A Study on Micellization of Cetyl Pyridinium Bromide in Mixed Solvent System

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Abstract: ***During the last few decades the study of micelle formation of surfactant solution and the activities of micelle have undergone an explosive growth.. In the present study, the micellization of cetylpyridinium bromide has been studied in aqueous medium, in ethylene glycol(EG) medium and in mixed solvent medium of varying proportions of both. CMC in mixed solvent systems of 5%, 10% and 15% EG/water medium is found to be same as that in pure aqueous medium. By changing the medium from aqueous to 20% EG / water system brings a rapid decrease in CMC value.The effect of ethanol for the micellization of CPBr is found to be very positive i.e. 5% ethanol decreases the CMC value from 9.0×10^{-4}mole/dm^3to1.0×10^{-4}mole/dm^3. The effect of additives (electrolytes) has also been studied. The effect of NaCl on CMC is found to be negligible but sodium sulphate decreases the CMC.***

Keywords: Cetylpyridinium bromide (CPBr), Micelles, Ethylene glycol,Critical Micelle Concentration (CMC).

1. Introduction

Micellar systems, have been widely investigated and have variety of chemical applications. These systems have been recognized as potentially useful model matrices to study the processes that occur in the complex plasma or cell membrane of living cells and also play a vital role in pharmaceutical industry and other industrial systems. The role of head group size, temperature,counter ion, solvent etc. in the formation of micelle in surfactant solution is important in the point of view of fundamental study and applied fields [1-4]. The minimum concentration of the surfactant at which the micellization starts is known as the critical micelle concentration (CMC).The CMC of surfactant can be affected by theadditives in solution [5]. The effect of additives on properties of surfactant solution has been a subject of great significance in a variety of industrial and technological fields.

2. Literature Survey

Akbas.H and Kartal.C(2006)havestudied the effect of co-solvent on micellization of hexadecyltrimethyl ammonium bromide (CTAB) in aqueous solution by conductivity method [6]. Kallol K. Ghosh and Vidyacharan bhagel(2008) have been studied the micellar properties of benzyldimethyldodecyl-ammonium bromide by conductivity method[7].Deepti and Kallol K. Ghosh(2009) studied the micellization behavior of gemini surfactants in binary aqueous-solvent mixtures [8].Nasiru, Tahirat(2011) et al. studied the CMC of sodium-*n*-dodecyl benzene sulfonate by UV-Visible Spectrophotometric method[9]. Prajapati.K and Patel.S(2012)have been studied the micellization of some surfactants in mixed solvent systems of different polarity[10].Segun E Olaseni et.al(2012) have been studiedmicellization of Cetyltrimethyl Ammonium Bromide in Aqueous -Organic Media. i.e the micellization behavior of cetyltrimethylammonium bromide (CTABr) in different mass fraction of ethylene glycol, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) water mixed solvents [11].May Essa Mahmood & Dhafer A. F. Al-Koofee (2013)studied the effect of temperature changes on critical micelle concentration for tween series surfactant by the fluorescence intensity technique[12].

3. Problem Definition

Cetylpyridinium bromide (C_{21}-H_{38}-N.Br) is a cationic surfactant having various applications as use in mouthwashes, as a disinfectant, as a germicide, deodorant, laboratory reagent, surfactant, and is also frequently used in analytical and physical chemistry. A study on the micellization properties of cetylpyridinium bromide in mixed solvent system of ethylene glycol and waterwill be of great importance as it is being used in various application fields.

4. Methodology

The cationic surfactant Cetylpyridinium bromide was obtained from SD fine chem. Ltd. Ethylene glycol and ethanol were purchased from Merck specialities pvt.Ltd. and used without purification. All other chemicals used were of Guaranteed Reagent grade. In order to determine the critical micelle concentration (CMC) of cetylpyridinium bromide(CPBr), the conductance measurements were carried out for solutions of varying concentrations of CPBr using a conductometer. Before starting the experiment, the conductivity cell was calibrated using KCl solution . The errors in the conductance measurement were within +/- 5 %.. The CMC is obtained from the graph plotted between conductance and concentration of the surfactant ..

5. Result and Discussion

CMC of CPBr

Determination of CMC of CPBr in pure water, in aqueous mixtures of EG (5%, 10%, 15%, 20%, 60%, 70%, 80%, 90%) and pure EG has been carried out through conductance measurements and the results are shown in Table -1 and Fig.1

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Table 1

	Specific Conductance (mS/cm)									
Concentration of CPBr (in Mole/ dm^3)	Aq. Medium	5% EG	10% EG	15% EG	20% EG	60% EG	70% EG	80% EG	90% EG	Pure EG
0.00001	0.18	0.155	0.140	0.120	0.100	0.024	0.022	0.018	0.015	0.001
0.00005	0.19	0.165	0.150	0.130	0.110	0.027	0.023	0.019	0.016	0.002
0.0001	0.20	0.175	0.160	0.140	0.120	0.030	0.027	0.022	0.017	0.003
0.0005	0.23	0.205	0.190	0.150	0.130	0.038	0.028	0.023	0.018	0.005
0.001	0.26	0.235	0.220	0.190	0.140	0.043	0.037	0.026	0.022	0.009
0.003	0.27	0.250	0.235	0.210	0.180	0.068	0.061	0.040	0.031	0.020
0.005	0.29	0.265	0.250	0.230	0.220	0.094	0.085	0.055	0.040	0.032

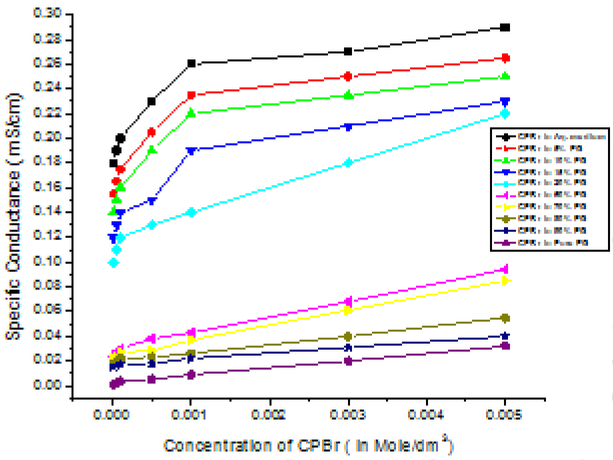

Figure 1: CMC Determination of CPBr

From the plot it is clear that the aggregation of surfactant molecules starts at a CPBr concentration of 1.0×10^{-4} mole/dm^3. But the formation of complete micelle occurs at 9.0×10^{-4} mole/dm^3. It is observed that by the addition of 5%, 10% and 15% ethylene glycol (EG) does not make any difference to the first and second break points of the plot obtained for the aqueous system. But for the 20% EG onwards, the sharpness of the second break point diminishes and found to be merging to the first break point.

6. Effect of Additives on CMC of CPBr in Aqueous System

The concentration of NaCl and Na_2SO_4 were kept constant (0.005 M).The effect of NaCl on CMC is found to be negligible while Na_2SO_4 decreases the CMC of CPBr from 9.0×10^{-4} to 2.0×10^{-4} (Fig.2).

7. Effect of Co-Solvent on Micellization

The effect of co-solvent , ethanol, has been studied by determining the CMC of CPBr in 5% ethanol water system and in varying proportions of ethanol, EG and water systems. The results reveal that 5% ethanol is sufficient to reduce the CMC of CPBr from 9.0×10^{-4} to 1.0×10^{-4}mol/dm^3(Fig.3)

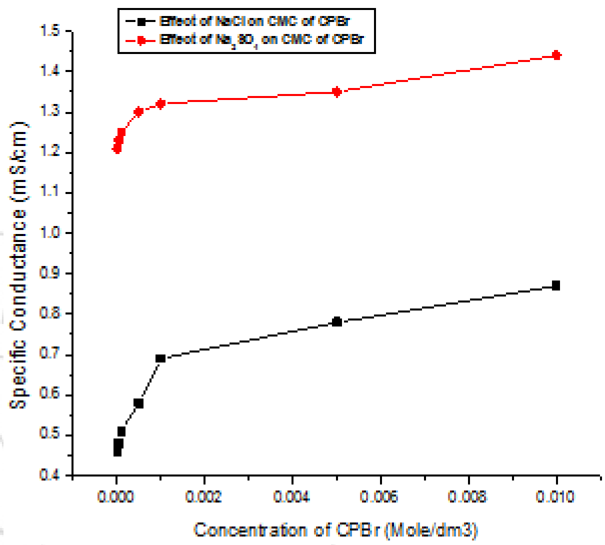

Figure 2: Effect of additives on CMC of CPBr in aqueous system

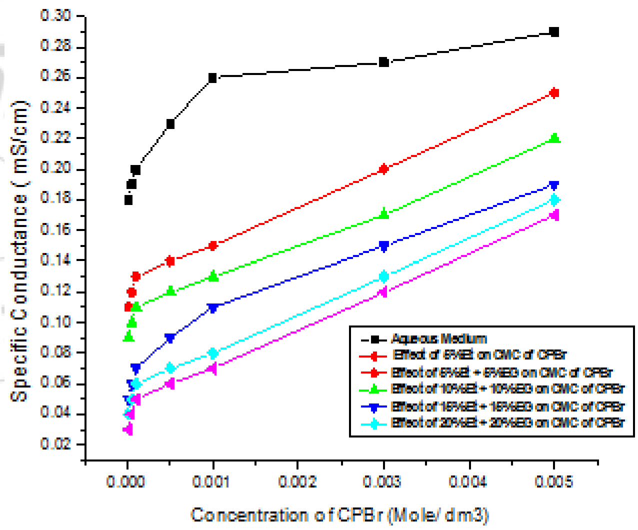

Figure 3: Effect of co-solvent on Micellization

8. Conclusion

From the observations, it is clear that in aqueous medium the formation of molecular aggregates (pre-micellar state) starts at a CPBr concentration of 1.0×10^{-4} Mole/dm^3 and complete micellar formation occurs at 9.0×10^{-4} Mole/dm^3, which is completely agreeable with literature value. The CMC value of CPBr in EG is found to be 1.0×10^{-4} mole/dm^3.The pre-micellar state is not observed in EG medium. CMC in mixed solvent system of 5%, 10% and 15% EG/water medium is found to be same as that in pure aqueous medium. But the

CMC in 20% EG and higher mixed solvent systems are found to be decreasing to the experimentally obtained CMC value of CPBr in pure EG.i.e. 1.0×10^{-4} mole/dm^3. This result is in contrast to that reported for CTABr in mixed solvent system of water and EG where the CMC increases with the increasing concentration of EG [6]. . Among various factors affecting CMC, the hydrophobic effect of hydrocarbon chain, the steric repulsions of the head group and the electrostatic interactions of polar head groups (for ionic surfactants) play great roles in micellization. In the case of CPBr, the steric repulsion of head groups and the electrostatic interaction of charged head groups may be responsible for the pre-micellar stage in aqueous system. Decrease in ionic head group interaction energy in mixed solvents decreases the CMC value. So the influence of the interaction energy of the ionic head groups on CMC of CPBr in mixed solvent system plays a major role in comparison to the role of tail transfer free energy. The effect of ethanol for the micellization of CPBr is found to be very positive i.e. 5% ethanol decreases the CMC value from 9.0×10^{-4}mole/dm^{3}to 1.0×10^{-4}mole/dm^3.The effect of NaCl on CMC of CPBr is negligible but sodium sulphate decreases the CMC. In the presence of sodium sulphate, the decrease of CMC is due to the decrease in electrostatic repulsion between the charged head groups. Free energy change increases by the addition of salt, as a result CMC decrease [13].Hence we conclude that the mixed solvent systems of 20% EG/Watersystem is a better system for micellization of CPBr.

9. Future Scope

The interaction between dyes and surfactants is a subject of some investigation now a days. The phenomenon of solubilization plays an important role in detergency, dyeing process in textile industries, in pharmaceutical applications etc. So the use of these micellar systems of CPBr for the solubilization purposes in different fields will be of great importance and further study is needed in this regard.

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