Asian Journal of Chemistry Vol. 20, No. 6 (2008), 4503-4510

Effect of Polymers on the Micellization of Surfactants by Conductance Measurements

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The micellization behaviour of anionic and cationic surfactants in the presence of charged (human serum albumin and ribonucleic acid) and neutral polyvinyl pyrrolidone polymers was investigated by means of conductance measurements. The plots of conductance *vs.* concentraton of surfactants exhibited sharp inflexion at critical micelle concentration (CMC). The conductance was found to increase with the progressive addition of the respective polymers, however the extent of increase was comparatively more in the premiceller than in the postmiceller regions as the polymer formed mixed micelles. The rise in conductance of surfactants-polymer mixt-ures was ascribed to the alteration in the nature of solvent as the polymer formed mixed micelles with the surfactants by the incorportion of the polar part of polymers in the micelles. Ribo-nucleic acid was found to increase the CMC of cationic surfactants while those for anionic, it was decrases. On the other hand, human serum albumin and polyvinyl pyrrolidone caused a decrease in CMC of both cationic and anionic surfactants. The mechanism has been suggested through electrostatic, hydrophobic and coop-erative types of linkage between surfactants and the polymers.

Key Words: Polymers, Micellization, Surfactants, Conductance.

INTRODUCTION

Owing to great significance of critical micelle concentration (CMC) of surfactants in a variety of industrial and technological fields[1-12]. Arora *et al.*[13-22] have made several binding studies on the linking of surfactants to many proteins employing different physico-chemical methods. Blei[23] investigated the solubilizing properties of sodium alkyl sulphates in the presence of human serum albumin and found that at any surfactant concentration below critical micelle concentration (CMC) the moles of dye solubilized increased with the protein concentration while no dye was solubilized in the absence of the protein. Gamboa *et al.*[24] investigated between anionic polyelectrolytes and cetyl trimethyl ammonium bromide micelles by potentiometrically.

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Arora *et al.*[25] have studied the effect of ovalbumins on the micellization of anionic and cationic surfactants using conductance measurements. Arora *et al.*[26] have also reported the binding constants of anionic and cationic surfactants-polyvinyl pyrrolidone (PVP) interaction by physico-chemical methods. Recently Chauhan *et al.*[27] have reported a conductometric study of interaction between gelatin and sodium dodecyl sulphate in aqueous rich mixtures of dimethyl sulphoxide. A survey of the published literature revealed that no much studies on the effect of polymers on the CMC of surfactants are made on this consideration, it was thought of interest of study the effect of human serum albumin (HSA), ribonucleic acid (RNA) and polyvinyl pyrrolidone (PVP), a neutral polymer, on the micellization of anionic and cationic surfactants employing conductance measurements.

EXPERIMENTAL

Crytalline human serum albumin (HSA, m.w. = 69,000) was obtained from Sigma Chemical Company. Its solution was prepared by dissolving it in deionized double distilled water. The concentration of protein solution was determined by evaporating a known aliquot in an oven at 100 ºC, as well as by a biuret method. Sodium salt of ribonucleic acid (RNA), a Sigma product, was dissolved in double distilled water to get a solution of known strength. Polyvinyl pyrrolidone (PVP, m.w. = 40,000) was obtained from Sigma chemicals and it solution was prepared in double distilled water by direct weighing. Sodium dodecyl sulphate (SDS) was obtained from Chemical De Universe, India, while triethanol amine lauryl sulphate (TEALS) was a product of HICO Pvt. Ltd. India. Its purity was checked by the standard method. The cationic surfactants *viz.*, cetyl pyridinium chloride (CPC) and cetyl trimethyl ammonium bromide (CTMAB), were BDH products and their stock solutions were prepared in double distilled water.

An Elico conductivity meter (Model-CM 180) and a dipping type conductivity cell with platinized electrode was used for measuring the conductance of the surfactants and surfactant-polymer mixtures. These were determined by direct concentration runs. All the conductance determinations were made at constant temperature in a water thermostatic bath.

Methods: Different fixed amounts of polymers (0.0 to 0.07 g/dl) were taken in 20 mL. and then titrated against the known solution of the respective surfactant. The conductivity values were recorded after mixing the solutions. The reproducibility of the determinations was checked by repeating the experiments several times. The reproducibility of the conductance reading was found to be 0.1 per cent. The critical micelle concentration (CMC) of surfactants was determined by means of conductance *vs.* surfactant concentration plots. The results of the dependence of the conductance of surfactant on the concentration of added polymers have been obtained by plotting the curves of conductance against concentration of surfactants.

RESULTS AND DISCUSSION

As critical micelle concentration (CMC) denotes that minimum concentration where a polyelectrolyte changes into a colloidal polyelectrolyte, hence the points of sharp inflection in any physical property *vs.* surfactant concentration curves would correspond to the CMC value of surfactant. The point of inflection in the curve is CMC of surfactant, the lower region of it is called as premicellar while the upper region postmiceller region. In this study the conductance is plotted against surfactant concentration in absence and presence of the added polymeric substances to study the effect of polymers on CMC of surfactants. It is observed that with rising amounts of polymer the angle of inflection regularly decreases and at a concentration of 0.06 g/dl in case of HSA, the inflection almost disappears and the plot assumes the nature of a straight line. Obviously the value of CMC at and beyond this concentration of polymer can't be deduced correctly. The CMC values of ionic surfactants determined in the presence of respective polymers are given in Tables 1 and 2.

It is established that interaction between surfactants and polyampholytes involves primary electrostatic attraction between oppositely charged ionic groups followed by mutual association of the non-polar residues due to vander Wall's forces between them[28]. The ionic interaction between similarly charged detergents and polyampholytes could also take place was pointed

TABLE-1
CRITICAL MICELLE CONCENTRATION (CMC) VALUES OF DETERGENTS IN THE PRESENCE AND ABSENCE OF RNA

RNA (g/dl)	Critical micelle concentration (CMC) × 10^4 M			
	CPC	CTMAB	TEALS	SDS
0.000	8	30	43	65
0.250	–	–	30	–
0.500	2	35	28	60
0.750	–	–	16	–
0.100	32	43	11	55
0.125	–	–	5	–
0.150	41	48	–	52
0.200	52	52	–	47
0.250	63	–	–	–
0.300	–	65	–	24
0.400	–	–	–	20
0.500	–	–	–	10

RNA = Ribonucleic acid, CPC = Cetyl pyridinium chloride, CTMAB = Cetyl trimethyl ammonium bromide, TEALS = Triethanol amine lauryl sulphate, SDS = Sodium dodecyl sulphate.

TABLE-2
CRITICAL MICELLE CONCENTRATION (CMC) VALUES OF DETERGENTS IN THE PRESENCE AND ABSENCE OF HSA

HSA (g/dl)	Critical micelle concentration (CMC) × 10^4 M			
	CPC	CTMAB	TEALS	SDS
0.00	8	30	43	65
0.01	7	25	40	60
0.02	6	19	35	55
0.03	5	15	29	50
0.04	4	10	25	40
0.05	2	5	20	35
0.06	–	–	15	25
0.07	–	–	10	15

HSA = Human serum albumin, CPC = Cetyl pyridinium chloride, CTMAB = Cetyl trimethyl ammonium bromide, TEALS = Triethanol amine lauryl sulphate, SDS = Sodium dodecyl sulphate.

out by previous workers[29] who stated that if one component of a mixture was protein and the other was a detergent, ionic interaction could occur to ranges of pH where both components possesses the same sign of net charge provide there still existed ionized groups on the protein having a sign of charge opposite to that of the net charge. This hypothesis received support from vast experimental work[30-32]. The formation of micelles of anionic surfactants can alter the conformation of protein due to the existance of strong electrostatic and hydrophobic interactions between the micelles and the proteins[33,34].

The decrease in CMC of ionic surfactants on addition of ampholyte may be explained in the light of the above generalizations. At any specific concentration of protein added, the surfactants binds to protein due to electrostatic attraction by the oppositely charged groups so long as it is present in small amounts when all the protein is thus used up, additional surfactants ions enter into combination as a unit with the protein-surfactants adduct already formed. The probable way in which this occurs is that an individual surfactant ion bound at a particular site on the protein molecule favours the binding of additional surfactant ions in its immediate vicinity through the hydrophobic interaction of the paraffin chain. The surfactants binding sites, thus act as nuclei for the formation of micellar cluster on the ampholyte[35]. This leads to the formation of micelles at relatively lower concentration of the surfactants. These micelles would obviously have protein molecules trapped in their structural frame-work.

A few workers have shown that SDS is able to solubilize *p*-aminoazobenzene at concentrations below the critical concentration for the micelle formation in the presence of 0.2 % of BSA while no dye is solubilized in

the absence of BSA and that the moles of dye solubilized at any surfactants concentration increases with increasing BSA concentration[23]. Since solubilization has been conclusively shown to occur through the agency of the surfactant micelles, these results indicate that surfactants molecules form a sort of aggregate of micelle on the protein. This view is in accordance with present results, which indicate substantial lowering of the CMC of the ionic surfactants in the presence of protein. These aggregates or micelles may consist of a single palisade layer of a few molecules clustered about a binding site on the protein. However, as the concentration of protein is increased, surfactants-protein complexes of many different compositions are formed[36] with the result that at a certain concentration of protein no sharp break corresponding to the micelle formation can be located.

Explanation may be offered for anionic surfactant-RNA system where CMC decreases as the concentration of RNA increase. The surfactants anions may combine with pyrimidine/purine bases partly by electrostatic attraction and partly through hydrogen bonding. Infact in aqueous solution sodium ribonucleate behaves as a strong polyanion of high negative charge density. It is because electostatic repulsion between surfactants anions and negatively charged phosphate groups will completely prevent ligand binding by the hydrophobic effect instead of the fact that surfactant anions contains 12 or more $-CH_2-$ groups in their molecules. However, in the present case the decrease of CMC by the RNA must be due to the involvement of the nitrogen atoms and the -OH groups, which are formed hydrogen bonds with the anionic surfactants. It may be assumed that in the presence of SDS, the common Na^+ ions from the surfactant suppresses the ionization of sodium ribonucleate. Owing to this fact electrostatic repulsion gets minimized and the extent of hydrophobic interaction increase. Due to increase in the hydrophobic nature of SDS-RNA complex micellization took place at least concentration of the surfactant. A critical point is reached when no micellization can be detected from conductance *vs.* concentration of surfactant curves. This concentration of RNA is called as its critical concentration, which abolished an inflection in the curve. In case of TEALS the number of $-CH_2-$ groups is larger than SDS, hence critical RNA concentration is less than SDS. Further TEALS contains three aliphatic -OH groups, which can form hydrogen bonds with sugar residues of RNA and thus accounts to its more reactivity than SDS. However, the case of cationic surfactant-RNA system was found to be entirely different from those of anionic surfactant-RNA systems. In aqueous solution there are a large number of anionic phosphate groups on the surface of RNA molecule, hence addition of surfactant cations would cause electrostatic attraction and a neutral RNA cationic surfactant complex will be salted out. The sharp inflection in the conductance *vs.* cationic surfactant concentration curves in presence of RNA indicates

the formation of a neutral complex. In any experiment when whole of RNA is consumed up micelle formation occurs, that is why CMC of cationic surfactants regularly increases on addition of increasing amount of RNA. Chatterjee *et al.*[37] have shown that at lower ligand concentration, binding or the long-chain cationic amines to DNA is mainly controlled by the electrostatic attraction between the phosphate site of the nucleotide and the cationic sites of the nucleotide and the cationic sites of the surfactant. However, at higher concentration of the ligand, binding is largely enhanced by the hydrophobic interaction between the large number of the $-CH_2-$ groups present in the bound cationic surfactant.

Besides electrostatic and other forces involved in increasing or decreasing the CMC values of surfactants one extra factor may be the change in the water structure of the medium caused by the presence of the dissolved polymer. The high viscosities of the aqueous solutions of the ampholytes suggest that they strengthen hydrogen bonds in the water structure as a result of which cohesive forces existing between the water molecules are increased consequently, the pushing out tendency for the hydrophobic moiety of the surfactant is enhanced causing its micellization to occur at lower concentrations. These conclusions are in line with the generalizations based on the results of a previous studies that changes in water structure are an important factor in the micelle formation of the synthetic surfactants[38-42]. Although PVP is a neutral polymer but its presence decreases the CMC of the surfactants as those of protein and RNA. It is observed that the conductance of surfactant increase with progressive addition of PVP, but the extent of increase is comparatively more in the premicellar than in the postmicellar regions. This increase in conductance may be due to the change in the nature of the solvent that PVP forms mixed micelles with TEALS by the incorporation of the $-CH_2-$ of PVP in the micelles. Owing to this the conductance *vs.* concentration of surfactant curves tend to converge in the post micellar regions causing the inflection to finally disappear. Prior to this stage the added PVP reduces the CMC of TEALS in proportions of its concentration. These are found to be 43, 30, 20 and 14×10^{-4} M for TEALS at 0, 0.01, 0.02 and 0.03 % PVP, respectively. On the other hand CTMAB has a CMC of 30×10^{-4} M in the absence of added PVP, but the addition of 0.02 to 0.080 g/dl of PVP reduces the CMC to a constant value of 25×10^{-4} M.

The decrease in CMC of TEALS by PVP can't be explained on the basis of electrostatic attraction of PVP as a neutral polymer. It appears that the added PVP reacts with a polar parts of TEALS to produce a negatively charged cluster. The additional TEALS ions enter into combination as a unit with the TEALS-PVP complex already formed, the probable way by which this occurs is that an individual surfactant ion adsorbed at a particular PVP segment favour the adsorption of additional TEALS in its immediate

vicinity through the hydrophobic interaction of the paraffin chain. The TEALS adsorption segment of PVP thus may act, as a nuclei for the formation of micellar clusters on the PVP molecule. This leads to the formation of micelles at relatively lower concentration of TEALS. These micelles would obviously have PVP molecules trapped in the structural framework. The slow rise of conductance in the postmicellar region would be due to the formation of mixed micelles of TEALS and PVP.

The dissolved PVP in surfactants solution may also cause lowering of critical micelle concentration of TEALS. The relatively higher conductivity values of aqueous solutions of PVP suggest that these increase the strength of hydrogen bridges in water, so the cohesive forces existing between water molecules are enhanced. This tendency caused the micellization to occur at lower tenside concentration. The lowering of CMC indicated that the micelle forming point of TEALS get diminished in presence of PVP. Thus, on progressive addition of PVP the premicellar region decreases and the postmiceller region corresponding to mixed micelles existed. The higher conductance of PVP-TEALS mixtures in the absolute postmiceller regions may be due to complete uncoiling of PVP and that all its hydrophobic groups are fully traped by TEALS micelles. The difference of conductance behaviour of TEALS and CTMAB may be owing to the different structures of the respective surfactants. The anionic surfactant TEALS besides having methylene groups in common to CTMAB also contains aliphatic-OH groups, which could form hydrogen bonds with PVP and as well as may enter into hydrogen bonding with the solvent water while such a possibility is entirely lacking in the case of CTMAB. Owing to this structural difference among two surfactants, the behaviour of TEALS is different from CTMAB. This conductance behaviour of surfactant-PVP mixtures ensure the formation of mixed and true micelles in their linking with the neutral molecule.

REFERENCES

1. M.E. Ginn and J.C. Harris, *J. Am. Oil Chem. Soc.*, **38**, 605 (1961).
2. D.M. Small, M. Bourges and D.G. Dervichian, *Nature*, **211**, 816 (1966).
3. D.M. Small, *Adv. Int. Med.*, **16**, 243 (1970).
4. D.M. Small, in eds.: P.P. Nair and D. Kritcheusky, In the Bile Acids-Chemistry, Physiology and Metabolism, Plenum Press, New York, Vol. 1, p. 249 (1971).
5. R.D. Stevens, *J. Lipid Res.*, **18**, 417 (1977).
6. K. Srikrishna and R. Paul, *Indian J. Biochem. Biophys.*, **16**, 255 (1979).
7. R. Paul and K. Sreekrishna, *Indian J. Biochem. Biophys.*, **16**, 257 (1979).
8. A. Albert, Selective Toxicology, New York, Willey, p. 97 (1965).
9. M.J. Schick and A.H. Gilbert, *J. Colloid Intuf. Sci.*, **20**, 464 (1962).
10. C. Tanford and P. Dey, *J. Boil. Chem.*, **236**, 1711 (1961).
11. P. Mukherji and A. Ray, *J. Phys. Chem.*, **67**, 190 (1963).
12. L. Benjamin, *J. Colloid Intuf. Sci.*, **22**, 386 (1966).
13. J.P.S. Arora, D. Soam, S.P. Singh and R. Kumar, *Tenside Detergents Surfactants*, **21**, 87 (1984).

14. J.P.S. Arora and S.P. Malik, *Studia Biophys.*, **100**, 181 (1984).
15. J.P.S. Arora, V.K. Singhal, S.P. Singh and R. Kumar, *Tenside Detergents Surfactants*, **21**, 1 (1984).
16. J.P.S. Arora, S. Jain, C. Pal, Laxmi and M. Chand, *Bull. Soc. Chim. (France)*, **1**, 58 (1989).
17. J.P.S. Arora and K.L. Balyan, *Tenside Surfactants Detergents*, **29**, 48 (1992).
18. J.P.S. Arora, Vineeta and R.P. Singh, *Tenside Surfactants Detergents*, **29**, 418 (1992).
19. J.P.S. Arora, Vineeta and M. Chand, *Tenside Surfactants Detergents*, **30**, 136 (1993).
20. J.P.S. Arora, R.P. Singh, D. Soam and S.P. Singh, *Bull. Soc. Chim. (France)*, **1-2**, 19 (1984).
21. J.P.S. Arora, S.P. Singh, V.K. Singhal and R. Kumar, *Tenside Detergents Surfactants*, **21**, 513 (1984).
22. J.P.S. Arora, S.P. Singh, V.K. Singhal and R. Kumar, *Tenside Detergents Surfactants*, **21**, 197 (1984).
23. J. Blei, *J. Colloid Sci.*, **14**, 358 (1959).
24. C. Gamboa, R. Barraza and A.F. Olea, *J. Chil. Chem. Soc.*, **49**, 303 (2004).
25. J.P.S. Arora, V. Verma and K.L. Balyan, *Tenside Surfactants Detergents*, **2**, 124 (1992).
26. J.P.S. Arora, S.K. Arora and A.K. Duggal, *Tenside Surfactants Detergents*, **35**, 24 (1998).
27. M.S. Chauchan, N. Kumar, S. Pathania, K. Sharma and G. Kumar, *Colloid Surfaces*, **293**, 157 (2007).
28. D. Waugh, *Adv. Proteins Chem.*, **9**, 426 (1954).
29. G.W. Schwer, F.W. Putnam and D.R. Briggs, *Arch. Biochem.*, **4**, 37 (1949).
30. H.P. Lundgren, *Text. Res. J.*, **15**, 335 (1945).
31. F.W. Putnam and H. Neurath, *J. Biol. Chem.*, **159**, 195 (1945).
32. W.H. Hardy and H.P. Lundgren, *J. Polym. Res.*, **1**, 22, (1946).
33. Y. Hagilava, D.P. Hong, M. Hoshino, K.I. Enjyoji, H. Kato and Y. Goto, *Biochemistry*, **41**, 1020 (2002).
34. R. Montserret, M.J. Mcleish, A. Bockmann, C. Geourjon and F. Penin, *Biochemistry*, **39**, 8362 (2000).
35. F. Karush and M. Sonenberg, *J. Am. Chem. Soc.*, **71**, 1369 (1949).
36. M.J. Pallansch and D.R. Briggs, *J. Am. Chem. Soc.*, **76**, 1396 (1954).
37. R. Chatterjee and D.K. Chattoraj, *Biopolymers*, **18**, 147 (1979).
38. M.J. Schick, *J. Phys. Chem.*, **67**, 1796 (1963).
39. K.W. Herman, *J. Phys. Chem.*, **66**, 295 (1962).
40. W. Bruning and A. Holtzer, *J. Am. Chem. Soc.*, **83**, 4865 (1961).
41. E.D. Goddard and G.C. Renson, *Can. J. Chem.*, **35**, 936 (1957).
42. E.M.S. Azzam, *J. Surfactants Detergents*, **10**, 13 (2007).

(*Received*: 29 June 2007; *Accepted*: 6 March 2008) AJC-6416