Effect of Glycol Additives on CMC of Imidazolium Cationic Surfactants

Madhu Chandel[1], Satwinderjeet Kaur[2] and Pankaj Patial*[3]

[1]P.G. Department of Botany, Khalsa College, Amritsar,
[2]Department of Botanical and Environmental Sciences, Guru Nanak Dev University, Amritsar, Punjab.
[3]Department of Chemistry, S.G.A.D College Khadoor Sahib, Tarn-Taran.

Abstract : Changes in critical micelle concentrations (cmc's) of six cationic surfactants 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride, 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium chloride, 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium chloride having different counter ions have been investigated by electrical conductivity and tensiometric measurements. It was found that increase in concentration of ethylene glycol, diethylene glycol and triethylene glycol added to surfactant aqueous solution caused an increase in cmc's of surfactants, provoked by the decrease in interfacial Gibbs energy. There is decrease in wavelength and increase in absorption with the increase in additive concentration. The effect on cmc was maximum in case of triethylene glycol.

Keywords: cationic surfactants, cmc, ethylene glycol, diethylene glycol, triethylene glycol, interfacial gibbs energy.

Introduction

Cationic surfactants are receiving extensive attention in both pure and applied science such as skin care, antibacterial regimens, construction of high porosity material, transdermal drug delivery and so on [1-3]. Surfactants are also being used in the removal of dyes from the effluents [4-6]. A considerable number of investigations have been reported on the synthesis of many cationic surfactants and study of their unusual physico-chemical properties including their surface activity, micelle structure and aberrant aggregation behavior [7-10]. Recently these compounds were also applicable in the solubilization of dyes and pigments in the textile industry [11], gene therapy [12], the synthesis of highly mesoporous materials [13], etc. Nowadays, they are one of the most interesting objects of surface science. In comparison with the amount of work done on the physico-chemical properties of the surfactants in water, polar solvent and apolar solvent, the study of the surfactants in polar solvent or its mixture with alcohol is a rather limited field. During the last years, interest in studying the aggregation of surfactants in polar solvent and mixed aqueous solution has been increased considerably [14-18]. Some new high effective pesticides, such as netenpyrem, thiamethoxam etc. can't solve in water or apolar solvent. In order to improve the efficiency, high security and environmentally friendly property, at first these technical materials must be solved in polar solvent, and then go into the making of the oil in water microemulsion [19].

The effects of various additives on micelle formation have been widely studied by various techniques such as conductivity measurements, surface tension measurements etc [20-22]. To understand the effect of additives, it is necessary to distinguish between two classes of organic materials that markedly affect the critical micelle concentration (cmc) of the aqueous solution of surfactant: (i) those materials that affect the cmc by being incorporated into the micelle, and (ii) those additives that change the cmc by modifying the solvent-micelle or solvent-surfactant interactions [23]. The presence of structure breakers in the aqueous phase may disrupt the organization of water structure resulting from dissolved hydrophobic groups [24], thereby increasing the entropy of micellization. Because of the fact that an increase in entropy disfavours the micellization, a higher bulk concentration of surfactant is required for micelle formation; that is, the cmc is increased [25-26]. There has been a considerable amount of research that involves the effects of nonaqueous polar solvents, such as glycerol, formamide and glycols, on the micellization process [27-29]. Glycols have fascinating solvation behavior, similar to that of water [30]. In the presence of water, glycol acts as a water structure breaker, which leads to the formation of new structure knitted with hydrogen bonding between the water

and glycol molecules. Such a combined structured phase also provides a complete hydrophobic environment for amphiphilic molecules of surfactants to assemble in a similar way as they do in pure water [31-34]. Therefore in view of the above facts, we opted to perform a systematic study on the micellization of six cationic surfactants (1-(decyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium bromide, (1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride, 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium chloride, 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium chloride in the presence of ethylene glycol, diethylene glycol and triethylene glycol at different concentrations, which are known for their high cohesive energies and considerable hydrogen bonding capabilities that favors the aggregation of surfactants monomers to form the micelle. It is expected that the different concentration of glycol additive will affect the micelle formation. The measurements of cmc have been performed with a conductivity technique which seemed to be most useful tool for determination of micelles. The cmc values and free energy of micellization were calculated.

Experimental

Materials/Methods

Chloroacetic acid (AR), bromoacetic acid (AR) and 1-methyl imidazole (AR) were purchased from Sigma-Aldrich Chemical co. USA. Decyl alcohol (Decanol AR), Lauryl alcohol (Dodecanol AR), Myristyl alcohol (Tetradecanol AR) and silica gel for T.L.C was purchased from S. D. Fine Chemicals Ltd; Mumbai India. Sulphuric acid (AR) was purchased from Merck, Germany. All the chemicals were used as received.

General Procedure

Preparation of decyl/dodecyl/tetradecyl 2-chloro/bromo acetate (1-6)

The preparation of these esters from halogenated fatty acids has earlier been reported [35]. However, we herein, report the modified procedure for their preparation with excellent yield, that too in a short time. Chloro/bromo acetic acids (0.01 mole; 0.94 g for chloroacetic acid and 0.137g for bromo acetic acid) was added in a fatty alcohol (0.01 mole; decyl 0.180 g; dodecyl 0.214g; tetradecyl 0.242g) followed by the addition of catalytic amount of sulphuric acid . Contents of the flask were then stirred for 2-3 hours at 60 ^{0}C. The progress of reaction was monitored by thin layer chromatography [silica gel G coated (0.25 mm thick) glass plates using hexane/ethyl acetate (98:5)

as mobile phase, the spots were visualized in iodine]. The reaction got completed in 3 hours. In each case the crude reaction mixture was extracted with 50 ml of chloroform and washed repeatedly (3 X 25ml) with water and then dried over sodium sulphate. Chloroform was removed from crude reaction mixture under reduced pressure in a rotary flash evaporator at 40 ^{0}C. An individual crude product was then purified using aqueous methanol (i.e. the crude compound was taken in a separating funnel and 10 ml of methanol was added with a drop of water which led to the settling of product at the bottom in its purest form). The yields of resulting esters are reported in parenthesis {decyl-2-chloroacetate (91%), dodecyl-2-chloro acetate (92%), tetradecyl-2-chloroacetate (92%), decyl-2-bromoacetate (92%), dodecyl-2-bromoacetate (94.4%) and tetradecyl-2-bromoacetate (90.1%)}.

Preparation of surfactants [7, 8 (a, b, c)]

Each resulting ester (1-6) was immediately reacted with 1-methyl imidazole in 1:1molar ratio (0.01mol) at 60 ^{0}C for 30 minutes (for chloro esters) and 15 minutes (for bromo esters) i.e. for 1, 2.792g; for 2, 3.072g; for 3, 3.353g; for 4, 2.347g; for 5, 2.628; for 6, 2.908g; and 1-methyl imidazole (0.821g) were taken. In each case the resulting crude product was crystallized with ether and subsequently recrystallized in cold acetone to get the pure compounds 7and 8 (a, b and c) which were characterized on the basis of ^{1}H, ^{13}C NMR, DEPT experiments and mass spectral analysis as 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium bromide(7a), 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide(7b), 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium bromide(7c), 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium chloride(8a), 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium chloride(8b), 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride)(8c). The scheme of the reaction is given in scheme 1.

Spectral results

1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide 7(b): white solid, Yield, 92.5%. Melting point is 72 ^{0}C. ^{1}H NMR (δ ppm, CDCl$_3$,): 0.85 (t, 3H, CH$_3$), 1.23(br, s, chain 16H, (-CH$_2$-)$_8$), 1.61 (m, 2H, CH$_2$ next to terminal methyl group), 2.01 (m, 2H, CH_2CH$_2$CO$_2$), 4.05 (t, 2H, CH_2CO$_2$), 4.16 (t, 3H, methyl group attached to imidazole), 5.44(t, 2H, CO$_2$$CH_2$) 7.29 and 7.41(2s, 1H and 1H, N$CHCH$N), 10.52(s, 1H, NCHN), 75MHz ^{13}C/DEPT NMR (δ ppm, CDCl$_3$): 14.08 (terminal methyl carbon), 22.63(CH$_3$$CH_2$), 25.81 ($CH_2CH_2CH_2CO_2$), 28.31(chain methylene carbons), 31.03(CH_2CH$_2$CH$_3$), 36.70(methyl carbon attached to imidazole), 50.09(CH_2CO$_2$), 66.30(CO$_2$$CH_2$), 123.30 and 123.63 (N$CHCHH$N),

138.01 (NCHN), 166.62(carbonyl carbon). ESI-MS positive ions m/z calculated for $C_{18}H_{33}N_2O_2$: 309.25 Found 309.61. The entire data well corresponds with the previous report [35].

Methods

Conductivity measurements [36-37]

The critical micelle concentrations (cmc) of these surfactants in the presence of additive were determined by the conductivity method. The conductance as a function of surfactant concentration was measured at 25^0C. Measurements were performed with an Equiptronic Conductometer (Auto temperature conductivity meter model E.Q.661) with stirring to control the temperature. The solutions were thermostated in the cell at 25^0C. The precise conductance of 7a, 7b, 7c, 8a, 8b, 8c in glycol+water containing 20% and 50% eg, deg and teg (w/v) in their respective binary mixture were measured at 25°C. The conductance measurements in pure water were also performed.
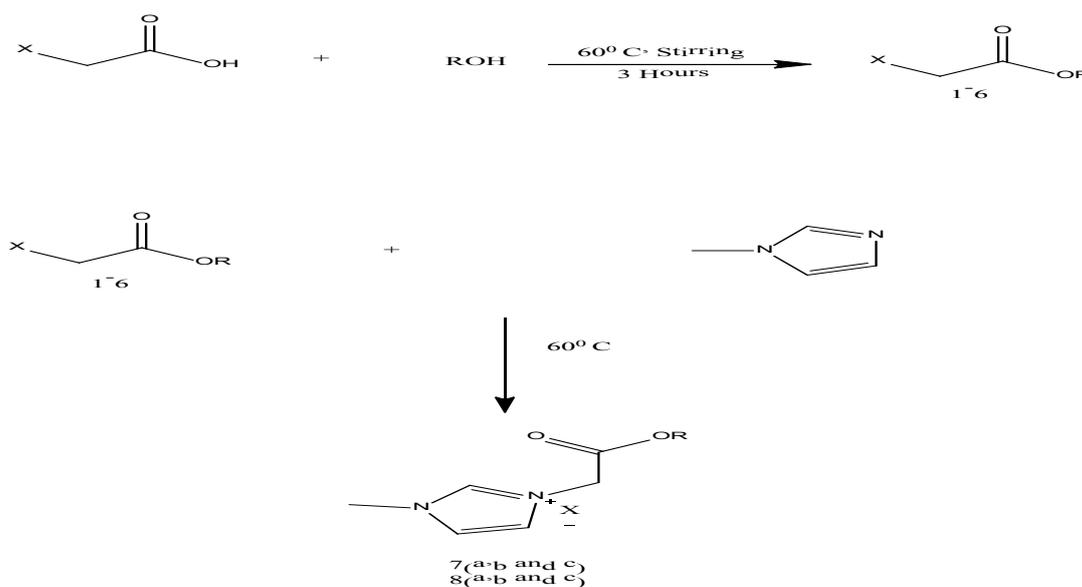
The error in conductance measurements was ±0.5%.

Surface Tension Measurements

Surface tension values were used to calculate cmc using a CSC Du-Nouy interfacial tensiometer (Central scientific Co., Inc.) equipped with platinum-iridium ring (circumference 5.992 cm) at 25 ^0C. The Tensiometer was calibrated using triple distilled water. For the determination of cmc and surface tension, adequate quantities of a concentrated solution of surfactant in glycol+water containing 20% and 50% eg, deg and teg (w/v) in their respective binary mixture were used.

UV measurements

UV absorption spectra of the six cationic imidazolium surfactants were recorded on a Shimadzu model UV-1800 double-beam spectrophotometer, equipped with 1.0 cm quartz cells thermostatted at 25.0 ± 0.1°C.

Scheme of reactions

Scheme 1

X = Cl, Br and R = $CH_3 (CH_2)_9$-; $CH3 (CH_2)_{11}$- and $CH3 (CH_2)_{13}$-.

RESULTS AND DISCUSSION

Surfactant molecules in aqueous solutions undergo aggregation in larger, oriented aggregates called micelles. In dilute solutions, these compounds exists as true electrolyte and in concentrated solutions, micelle formation occurs at a particular concentration {called the critical micelle concentration (cmc)}. In general, it is believed that the interaction between alcohol and water molecules forms hydrogen bonds. Such strong interaction impacts on the formation of the water structure (*iceberg structure*) near the micelle, which weakens the surfactant hydrophobic effect and the ability to form micelles, leading to the increase in cmc.

Effect of additives on the absorption spectra's of surfactants

The data of the absorption as the function of λmax of all the surfactants in water is given in Fig. 1. The effects of additives on UV spectra of surfactant 7 b are shown in Fig. 2, 3, 4, 5. The variation of λmax and absorbance for all the surfactants is reported in Table 1. The table reveals that the absorption increases with the increase in concentration of the additives. The data for deg was out of range, so not given in the Table 1.

Table1: Effect of additive on the absorbance and λmax of cationic surfactants 7and 8 (a, b and c)

Additive (w/v%)	λmax	Absorbance
7a	190.00	1.613
Eg		
20	193.90	3.200
50	196.60	3.284
Teg		
20	198.60	3.306
50	200.40	3.788
7b	193.80	2.470
Eg		
20	197.30	3.183
50	197.80	3.253
Teg		
20	198.70	3.282
50	200.30	3.884
7c	196.20	2.928
Eg		
20	196.70	3.128
50	197.80	3.344
Teg		
20	199.00	3.302
50	200.00	3.825
8a	210.20	0.641
Eg		
20	195.10	2.939
50	195.90	3.158
Teg		
20	198.50	3.329
50	200.90	3.830
8b	211.20	0.770
Eg		
20	193.80	2.878
50	195.30	3.199
Teg		
20	199.40	3.328
50	197.90	3.357
8c	212.20	3.222
Eg		
20	194.80	3.111
50	196.90	3.318
Teg		
20	198.80	3.363
50	199.70	3.771

Figure captions:

Fig. 1 Plot of absorbance v/s λmax of 7, 8 (a, b and c) in pure water.
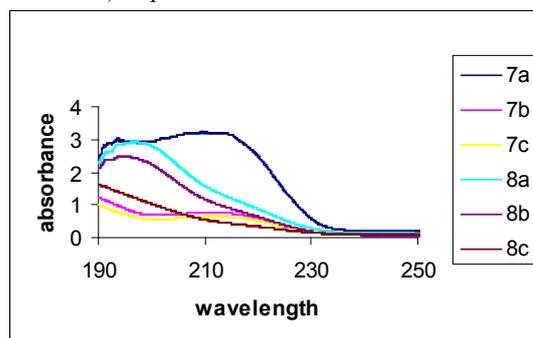

Fig. 1

Fig. 2 Plot of absorbance v/s λmax of 7 (b$_1$, b$_2$ and b$_3$) in (eg)/water mixture in 20% and 50% concentration (w/v).
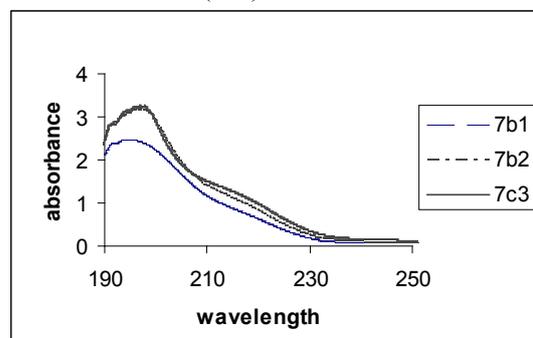

Fig. 2

Fig. 3 Plot of absorbance versus λmax of 7 (b$_1$, b$_4$ and b$_5$) in (teg)/water mixture in 20% and 50% concentration (w/v).
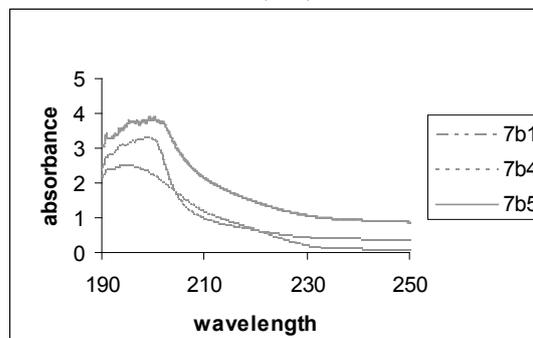

Fig. 3

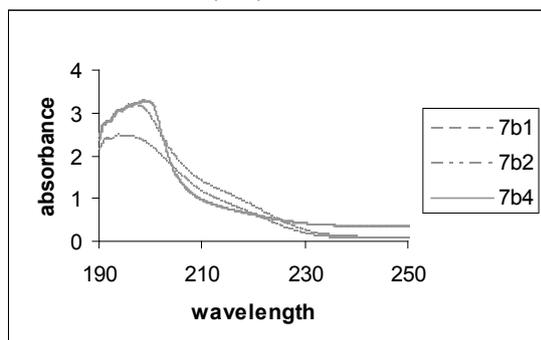**Fig. 4** Plot of absorbance versus λmax of 7 (b₁, b₂ and b₄) in water, (eg)/water, (teg)/water mixture in 20% concentration (w/v).

Fig. 4

Fig. 5 Plot of absorbance versus λmax of 7 (b₁, b₃ and b₅) in water, (eg)/water, (teg)/water mixture in 50% concentration (w/v).
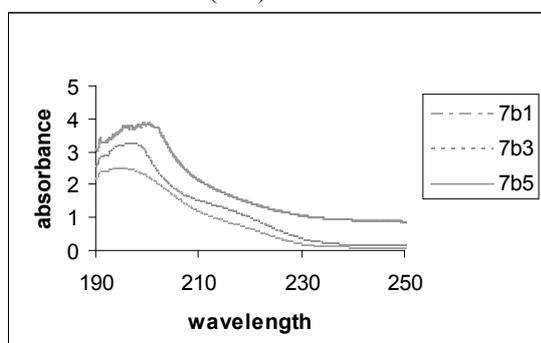

Fig. 5

The Fig. 1 reveals that the surfactants having chlorides as counter ion have less absorbance than the surfactants with bromides as the counter ions. In all the six surfactants as the chain length decreases, λmax shifts toward higher wavelength and the absorbance increases with decrease in chain length. The above figures show that as the concentration of eg and teg is increased from 20% to 50% the absorbance increases and the λmax shows bathochromic shift. However in case of surfactants with chlorides as counter ions, on addition of glycols, there is hypsochromic shift. But on increasing the concentration of glycols slight bathochromic shift was obtained. The hypsochromic shift is more in case of eg than in teg. The absorbance shows an increase with the change from eg to teg.

To corroborate these effects on the addition of additives to surfactant solutions conductivity and surface tension measurements were carried. Gibbs free energy (ΔG_m) was also calculated to support the effect of additives. The data is reported in Table 2. The effect of additives on the cmc of the surfactant solution is depicted in Fig. 6 and the effect on the surface tension behavior is depicted in Fig. 7.

The values of *cmc, surface tension*, ΔG_m are all summarized in Table 2.

Table2. Data reporting the *cmc* values by conductivity and surface tension measurements, surface tension at cmc and Gibbs free energy of micellization (ΔG_m) at 25°C for surfactants and surfactants /additives.

Additive (w/v%)	Cmc by conductivity (mM)	Cmc by surface tension (mM)	Surface tension at cmc (mN/m)	ΔG_{mic} kJ/mol
7(a)	0.038	0.034	51.3	-35167.41
eg				
20	0.062	0.05	41.4	-33954.52
50	0.14	0.12	39.2	-31936.52
deg				
20	0.13	0.11	39.4	-32120.13
50	0.17	0.16	37.1	-31455.48
teg				
20	0.19	0.17	36.8	-31179.92
50	0.23	0.21	34.9	-30706.56
7(b)	0.21	0.20	49.7	-30931.95
eg				
20	0.41	0.37	35.1	-29274.33
50	0.45	0.40	33.5	-29043.69
deg				
20	0.47	0.43	33.4	-28935.96
50	0.57	0.53	31.9	-28638.29
teg				
20	0.57	0.54	31.9	-28458.02
50	0.64	0.61	31.3	-28171.04
7(c)	0.70	0.68	30.4	-27949.04

eg				
20	0.81	0.77	29.7	-27587.41
50	0.93	0.88	27.4	-27245.13
deg				
20	1.05	1.01	26.9	-26944.45
50	1.40	1.29	26.4	-26231.70
teg				
20	1.9	1.50	27.1	-25475.05
50	2.1	1.91	27.3	-25227.13
8a	0.04	0.038	39.3	-34979.15
eg				
20	0.12	0.11	38.1	-32318.44
50	0.36	0.34	37.7	-29596.55
deg				
20	0.14	0.11	38.3	-31936.52
50	0.41	0.39	36.6	-29274.33
teg				
20	0.17	0.14	38.1	-31455.48
50	0.19	0.17	37.9	-28638.29
8b	0.31	0.30	35.6	-29967.02
eg				
20	0.58	0.55	34.9	-28414.93
50	0.69	0.65	32.5	-27984.60
deg				
20	0.70	0.66	32.5	-28171.04
50	0.81	0.77	31.4	-28587.41
teg				
20	0.93	0.91	30.6	-27245.13
50	1.02	0.98	30.4	-27040.68
8c	0.79	0.76	26.1	-27649.35
Eg				
20	0.83	0.79	25.7	-27526.98
50	0.95	0.91	24.1	-27192.42
deg				
20	1.41	1.12	22.5	-26214.07
50	2.01	1.97	22.1	-26227.13
teg				
20	2.10	1.99	22.1	-25203.65
50	2.56	2.12	21.9	-24736.40

Effect of Additive on cmc

Ethylene glycol (eg), diethylene glycol (deg) and triethylene glycol (teg) as additives have a profound effect on the cationic surfactant micellar properties. Ethylene glycol is highly water soluble and has less impact on the structure of water than deg which has less than teg so eg shifts cmc lesser than deg which is lesser than teg.

Conductance measurement

The cmc values from specific conductance (κ) vs concentration plot (Fig. 6) of cationic surfactants with different head groups in the presence of eg, deg and teg with different concentration at a constant temperature of 25 ^{0}C were determined from the breakpoint obtained by extrapolating the slopes. The experimental cmc value of these cationic surfactants without any additive was found to be in a good agreement with the literature value.

It is found that the surfactants with chlorides as counter ion have higher cmc as compared to the surfactants with bromides as counter ions [38]. It is found that cmc increases with increase in concentration of eg, deg and teg [39]. For all surfactants at the range of surfactant concentrations studied, κ increases as concentration increases. However, the rate of increase of κ, relative to concentration, is different below and above the cmc. The rate of increase of κ is higher below the cmc than that above the cmc. It is caused by different degree at which surfactant molecules are ionized. Above the cmc, portions of counter ions are bound to micelles, which result in a reduction in effective charge of the micelle. Thus, the slope of κ vs C above the cmc is smaller than that below the cmc (Fig. 6).

Surface tension measurements

As can be seen in Fig. 7 for all surfactants, two curves intersect at the concentration corresponding to the micelle formation, which allows identification of the cmc. A clear break is observed in all the cationic imidazolium surfactants. On the addition of glycols the decrease in surface tension is enhanced and the breakpoint value is extended to higher concentration indicating an increase in cmc value from eg to deg to teg. Further it is observed from the Fig. 7 that cationic imidazolium surfactants having bromine as a counter ion have low cmc values as compared to the cationic imidazolium surfactants having chlorine as a counter ion. The values for both the conductivity methods and surface tension method, corresponds well with each other.

Gibbs free energy: The Gibbs free energy of micellization for each system was obtained by using the following relation [40]
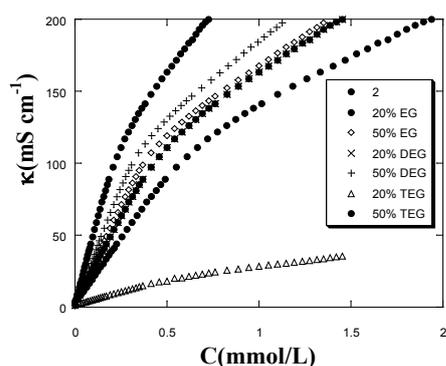
$$\Delta G_m = - RT \ln (cmc)$$

Fig. 6

Fig. 6 Plot of specific conductivity (κ) versus total concentration of 7b in water, eg/water, deg/water and teg/water mixtures in 20% and 50% concentration (w/v)
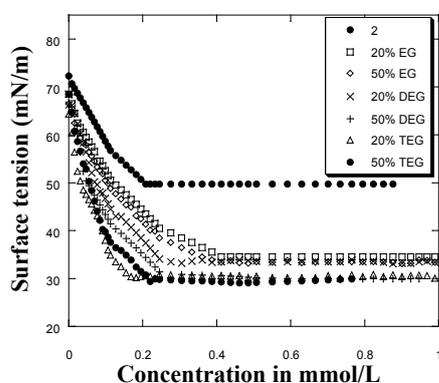

Fig. 7

Fig. 7 Plot of surface tension versus total concentration of 7b in water, eg/water, deg/water and teg/water mixtures in 20% and 50% concentration (w/v)

Conclusions

The absorbance of synthesized imidazole based surfactants having bromide as counter ion with lower cmc was found to be more than the surfactants having chlorine as counter ion. The additives like eg, deg and teg were found to increase the cmc for all the surfactants. The maximum effect is observed in case of teg which was corroborated by the maximum decrease in free energy on the addition [39].

Acknowledgement

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