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Synthesis and characterization of Imidazolium Monomeric Surfactants and to study the effects of additives on their properties

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Abstract
Variations in critical micelle concentrations (cmc's) of six cationic surfactants 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride,1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium chloride, 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride,1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide, 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium bromide having different counter ions have been examined by tensiometric and electrical conductivity measurements. It was observed that increase in concentration of ethylene glycol added to surfactant aqueous solution caused an increase in cmc's of surfactant, followed by the decrease in interfacial Gibbs energy.

Keywords: *Surface Tension, Critical Micelle Concentration, conductivity, ethylene glycol, methyl imidazole.*

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I. Introduction:

A considerable number of investigations have been reported on the synthesis of many cationic surfactants and their unusual physico-chemical properties including their surface activity, unusual micelle structure and aberrant aggregation behavior [1-4]. Furthermore cationic surfactants are receiving extensive attention in both pure and applied science such as skin care, antibacterial regimens, construction of high porosity material, and transdermal drug delivery and so on [5-7].

The effect of various additives have been widely studied by various techniques such as conductivity measurements, surface tension measurements etc [8-10]. In an aqueous solvent, the addition of surfactant results in the removal of the hydrocarbon chain from contact with water via micellization which consequently produces an increase in entropy of the system. The presence of additives in aqueous phase may disrupt the organization of water structure resulting from dissolved hydrophobic group; thereby increasing the entropy of micellization. Because of the fact that an increase in entopy disfavours the micellization, a higher bulk concentration of surfactant is required for micelle formation that is, the cmc is increased [11-12]. Polar organic molecules added to aqueous micellar solutions will alter the tendency of the surfactants molecule to avoid contact with solvent; therefore it is expected to affect the value of surfactant concentration at which aggregation occurs as well as polarity and solvent content in the interfacial region. The presence of polar organic solvents is expected to alter the cmc of surfactants [13-14]. 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 at different concentrations, which are known for their high cohesive energies and considerable hydrogen bonding capabilities that favours the aggregation of surfactants monomers to form the micelle. It is expected that the different concentration of glycol additive will affect the micelle formation [15-20]. 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.

II. Experimental Section:

2.1 Materials:

Chloroacetic acid, bromoacetic acid and 1, methyl imidazole were purchased from Sigma-Aldrich Chemical co. USA. 1-Decanol, Dodecanol, Tetradecanol and silica gel for T.L.C were purchased from S. D. Fine Chemicals

Ltd; Mumbai India. Sulphuric acid was purchased from Merck, Germany. All the chemicals were used as received.

2.2 Methods:

Conductivity measurements [21-22]: Conductivity water having a specific conductance of 4.8 x 10^{-7} S cm^{-1} was used in the preparation of all solutions. The precise conductance of (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 glycol+water containing 20% and 50% ethylene glycol (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 ^{0}C. 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% ethylene glycol (w/v) in their respective binary mixture were used.

2.3 General Procedure:

Preparation of decyl/dodecyl/tetradecyl/2-chloro/bromo acetate: The preparation of these esters from halogenated fatty acids has earlier been reported [23]. 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; 0.94g for chloroacetic acid and 0.137g for bromo acetic acid) was added in a fatty alcohol (0.01mole; decyl 0.158g; dodecyl 0.180 g; tetradecyl 0.214g; 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 (92%), dodecyl-2-chloroacetate (91%), tetradecyl-2-chloro acetate (92%), decyl-2-bromoacetate (90.1%), dodecyl-2-bromoacetate (92%), and tetradecyl-2-bromoacetate (94.4%)}.

Each resulting ester immediately reacted with 1 methyl imidazole in 1:1 ratio at 60 ^{0}C for 35 minutes (for chloro esters) and 20 minutes (for bromo esters). In each case the resulting crude product was crystallized with ether and subsequently recrystallized in cold acetone to get the pure compounds.

III. Results and discussion:

Ethylene glycol as an additive has a profound effect on the cationic surfactant micellar properties. In ionic surfactants the repulsive forces originate from electrostatic repulsion between the polar head groups whereas attractive interactions have generally contributes to the hydrophobic interaction between the non polar tails of surfactant molecule. Therefore an ethylene glycol, additive has significant influence on surfactant micellar properties.

3.1 Critical micelle concentration: Fig. (1-18) represents the plots of conductance versus the total concentration of cationic surfactants with different head groups in the presence of ethylene glycol with different concentration at a constant temperature of 25^{0}C. The break point in each plot is taken as the cmc of the cationic surfactants. 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 cmc increases with increase in concentration of ethylene glycol.

3.2 Surface tension measurements: The cmc of new imidazolium cationic surfactants in glycol+water containing 20% and 50% ethylene glycol (w/v) were calculated by using surface tension measurements at the cmc. The graphs of the surface tension v/s concentration as shown in Fig. (21-38). A clear break is observed in all the cationic imidazolium surfactants. It is observed from the graphs 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 cmc values are reported in table for all the cationic surfactants. The values for both the conductivity methods and surface tension method, corresponds well with each other.

3.3 Gibbs free energy: The Gibbs free energy for micelle formation for each system was obtained by using the following relation

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

In addition, the effect of a cosolvent or additive on the micellization process can be studied by means of so-called free energy of transfer, ΔG_{trans} which is defined by [24]

$\Delta G_{trans} = (\Delta G_{mic})_{GLYCOL\ +\ WATER} - (\Delta G_{mic})_{WATER}$

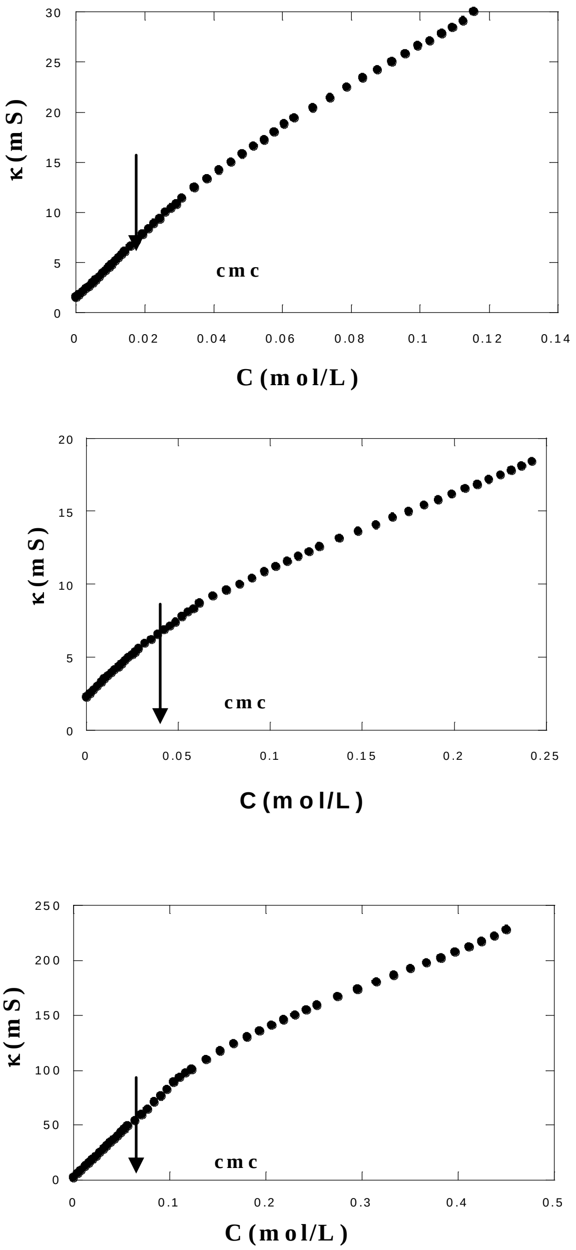
The values of *cmc*, *surface tension,* ΔG_{mic} and ΔG_{trans} are all listed in Table 1.

Table1. Critical micellar concentration (*cmc*) by conductivity measurements, cmc by surface tension measurements, surface tension at cmc and Gibbs free energy for micellization (ΔG_{mic}) at 25°C for surfactants and surfactants /additives, free energy of transfer ΔG_{trans} at 25°C

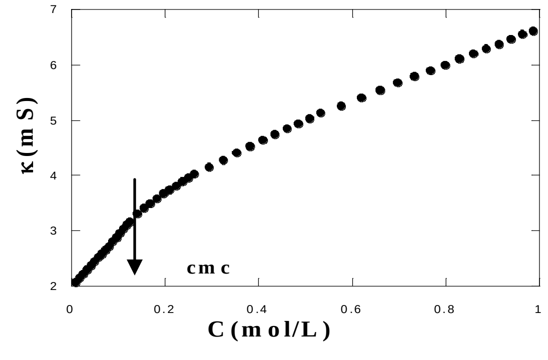
Additive (W/v %)	cmc by Conductivity	cmc by surface tension	surface tension at cmc	ΔG_{mic} kJ/mole	ΔG_{trans} kj/mole
1	0.038	0.034	51.3	-8103.53	
EG					
20	0.062	0.057	41.4	-6890.42	1213.11
50	0.14	0.12	39.2	-4872.06	3231.47
2	0.21	0.20	49.7	-3867.313	
EG					
20	0.41	0.37	35.1	-2209.39	1657.92
50	0.45	0 .40	33.5	-1978.71	1888.60
3	0.70	0.68	30.4	-883.84	
EG					
20	0.81	0.77	29.4	-552.95	330.89
50	0.93	0.88	27.4	-179.83	704.01
4	0.041	0.038	39.3	-7915.24	
EG					
20	0.12	0.11	38.1	-5254.05	2661.19
50	0.36	0.34	37.7	-2531.67	5383.57
5	0.31	0.30	35.6	-2902.21	
EG					
20	0.58	0.55	34.9	-1349.84	1552.37
50	0.69	0.65	32.5	-919.50	1982.71
6	0.79	0.76	26.1	-584.12	
20	0.83	0.79	25.7	-461.72	122.40
50	0.95	0.91	24.1	-127.10	457.02

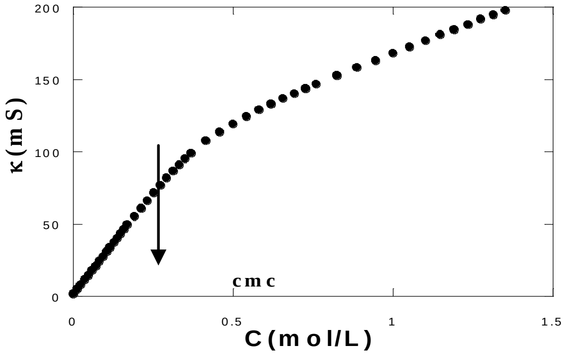
Figure captions:

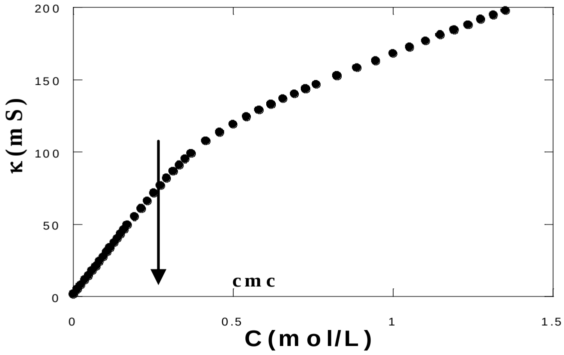
1. Plot of conductance (κ) versus total concentration of 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium bromide in pure water fig (1) and Ethylene glycol (EG)/water mixture fig (2-3) in 20% and 50% concentration (w/v).
2. Plot of conductance (κ) versus total concentration of 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide in pure water fig (4) and Ethylene glycol (EG)/water mixture fig (5-6) in 20% and 50% concentration (w/v).
3. Plot of conductance (κ) versus total concentration of 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium bromide in pure water fig (7) and Ethylene glycol (EG)/water mixture fig (8-9) in 20% and 50% concentration (w/v).
4. Plot of conductance (κ) versus total concentration of 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium chloride in pure water fig (10) and Ethylene glycol (EG)/water mixture fig (11-12) in 20% and 50% concentration (w/v).
5. Plot of conductance (κ) versus total concentration of 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium chloride in pure water fig (13) and Ethylene glycol (EG)/water mixture fig (14-15) in 20% and 50% concentration (w/v).
6. Plot of conductance (κ) versus total concentration of 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride in pure water fig (16) and Ethylene glycol (EG)/water mixture fig (17-18) in 20% and 50% concentration (w/v).



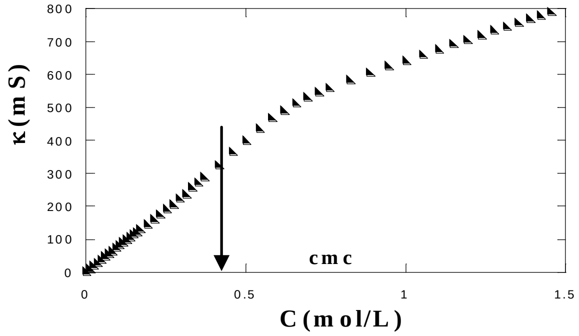
Specific conductivity v/s concentration plot of cationic surfactants (1) and surfactant / additive (2-3).

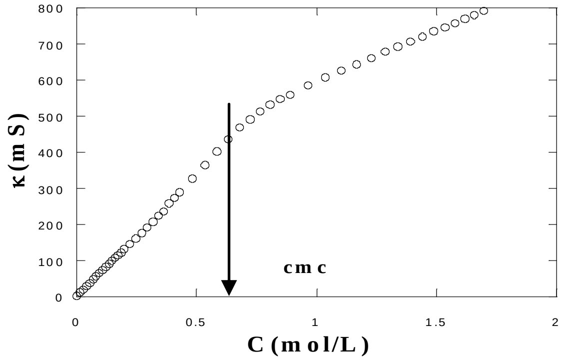


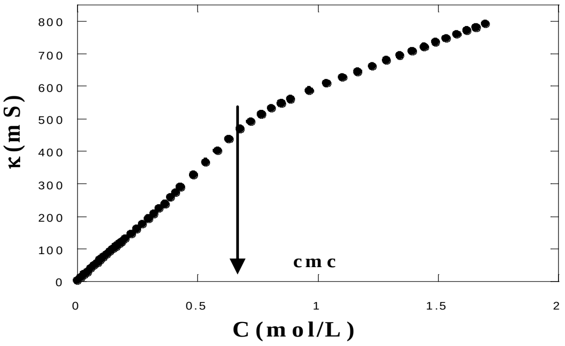




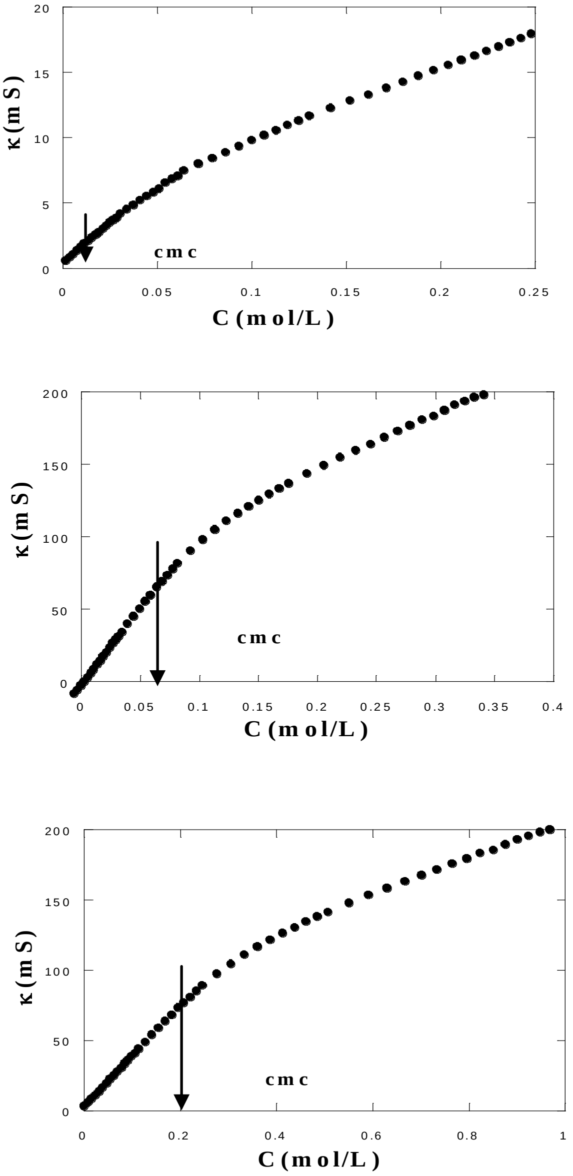
Specific conductivity v/s concentration plot of cationic surfactants (4) and surfactant / additive (5-6).



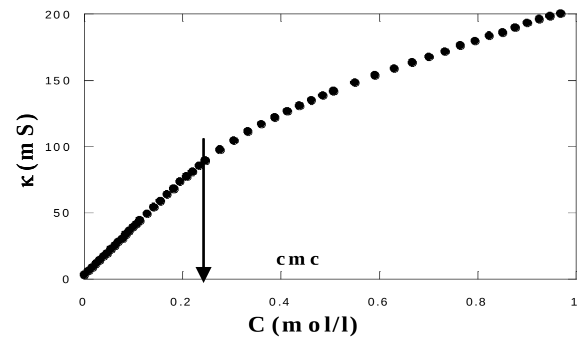


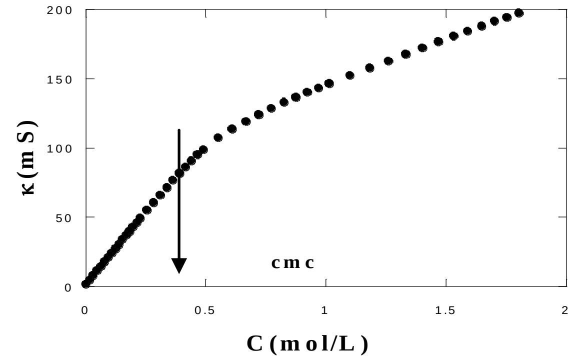


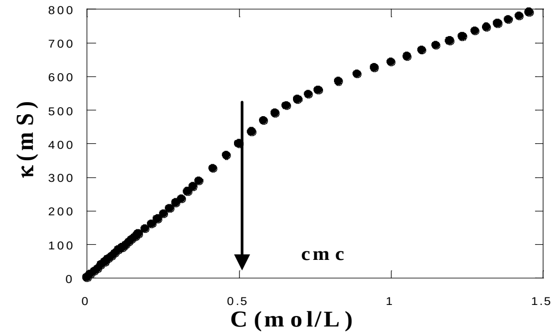
Specific conductivity v/s concentration plot of cationic surfactants (7) and surfactant / additive (8-9).



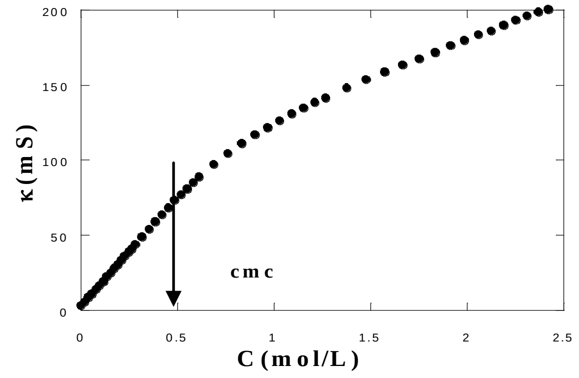
Specific conductivity v/s concentration plot of cationic surfactants (10) and surfactant / additive (11-12).

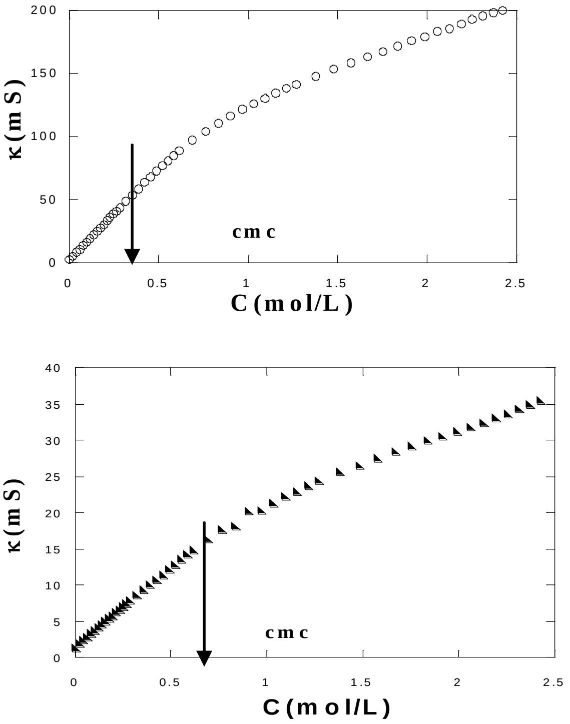






Specific conductivity v/s concentration plot of cationic surfactants (13) and surfactant / additive(14-15).

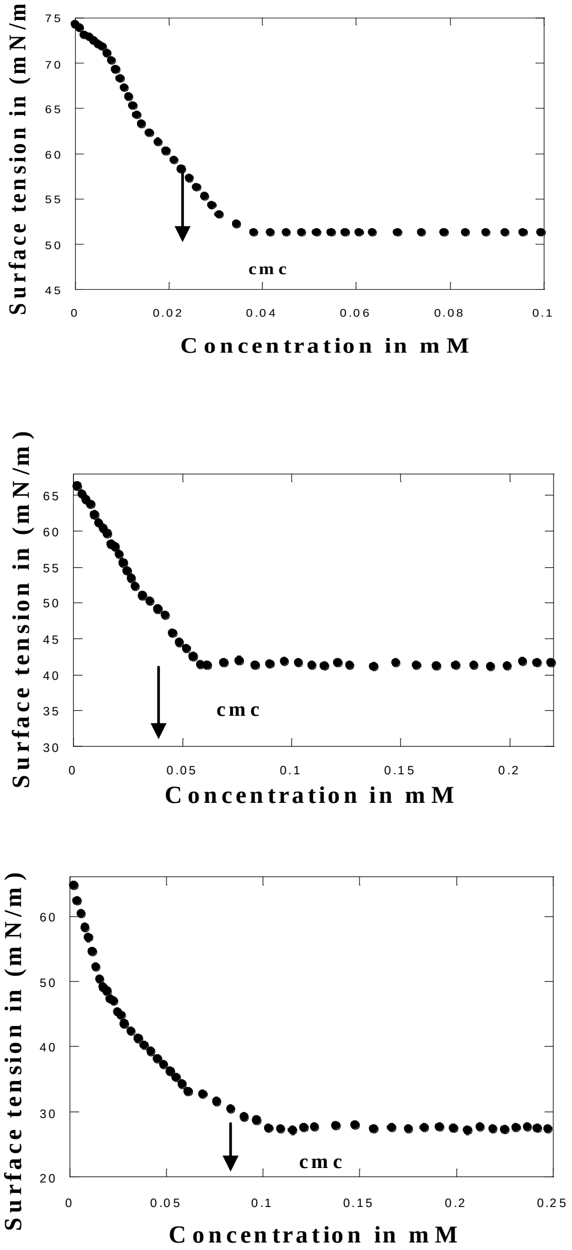




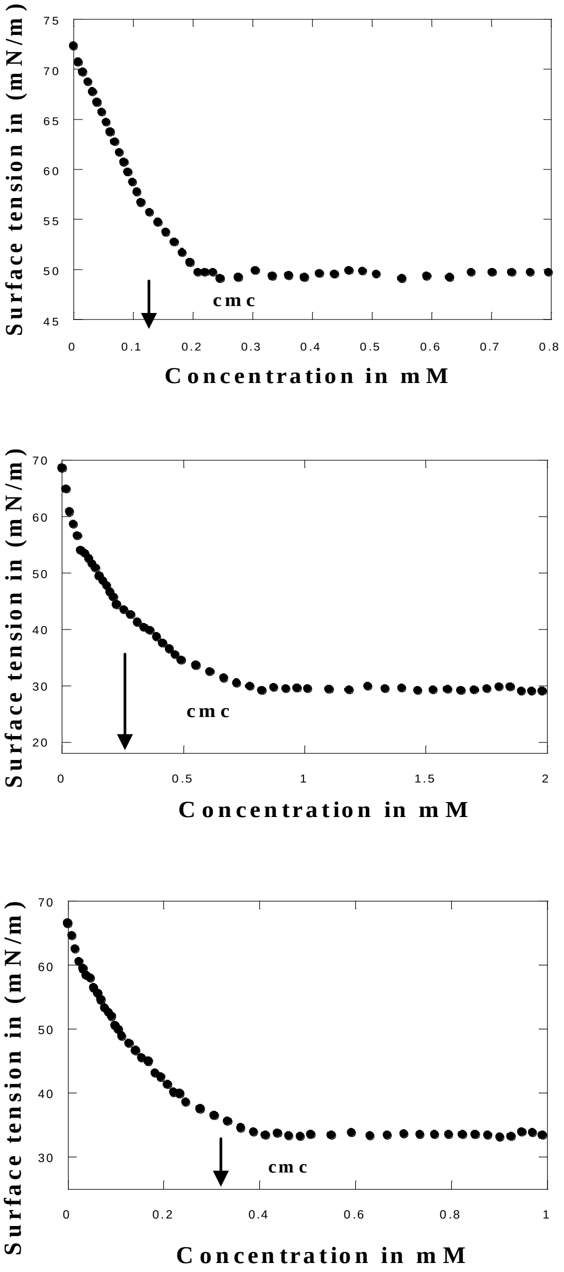
Specific conductivity v/s concentration plot of cationic surfactants (16) and surfactant / additive (17-18).

Figure captions:

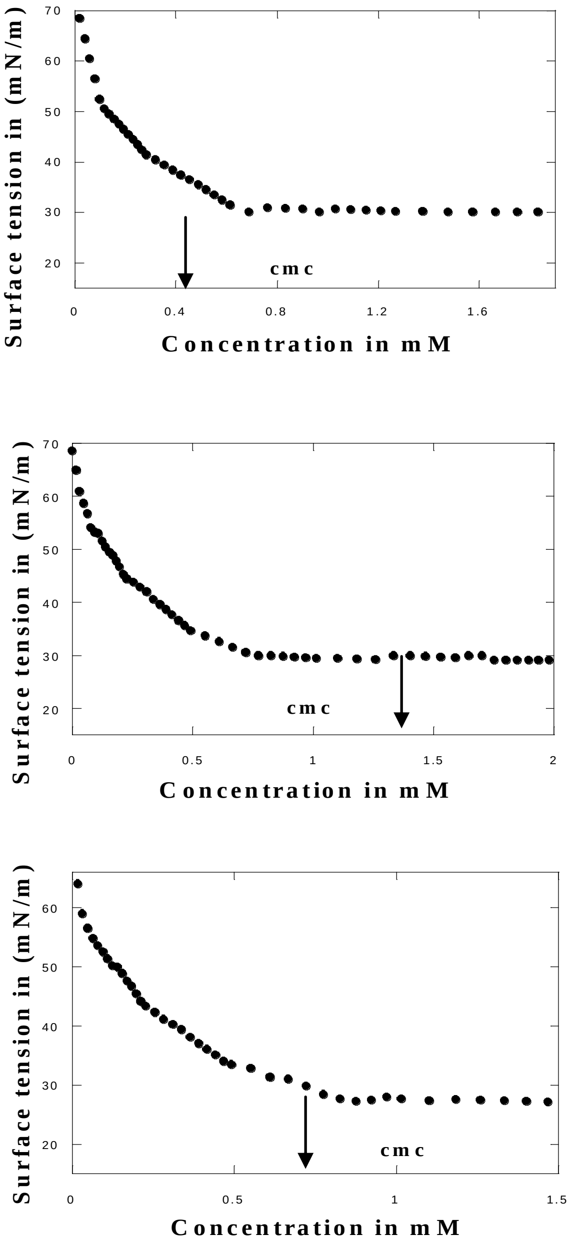
1. Plot of surface tension versus total concentration of 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium bromide in pure water fig (21) and Ethylene glycol (EG)/water mixture fig (22-23) in 20% and 50% concentration (w/v).
2. Plot of surface tension versus total concentration of 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium bromide in pure water fig (24) and Ethylene glycol (EG)/water mixture fig (25-26) in 20% and 50% concentration (w/v).
3. Plot of surface tension versus total concentration of 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium bromide in pure water fig (27) and Ethylene glycol (EG)/water mixture fig (28-29) in 20% and 50% concentration (w/v).
4. Plot of surface tension versus total concentration of 1-(tetradecyl oxy carbonyl methyl)-3-methyl imidazolium chloride in pure water fig (30) and Ethylene glycol (EG)/water mixture fig (31-32) in 20% and 50% concentration (w/v).
5. Plot of surface tension versus total concentration of 1-(dodecyl oxy carbonyl methyl)-3-methyl imidazolium chloride in pure water fig (33) and Ethylene glycol (EG)/water mixture fig (34-35) in 20% and 50% concentration (w/v).
6. Plot of surface tension versus total concentration of 1-(decyl oxy carbonyl methyl)-3-methyl imidazolium chloride in pure water fig (36) and Ethylene glycol (EG)/water mixture fig (37-38) in 20% and 50% concentration (w/v).



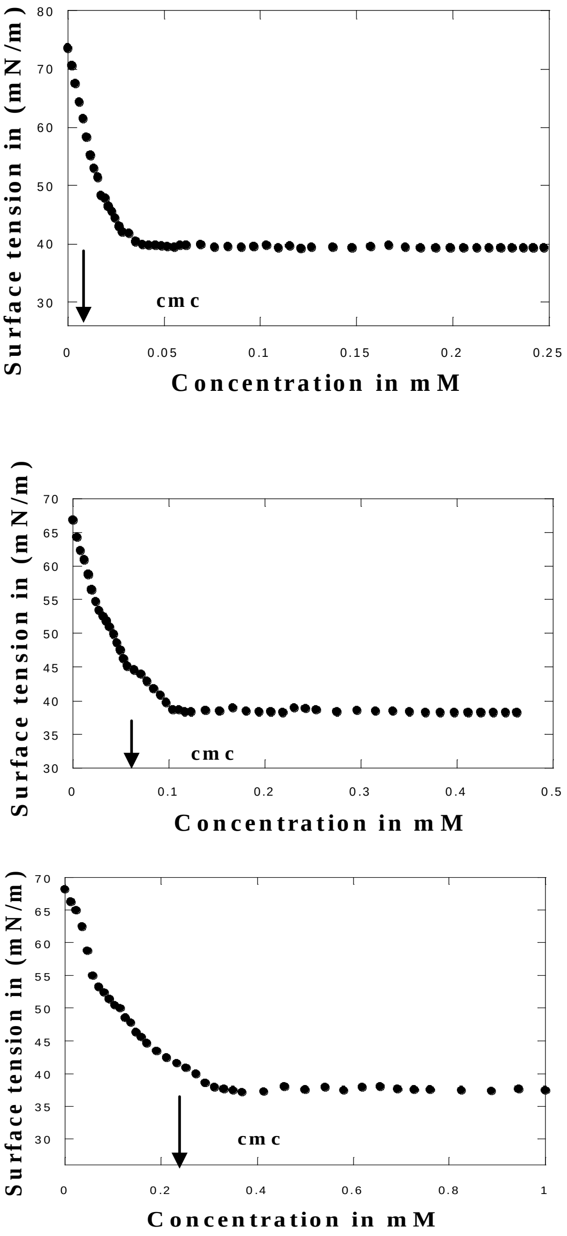
Plot of Surface tension v/s Surfactant concentration of cationic surfactants (21) and surfactant with additive (22-23).



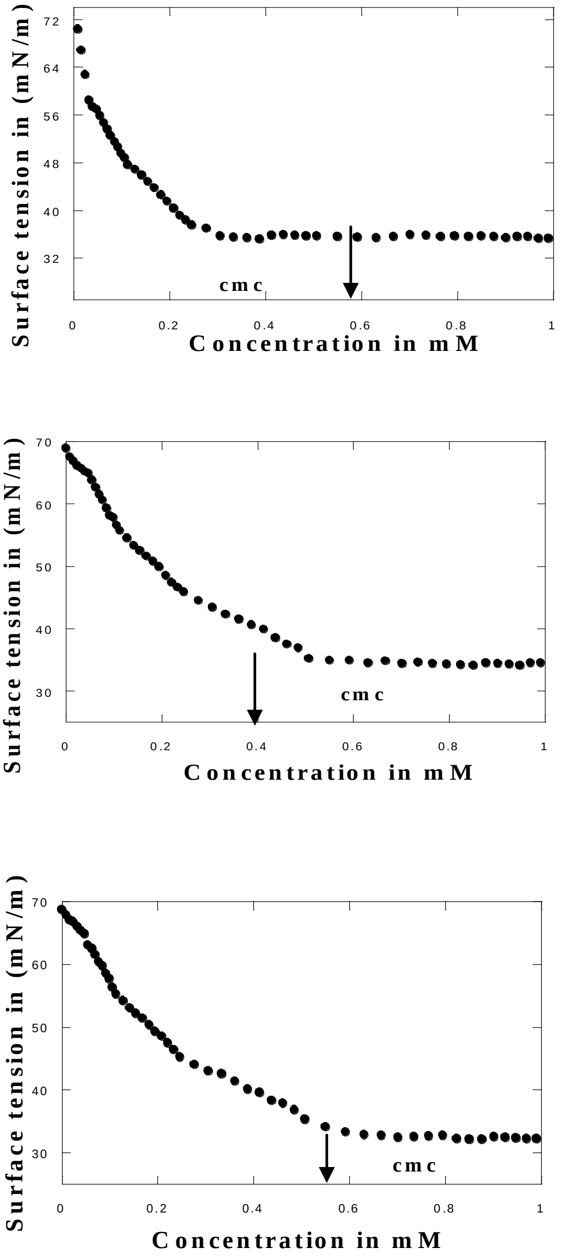
Plot of Surface tension v/s Surfactant concentration of cationic surfactants (24) and surfactant with additive (25-26).



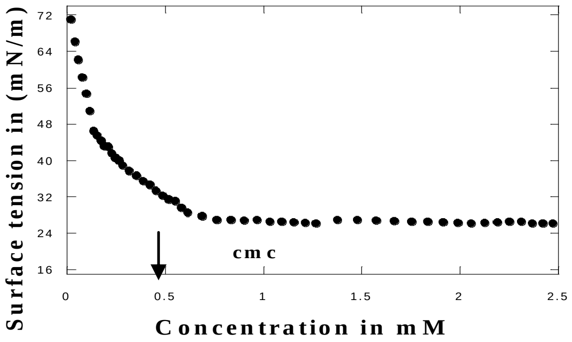
Plot of Surface tension v/s Surfactant concentration of cationic surfactants (27) and surfactant with additive (28-29).

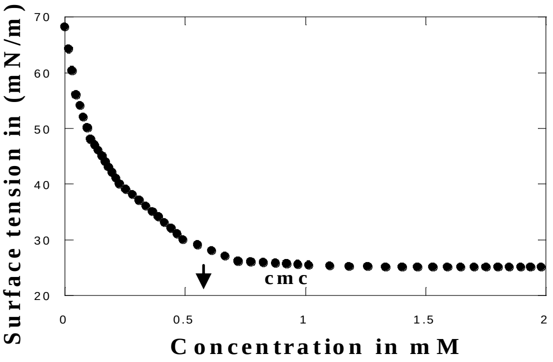


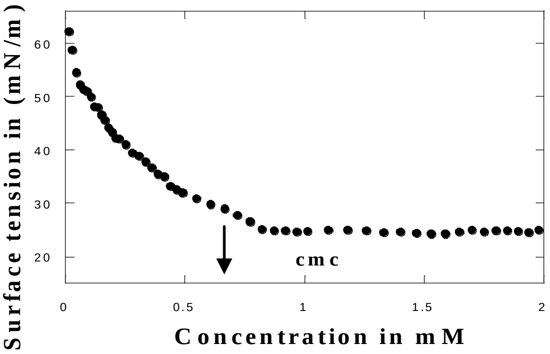
Plot of Surface tension v/s Surfactant concentration of cationic surfactants (30) and surfactant with additive (31-32).



Plot of Surface tension v/s Surfactant concentration of cationic surfactants (33) and surfactant with additive (34-35).







Plot of Surface tension v/s Surfactant concentration of cationic surfactants (36) and surfactant with additive (37-38).

IV. Conclusion:

Ethylene glycol used as an additive has significant influence on surfactant micellar properties. After all study, it is found that cmc value increases with increased ethylene glycol concentration. It is found that cationic imidazolium surfactants having bromine as a counter ion have low cmc values than cationic imidazolium surfactants having chlorine as a counter ion.

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