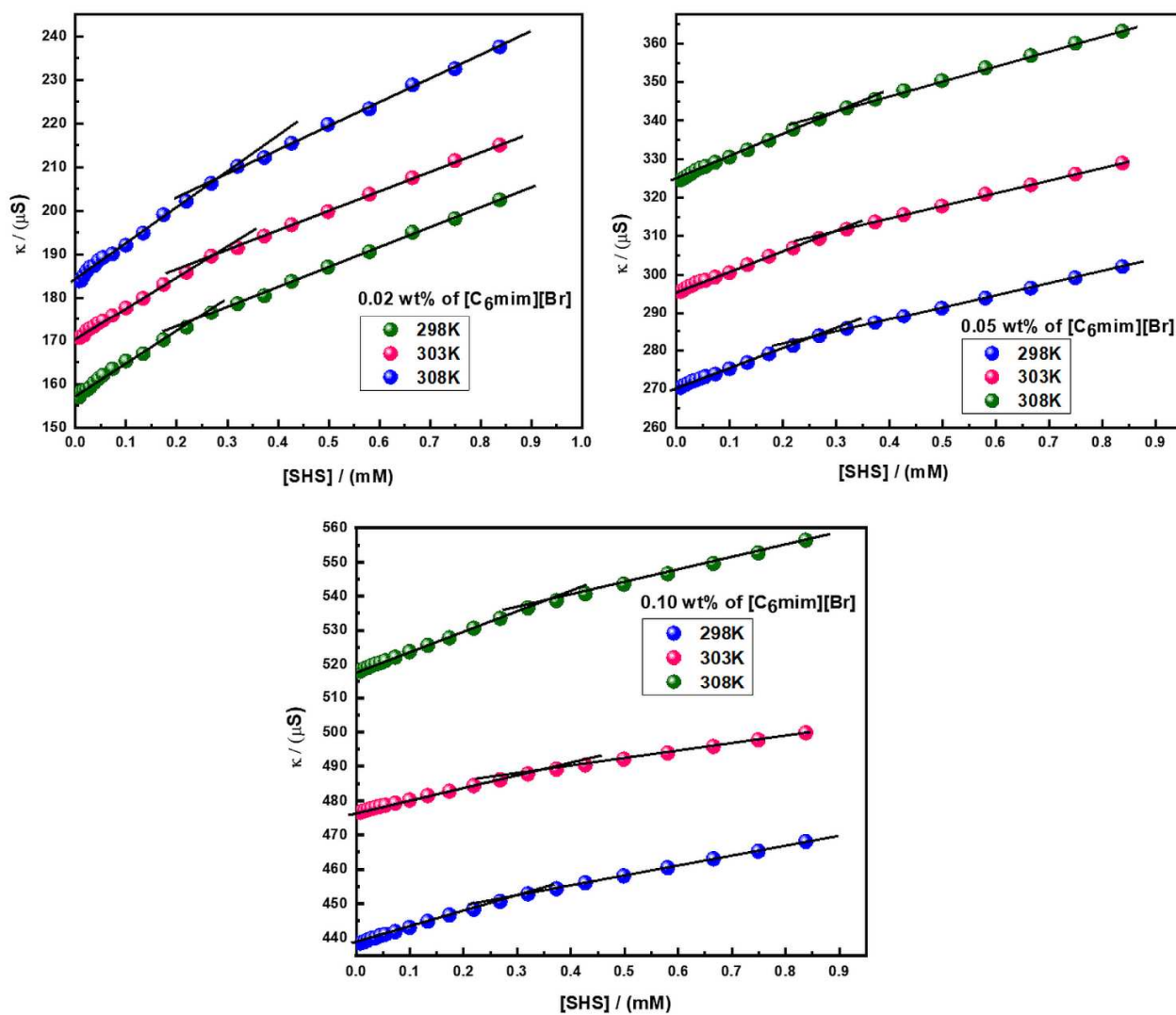
Figure 2 Specific conductance (κ) versus concentrations of SHS in (0.02, 0.05 and 0.10) wt. % of aqueous [C₆mim][Br] solutions at temperatures (298.15, 303.15 and 308.15) K
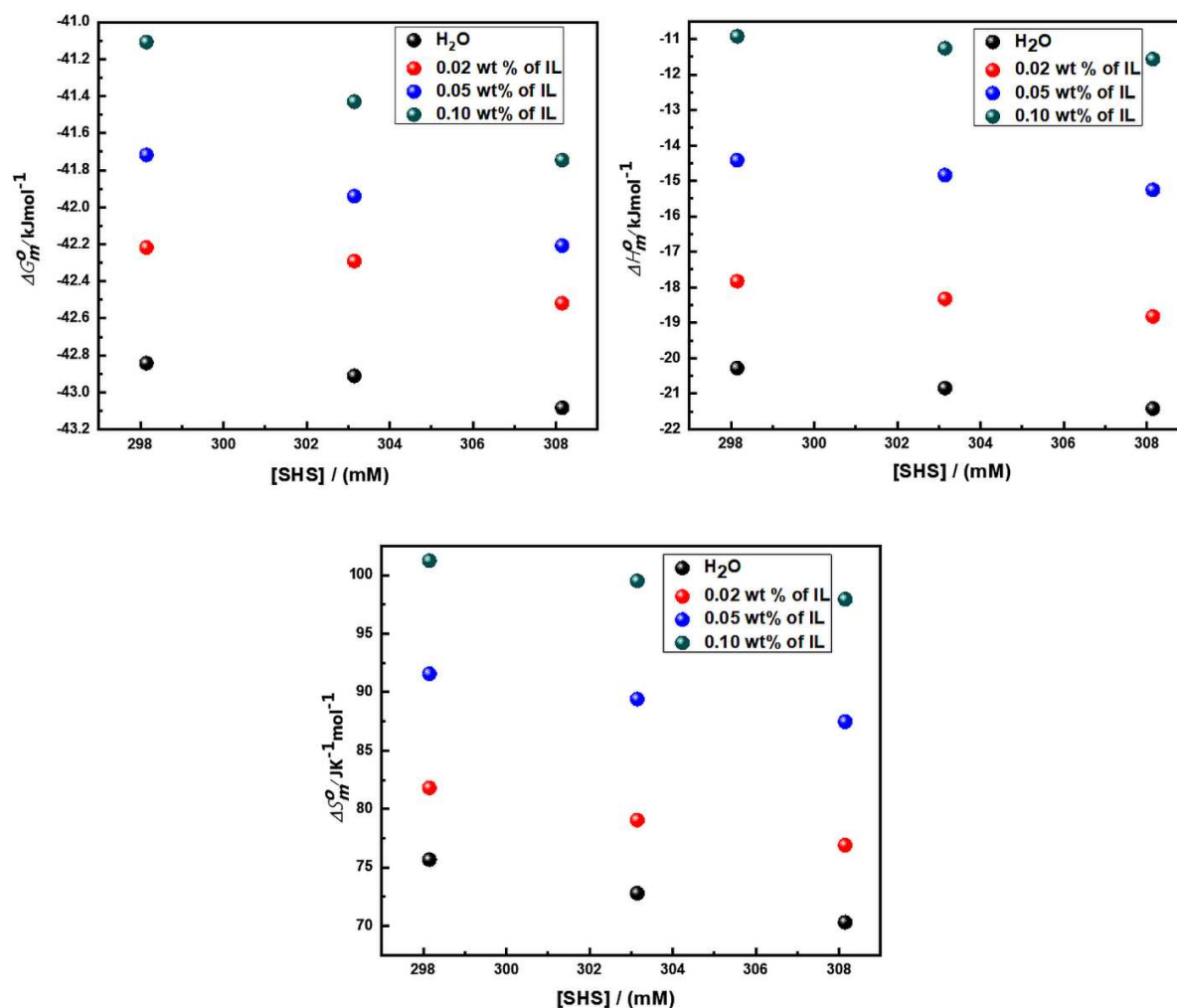
Figure 3 Plot of standard free energy of micellization ΔG^0_m, standard enthalpy of micellization ΔH^0_m and standard entropy of micellization ΔS^0_m of SHS solutions in water and in the presence of (0.02, 0.05 and 0.10) wt. % of aqueous [C$_5$mim][Br] solutions at temperatures (298.15, 303.15 and 308.15) K in the aqueous media

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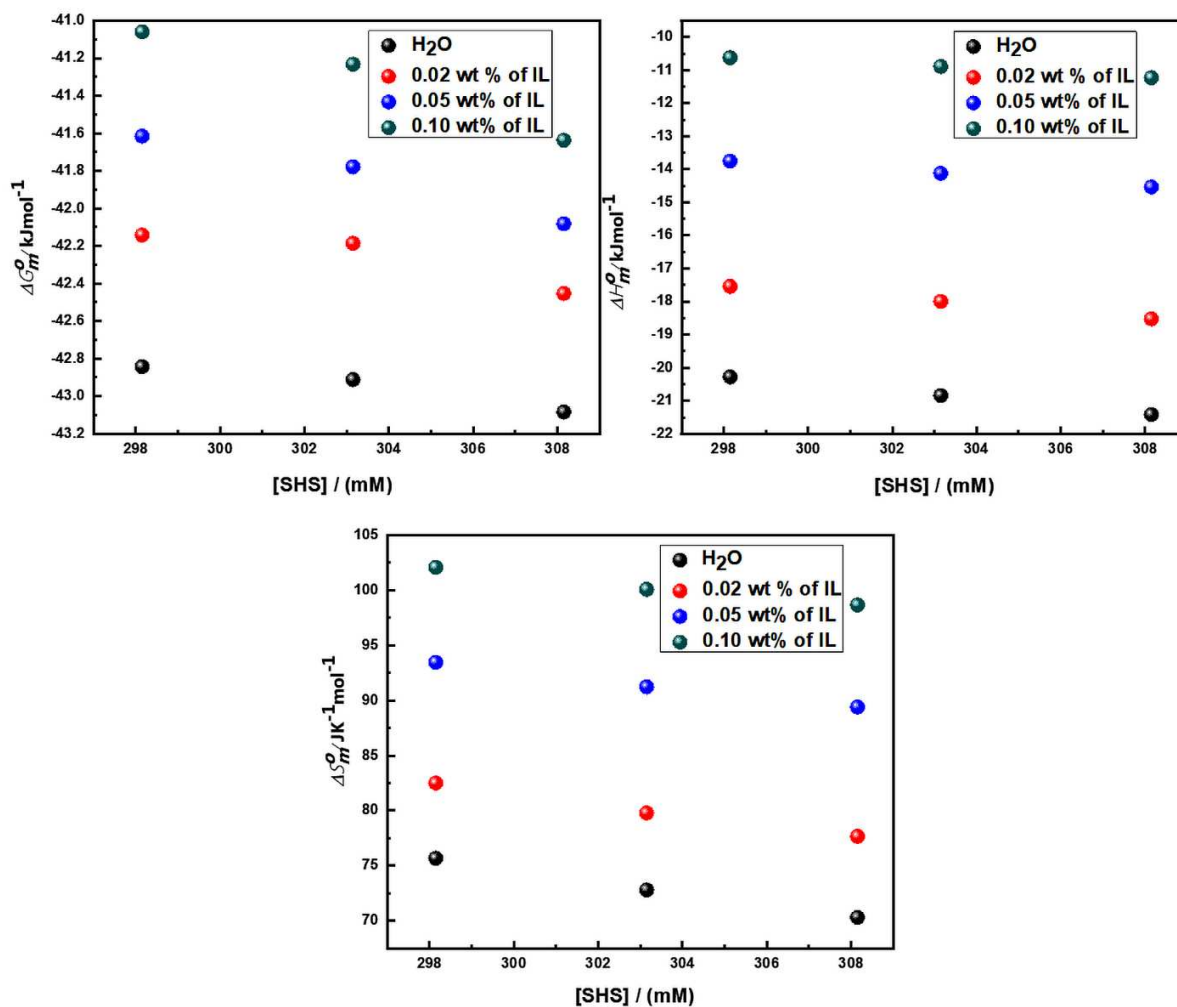
Figure 4 Plot of standard free energy of micellization ΔG^0_m, standard enthalpy of micellization ΔH^0_m and standard entropy of micellization ΔS^0_m of SHS solutions in water and in the presence of (0.02, 0.05 and 0.10) wt. % of aqueous [C$_6$mim][Br] solutions at temperatures (298.15, 303.15 and 308.15) K in the aqueous media

25
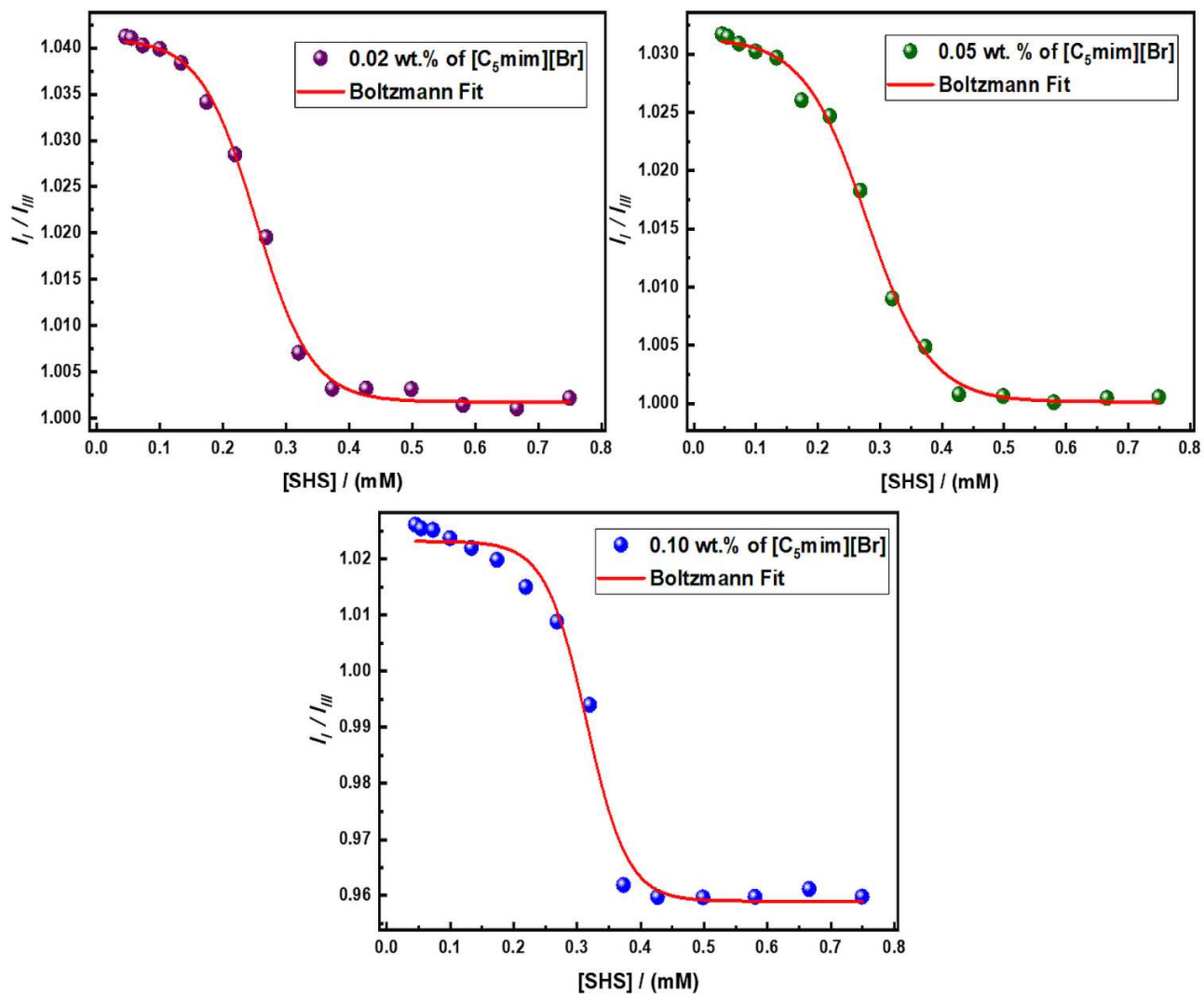
Figure 5 Pyrene I_I / I_{III} versus [SHS] in presence of (a) 0.02 wt. % (b) 0.05 wt. % (c) 0.10 wt. % of [C₅mim][Br] in the aqueous media, λ_{ex}=320 nm.
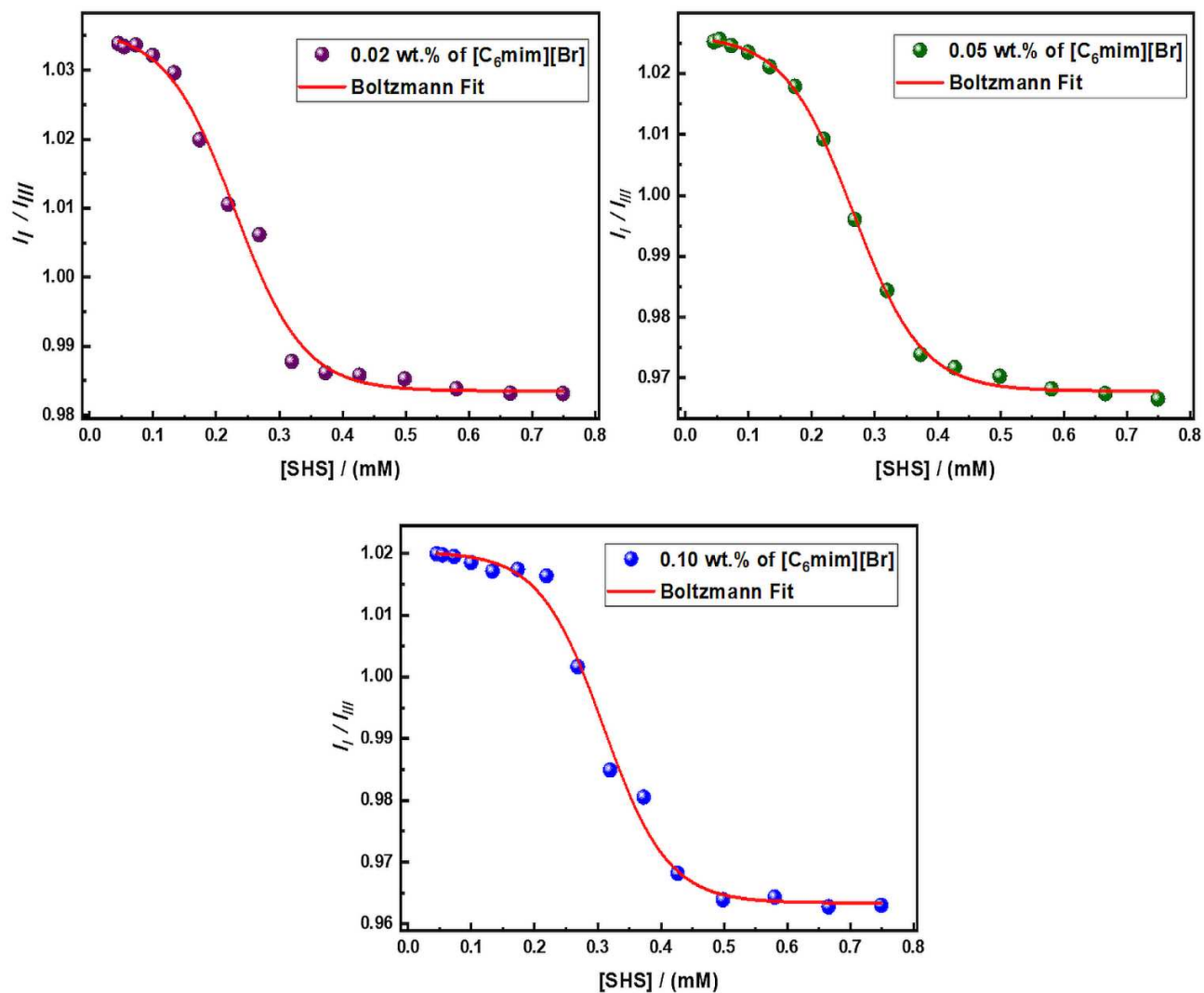
Figure 6 Pyrene I_I / I_{III} versus [SHS] in presence of (a) 0.02 wt. % (b) 0.05 wt. % (c) 0.10 wt. % of [C_6mim][Br]] in the aqueous media, λ_{ex}=320 nm.
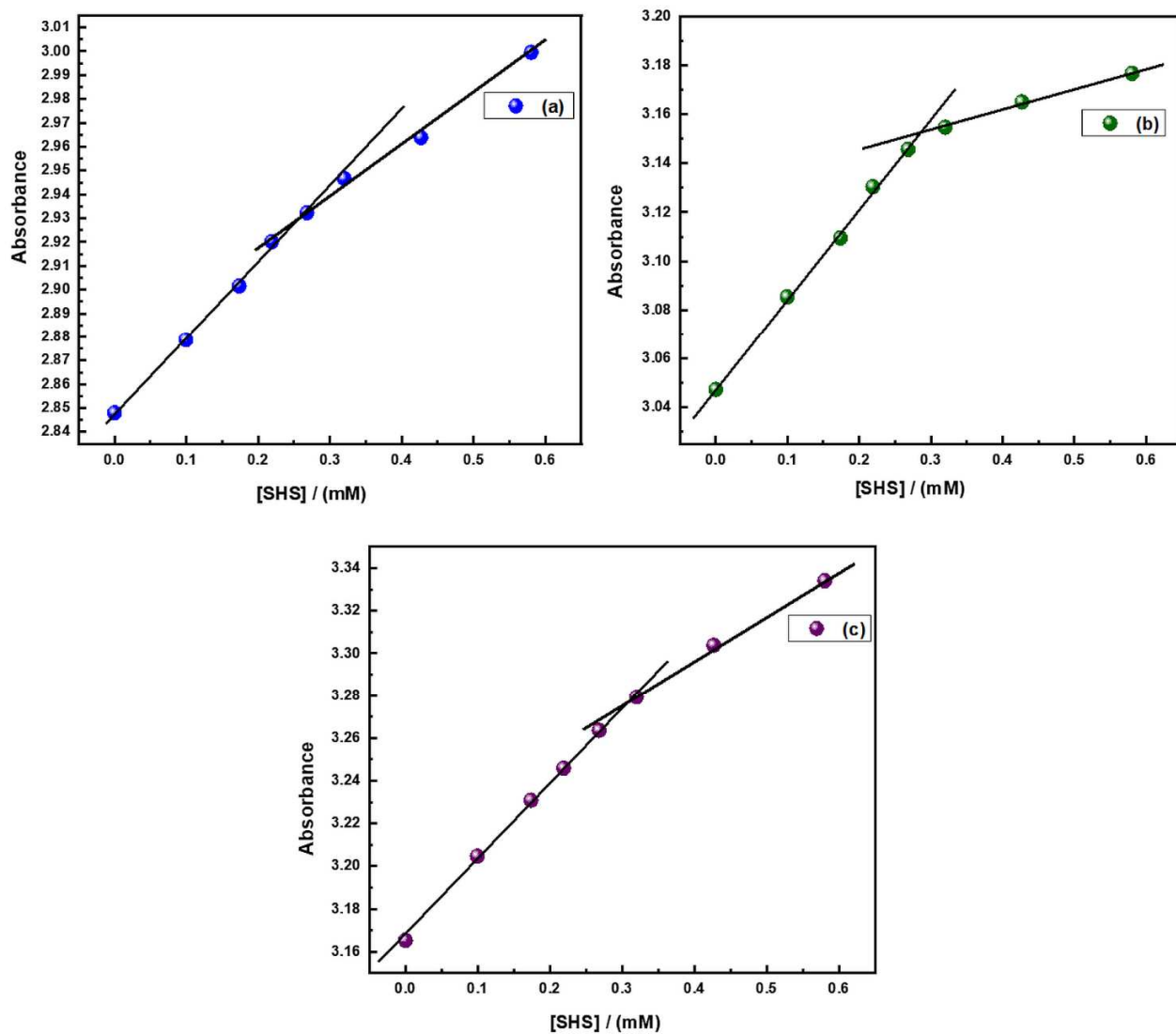
Figure 7 Variation of absorbance with concentration of SHS in presence of (a) 0.02 wt. % (b) 0.05 wt. % (c) 0.10 wt. % of [C$_5$mim][Br] in the aqueous media.
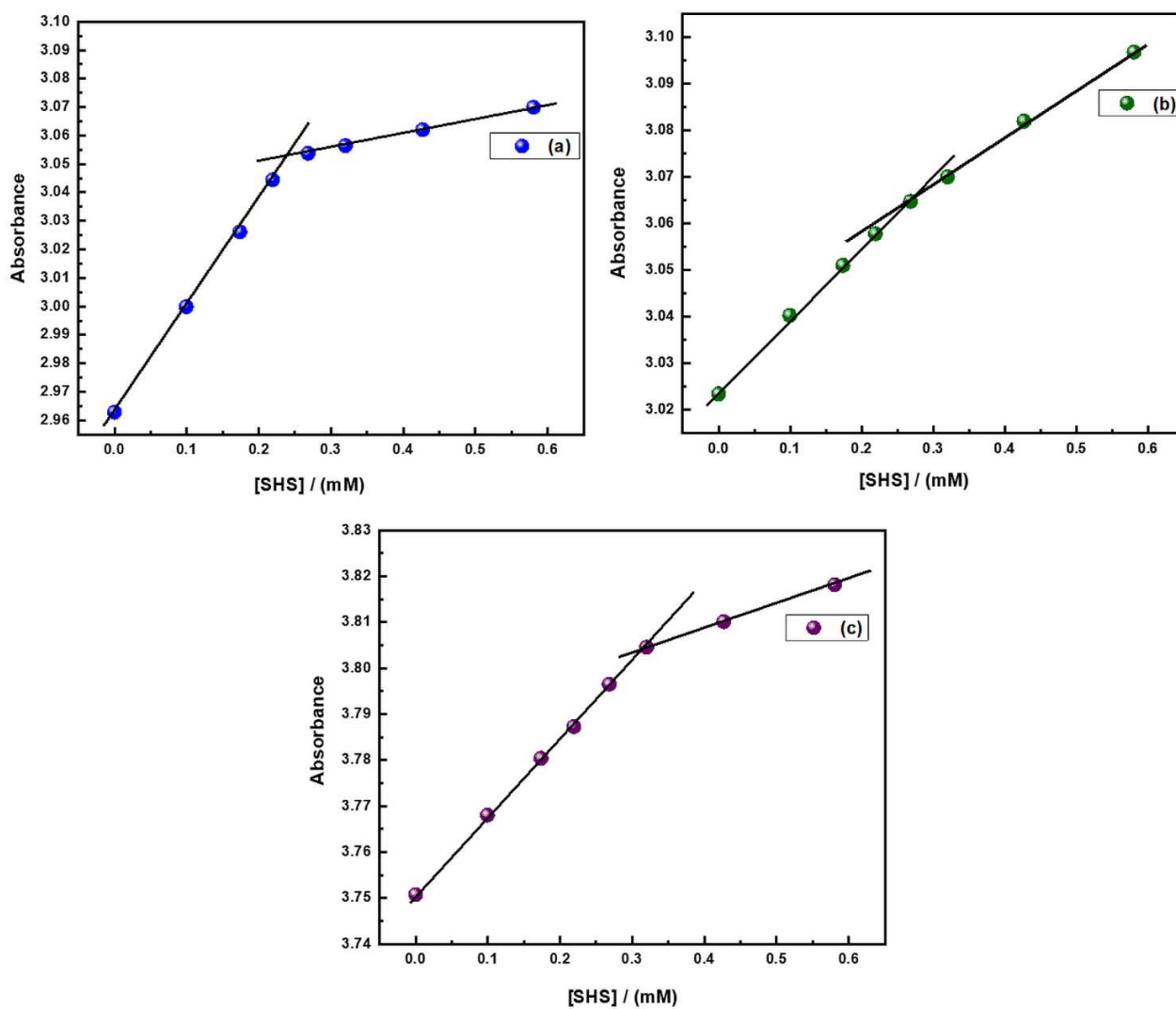
Figure 8 Variation of absorbance with concentration of SHS in presence of (a) 0.02 wt. % (b) 0.05 wt. % (c) 0.10 wt. % of [C$_6$mim][Br] in the aqueous media.
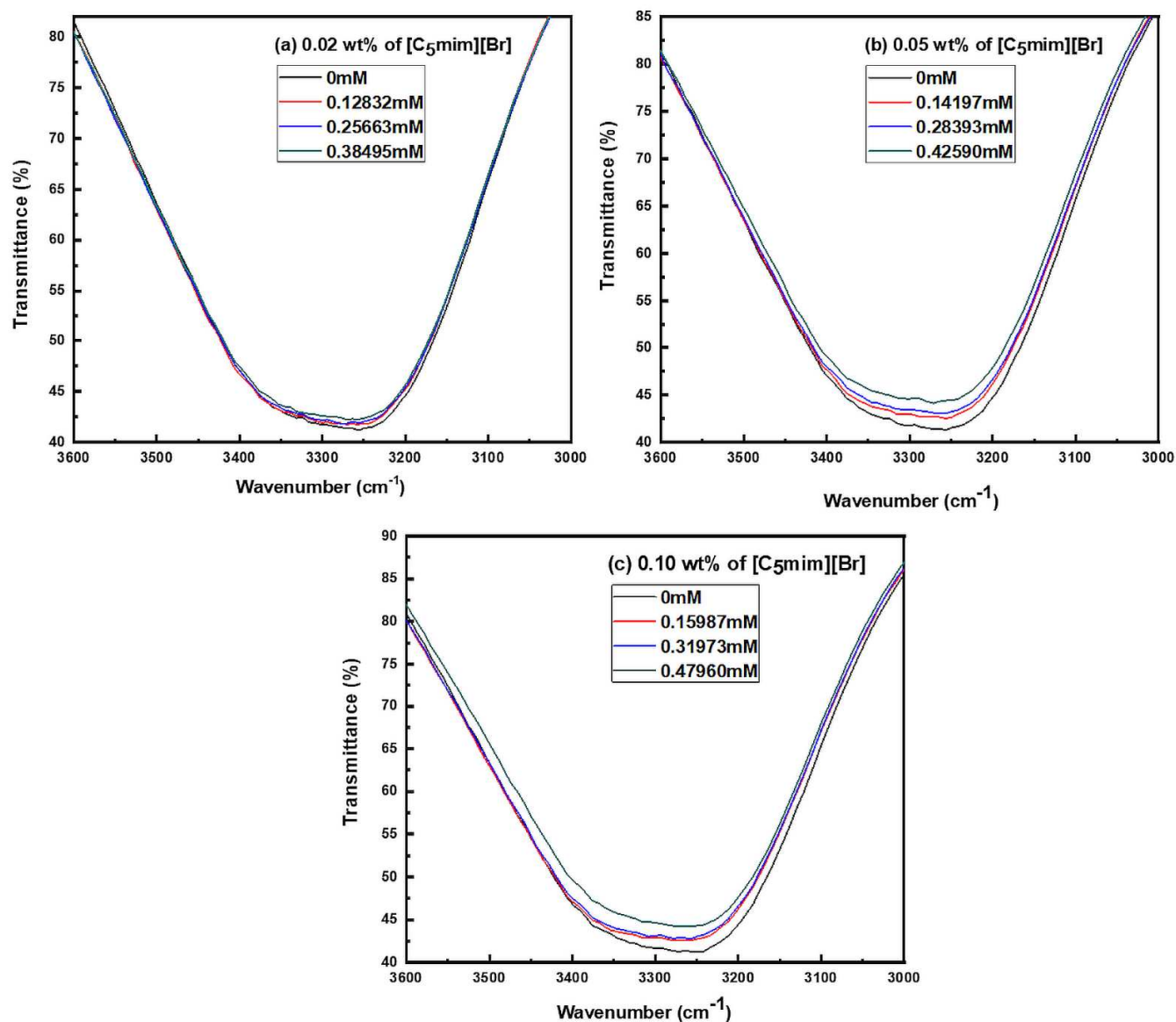
Figure 9 FT-IR spectra of SHS in (a) 0.02 wt. % (b) 0.05 wt. % (c) 0.10 wt. % of [C$_5$mim][Br] in the wavenumber range 3000-3600 cm^{-1} at different concentrations of SHS.

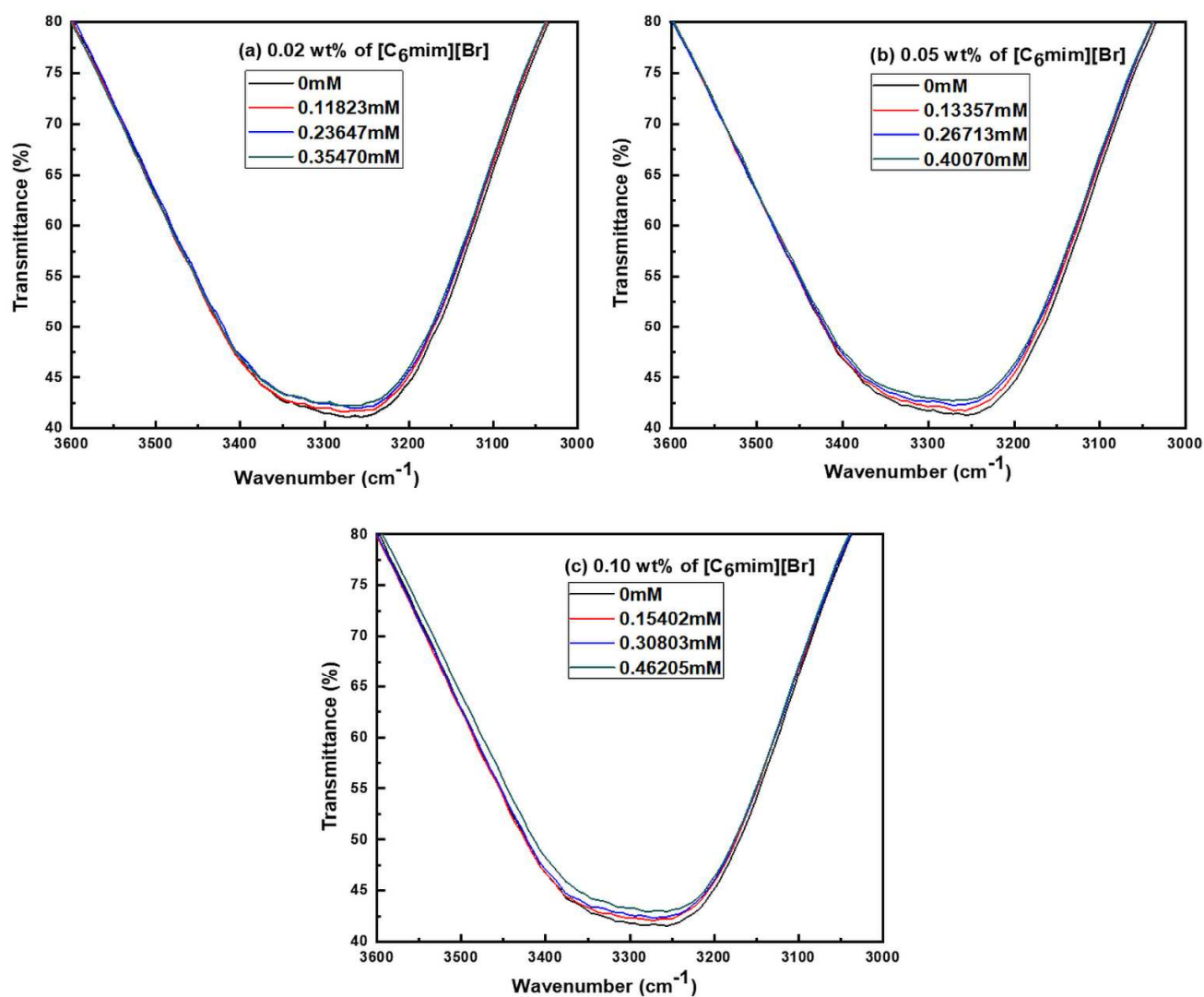**Figure 10** FT-IR spectra of SHS in (a) 0.02 wt. % b) 0.05 wt. % (c) 0.10 wt. % of [C$_6$mim][Br] in the wavenumber range 3000-3600 cm^{-1} at different concentrations of SHS.

Research Highlights

- Conductivity measurement of [C$_5$mim][Br] and [C$_6$mim][Br] with sodium hexadecyl sulfate (SHS).

- Fluorescence, UV-visible and FT-IR spectral analysis of solutions

- Continuous increment in CMC value with the increase in concentration of ILs and temperature.

- Micellization of SHS is more in presence of [C$_6$mim][Br] as compared to [C$_5$mim][Br].

- Thermodynamic parameters of micellization such as, ΔG_m^0, ΔH_m^0 and ΔS_m^0 have been evaluated.

Deciphering aggregation behavior and thermodynamic properties of anionic surfactant sodium hexadecyl sulfate in aqueous solutions of ionic liquids [C$_5$mim][Br] and [C$_6$mim][Br]

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Conflict of Interest

Authors declare no conflict of interest.

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