

Organization of amphiphiles

Part IV. Characterization of the microstructure of the adsorbed layer of decylethoxyethylene nonyl phenol

Pramila K. Misra^{a,*}, Bijay Kumar Mishra^a, P. Somasundaran^b

^a Centre of Studies in Surface Science and Technology, Department of Chemistry, Sambalpur University, Jyoti Vihar 768019, India

^b Langmuir Center for Colloids and Interface, Henry Krumb School of Mines, Columbia University, NY 10027, USA

Received 19 December 2003; accepted 8 August 2004

Available online 25 November 2004

Abstract

A systematic study on the adsorption behavior of decylethoxyethylene nonyl phenol (NP-10) on silica has been carried out in order to elucidate the mechanism that governs the formation of the adsorbed layer of the nonionic surfactants. Effects of pH and silica–water ratio on adsorption isotherm indicate that the adsorption of NP-10 at silica–water interface results from the contribution of both hydrophobic and hydrophilic parts of the surfactant and the surface charge of silica. The cooperative association of the hydrocarbon chain at silica–water interface has been proposed. Measurements of the electrokinetic properties of the silica with adsorbed surfactants reveal the adsorbed layer to mask the surface charge of silica significantly.

© 2004 Published by Elsevier B.V.

Keywords: Polyoxyethylated alkyl phenols; Zeta potential; Hemimicellar aggregation number

1. Introduction

Adsorption of surfactants at the solid/liquid and the liquid/gas interface plays a very important role in many industrial processes [1–3]. The polyoxyethylated alkyl phenols show strong adsorption on silica but not on alumina [2,4,5]. Such preferential adsorption on silica renders a great advantage for the beneficiation of minerals and the separation of surfactants from mixtures [6–8]. In our earlier studies [9–12], we have reported the organization of nonionic surfactants in homogeneous and microheterogeneous media. In the present paper, a systematic study of the adsorption behavior of NP-10 at silica–water interface has been carried out with a view to investigate the microstructure of the adsorbed layer of decylethoxyethylene nonyl phenol (NP-10) at silica–water in-

terface and to know the orientation of the surfactants at the silica–water interface.

2. Experimental

2.1. Materials

2.1.1. Silica

Synthetic silica used for experiments were spherosil XOB75 (Rhone-Poulenc, Lyon, France) with diameter of 2.5–64 μm and a BET surface area of 100 m^2/g with a spherical ball like structure. The average pore size on silica surface was specified to be 1200 \AA^2 .

2.1.2. Surfactant

The decylethoxyethylated nonyl phenol surfactants were obtained from Nikko chemicals, Tokyo, Japan under the product name NP-10 (**I**). These surfactants were used to study with-

* Corresponding author. Tel.: +91 663 243 1078; fax: +91 663 243 0158.
E-mail address: pramilamisra@rediffmail.com (P.K. Misra).

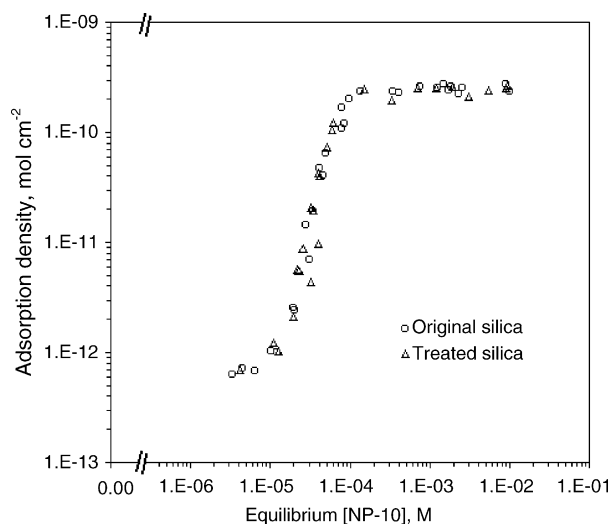


Fig. 4. Adsorption isotherm of NP-10 in original spherosil XOB75 and treated silica [$S/L=0.01$, $I=0.01$, temperature = $23 \pm 0.2^\circ\text{C}$, pH 5.0 ± 0.2].

3.2. Measurement of zeta potential of silica

The zeta potential of silica in 0.01 M NaCl was measured at $23 \pm 0.2^\circ\text{C}$ using a PEN KEM, Inc. Bedford Hills, Laser Zee Zeta meter model 501 system before and after adsorption of surfactants onto it. The virgin silica particle settled down immediately when it was subjected to zeta potential measurements. To obtain a suitable size for zeta potential measurement the supplied silica was subjected to stirring using a bar for ~ 72 h to break down the aggregate. The resulting silica particles were allowed to settle down and were dried in oven at about 140 – 160°C for 24 h. The BET surface area of this treated silica was also found to be $100\text{ m}^2/\text{g}$ and the particle size was $<1\text{ }\mu\text{m}$. Dispersion of the silica aggregates was found not to affect its surface properties as the adsorption density of NP-10 on this treated sample was found to be same as that on the original silica (Fig. 4).

4. Results and discussion

4.1. Effect of silica/water ratio

Adsorption of NP-10 on silica was determined at a given initial concentration ($C_i = 2.1 \times 10^{-4}\text{ M}$) as a function of silica–water ratio (0.01–0.125) to investigate the effect of solid to liquid ratio on adsorption and the result obtained is shown in Fig. 5. Interestingly, the adsorption density of the surfactant is found to decrease with increase in silica–water ratio. This behavior can be rationalized by considering the dominance of the particle–particle interaction of silica over silica particle–surfactant interaction at a higher solid–liquid ratio. The silica/water ratio was maintained at 0.01 for all subsequent experiments.

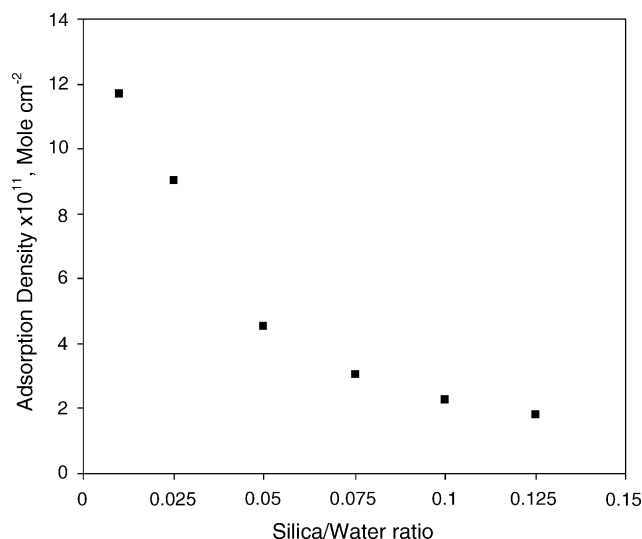


Fig. 5. Effect of silica/water ratio on the adsorption of NP-10 on silica [$I=0.01$, temperature = $23 \pm 0.2^\circ\text{C}$, pH 5.0 ± 0.2 , $C_i(\text{NP-10}) = 2.1 \times 10^{-4}\text{ M}$].

4.2. Effect of pH

The effect of pH on the adsorption of NP-10 on silica was obtained at the two initial concentrations at the silica/water ratio of 0.01. The results obtained are shown in Fig. 6. The adsorption density remains constant in the pH range of 2.5–7.0 and decreases above pH 8.0. The adsorption of NP-10 on silica depends on H-bond formation of silanol groups with the oxygen of the ethoxyl units of the surfactants [17]. At low pH, the ethoxyl oxygens are protonated [18], and as a result, probability of formation of H-bond between ethereal linkage of NP-10 and silanol –OH group is lower. With increase in pH, the ionization of silanol groups, on the other hand, increases (point of zero charge of silica = 2.0 [19], Fig. 7) and therefore, their proton-donating ability decreases, result-

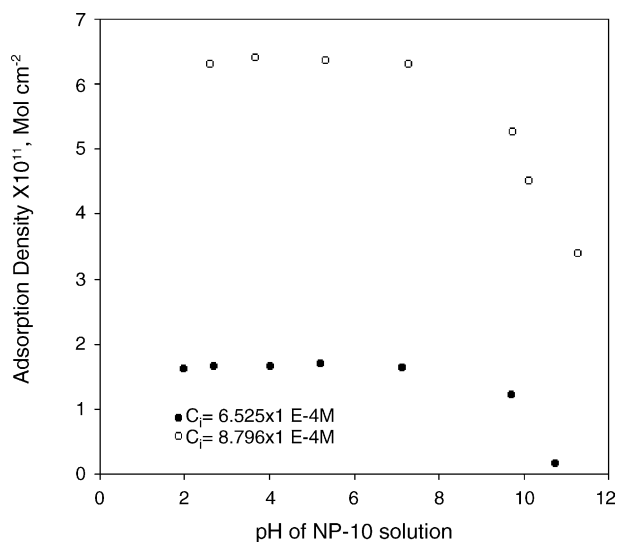


Fig. 6. Variation of adsorption density of NP-10 with pH [$S/L=0.01$, $I=0.01$, temperature = $23 \pm 0.2^\circ\text{C}$, pH 5.0 ± 0.2].

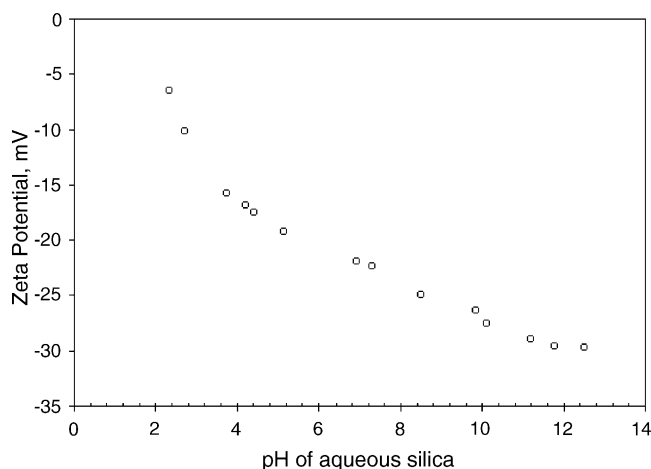


Fig. 7. Variation zeta potential of naked silica with pH [$S/L = 0.01$, $I = 0.01$, temperature = $23 \pm 0.2^\circ\text{C}$].

ing in a decrease in adsorption density. Thus, in this system two competing forces, i.e. ionization of silanol $-\text{OH}$ (SiOH) groups leading to decrease in adsorption and deprotonation of ethoxyl oxygen leading to increase in adsorption, operate. As a result the adsorption density remains constant till pH ~ 7.0 . With increase in pH above 7.0, increased ionization of the silanol groups predominates resulting in decrease of adsorption of the surfactants. This experimental findings suggest that adsorption of nonionic surfactants at silica surface is mainly because of the H-bonding between oxygen of the polyoxyethylene group of the surfactants and the hydrogen of the silanol group. Somasundaran et al. [20] and Keller and David [21] have also suggested a hydrogen bonding between the ethereal oxygen of the ethylene oxide group and the surface silanol groups.

4.3. Adsorption isotherm

The adsorption isotherm of NP-10 was obtained at different pH values at the ionic strength (0.01 M NaCl), and silica–water ratio 0.01. The adsorption density of NP-10 is found to be unchanged within the range of experimental pH. The adsorption isotherms at various pHs are also constructed. The adsorption isotherms in all cases are found to be sigmoidal nature (Figs. 4 and 8). At very low concentrations of the surfactant, the adsorption density is low, followed by a sharp increase and finally reaching a plateau. At the beginning of the adsorption isotherm the adsorption of surfactant is attributed to the monomeric adsorption of the surfactant at the surface of silica through H-bonding [17]. The conspicuous increase in adsorption density in the pre-plateau region is attributed to the cooperative association of the hydrophobic groups of the surfactants through lateral interaction. This type of cooperative association has been observed by earlier workers [22–27] and the aggregate on the surface colloid has been called “Hemi-micelle and Solloid” [28].

The onset of plateau in adsorption isotherm (Figs. 4 and 8) is found to be at the CMC of the surfactants [11,29]. This sug-

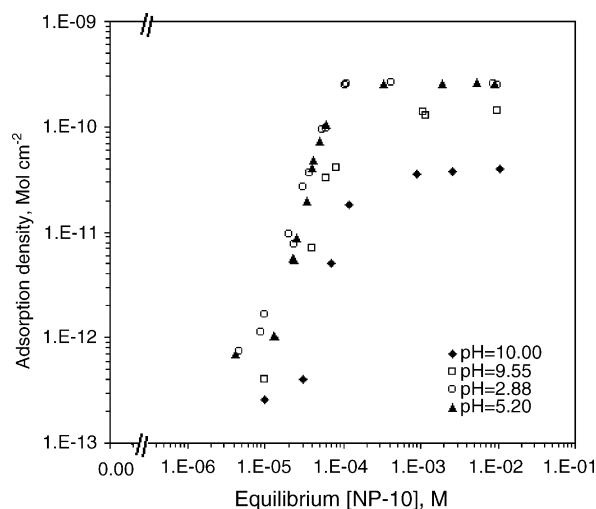


Fig. 8. Adsorption isotherm of NP-10 at various pH [$S/L = 0.01$, $I = 0.01$, temperature = $23 \pm 0.2^\circ\text{C}$].

gests that the appearance of plateau adsorption in adsorption isotherm is a micellar limited phenomenon. The formation of micelles, limits the monomer activity in solution which leads to the leveling up of the adsorption isotherm. It has been also suggested by many workers that the adsorption of surfactants involves surfactant monomer rather than micelles [30,31].

Effect of ionic strength was determined by carrying out adsorption studies at high ionic strength (1 M NaCl). The adsorption density is found to overlap on the adsorption isotherm at 0.1 M NaCl at low and relatively moderate concentration of NP-10. Near and above the onset of plateau the adsorption density increased remarkably with increase in ionic strength (Fig. 9). This may be attributed to the salting out of NP-10 from the water clusters. Such salting out of the surfactants from aqueous phase due to increase of salinity has been observed [32,33].

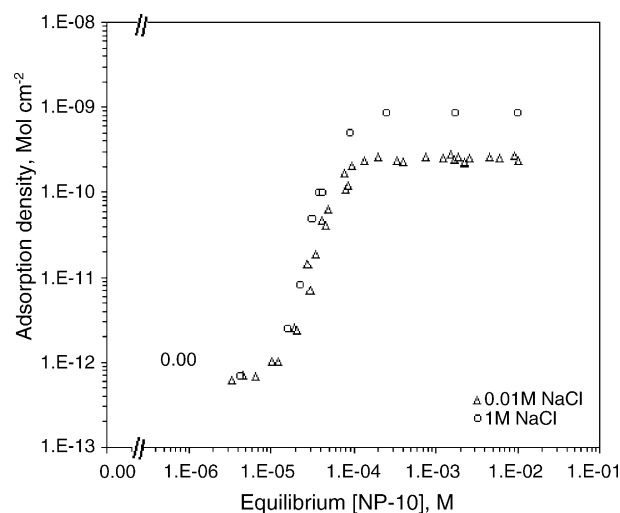


Fig. 9. Adsorption isotherm of NP-10 with different ionic strength [$S/L = 0.01$, temperature = $23 \pm 0.2^\circ\text{C}$, pH 5.0 ± 0.2].

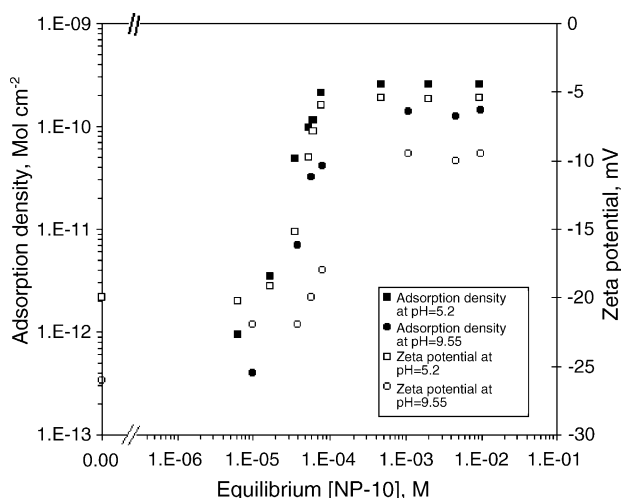
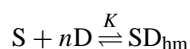


Fig. 10. Variation of zeta potential of silica along the adsorption isotherm of NP-10 [$S/L=0.01$, $I=0.01$, temperature = $23 \pm 0.2^\circ\text{C}$, pH 5.0 ± 0.2].

4.4. Hemi-micellar aggregation number

The aggregation number of hemi-micelles was determined by applying mass action model to the formation of hemi-micelle as shown below [34].



where S is the solid site, i.e. silica site, D is the surfactant monomer, SD_{hm} is the surfactant aggregate at the interface (hemi-micelle), n is the number of surfactants constituting a hemi-micelle and

$$K = \Gamma / (\Gamma_\infty - \Gamma) C^n \quad (2)$$

Γ is the amount of surfactant adsorbed at concentration C and Γ_∞ is the amount adsorbed in the limiting adsorp-

tion at high concentrations. The logarithm of Eq. (2) results in Eq. (3)

$$\log[\Gamma / (\Gamma_\infty - \Gamma)] = \log K + n \log C \quad (3)$$

The $\log K$ and n values obtained from the plots $\log[\Gamma / (\Gamma_\infty - \Gamma)]$ versus $\log C$ for the adsorption of the on silica surface are found to be 14.99 and 3.60, respectively (correlation coefficient $R^2=0.99$). This suggests that during the hemi-micellization in pre-plateau region, three to four surfactant molecules are attached laterally to form the two-dimensional closely packed aggregates, hemi-micelle [22–27].

4.5. Zeta potential

The adsorption isotherms of NP-10 at pH 5.2 and 9.55 are given in Fig. 10 along with the zeta potential. The naked silica has a negative zeta potential in the complete pH range and attains a value of -30 mV (Fig. 7) at pH 12.0. Upon adsorption of surfactant the negative potential of silica decreases and it exactly follows the adsorption isotherm, and finally attains a constant value in the plateau region (Fig. 10). The minimum zeta potential at pH 5.2 is around -5.5 and -10 mV at pH 9.55. It can be seen that the zeta potential change parallels the adsorption isotherms. The decrease in zeta potential can be attributed to covering the silica surface by the sheet of polyoxyethylene (Fig. 11) layer, leading to the displacement of the shear plane thus, reducing the surface charge of silica. Above the plateau, masking of surface charge of silica remains same due to constant adsorption in this region. This is in line with our earlier observation for the adsorption of octaethylene glyco mono- n -dodecyl ether on silica surface [35]. The structure of hemi-micelle of NP-10 on the surface of silica is represented in Fig. 11.

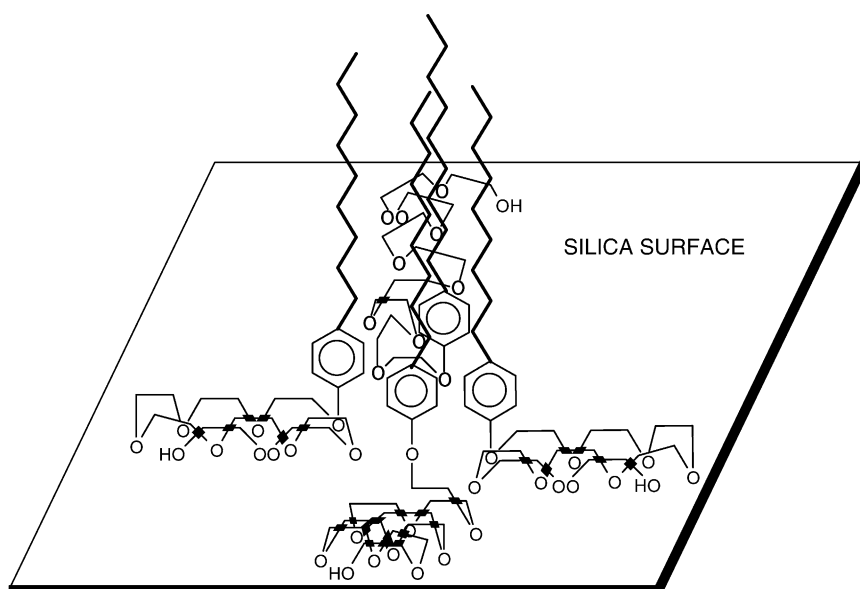


Fig. 11. Schematic representation of NP-10 hemi-micelle at silica–water interface.

Thus, the adsorption of nonionic surfactant NP-10 is very different from that of the ionic surfactants. NP-10 adsorbs on silica mainly due to hydrogen bonding and lateral alkyl chain association, the latter leading to masking of the surface potential. NP-10 evolves hemi-micelles of lower aggregation number at silica–water interface compared to ionic surfactants with relatively small head groups, such as sodium dodecyl sulfate at alumina–water interface [36] possibly due to size of the large polyoxyethylene head group of the former.

Acknowledgements

The authors thank Department of Science and Technology, Govt. of India, Columbia University, New York, USA and the Department of Energy and National Science Foundation for providing financial support and laboratory facilities to one of the author (P.K.M.).

References

- [1] P.S. Stenby, in: W.G. Cutler, R.C. Davis (Eds.), *Detergency: Theory and Test Methods Part III*, Dekker, New York, 1981, p. 766.
- [2] Ed. Fu, Adsorption of anionic–nonionic surfactant mixtures on oxide minerals, Ph.D. thesis, Columbia University, New York, 1987.
- [3] B. Idson, in: M.M. Reiger (Ed.), *Surfactants in Cosmetics*, Dekker, New York, 1985.
- [4] S. Patryka, S. Zains, M. Lindheimer, B. Brun, *Colloid Surf.* 12 (1984) 255.
- [5] S.A. Lawrence, J.A. Pilc, J.R. Readman, P.A. Sermon, *J. Chem. Soc. Commun.* (1987) 1035.
- [6] Ed. Fu, P. Somasundaran, *Int. J. Miner. Process.* 18 (1986) 287.
- [7] P. Somasundaran, *Proceeding of the Pacific Region Meeting of Fine Particle Society*, vol. 124, 1983.
- [8] R.J. Pugh, K. Tjus, *Colloid Surf.* 12 (1990) 179.
- [9] L. Sahoo, J. Sarangi, P.K. Misra, *Bull. Chem. Soc., Jpn.* 75 (2002) 859.
- [10] L. Sahoo, P.K. Misra, *SUJSc. Tech.* 13B (2001) 18.
- [11] L. Sahoo, P.K. Misra, P. Somasundaran, *Indian J. Chem.* 41A (2002) 1402.
- [12] L. Sahoo, G.D. Hota, P.K. Misra, *Indian J. Chem. Tech.* 10 (2003) 269.
- [13] T. Okano, T. Tamura, Y. Abe, T. Tasuchida, S. Lee, G. Sugihara, *Langmuir* 16 (2000) 1508.
- [14] (a) P.K. Misra, B.K. Mishra, P. Somasundaran, *J. Colloid Interf. Sci.* 265 (2003) 1;
(b) P.K. Misra, P. Somasundaran, *J. Surfactant Detergent*, in press.
- [15] T.T. Ndou, R. von Wandruszka, *Anal. Lett.* 21 (1988) 2091.
- [16] D. Patra, S. Mohapatra, P.K. Behera, B.K. Mishra, *Colloid Surf.*, accepted for publication.
- [17] H. Rupperecht, H. Liebl, *Kolloid Z. Z. Polym.* 250 (1972) 719.
- [18] J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley Interscience, New York, 1978, p. 47.
- [19] E. Koksai, R. Ramachandran, P. Somasundaran, C. Maltesh, *Powder Technol.* 62 (1990) 251.
- [20] P. Somasundaran, E.D. Snell, Q. Xu, *Colloid Interf. Sci.* 144 (1991) 165.
- [21] E. Keller, J. David, *J. Colloid Interf. Sci.* 155 (1994) 124.
- [22] P. Somasundaran, N.J. Turro, P. Chandar, *Colloid Surf.* 20 (1986) 145.
- [23] K.C. Waterman, N.J. Turro, P. Chandar, P. Somasundaran, *J. Phys. Chem.* 90 (1986) 6830.
- [24] P. Chandar, P. Somasundaran, K.C. Waterman, N.J. Turro, *J. Phys. Chem.* 91 (1987) 148.
- [25] S.K. Parida, P.K. Misra, B.K. Mishra, *Indian J. Chem.* 38A (1999) 639.
- [26] S.K. Parida, B.K. Mishra, *Indian J. Chem.* 37A (1998) 618.
- [27] P. Somasundaran, D.W. Fuerstenau, *J. Phys. Chem.* 79 (1966) 90.
- [28] P. Somasundaran, J.T. Kunjappu, *Colloid Surf.* 20 (1989) 245.
- [29] J. Sarangi, U.B. Mohapatra, P.K. Misra, *Sambalpur Univ. J. Sci. Tech.* XI (1999) 15.
- [30] H. Kolbel, K. Horig, *Angew. Chem.* 71 (1959) 691.
- [31] J.C. Griffith, A.E. Alexander, *J. Colloid Interf. Sci.* 25 (1967) 311.
- [32] P. Somasundaran, Adsorption From Flooding Solutions in Porous Media, Annual Report, submitted to DOE, NSF and Consortium of supporting Industrial Organization, Columbia University, New York, 1982.
- [33] H.S. Hanna, P. Somasundaran, in: D.O. Shah, R.S. Schechter (Eds.), *Improved Oil Recovery by Surfactant and Polymer Flooding*, Academic Press Inc., New York, 1977.
- [34] T. Gu, B. Zhu, *Colloid Surf.* 44 (1990) 81.
- [35] P. Somasundaran, E. Fu, Q. Xu, *Colloid Surf.* 63 (1992) 49.
- [36] P. Chander, P. Somasundaran, N.J. Turro, *J. Colloid Interf. Sci.* 117 (1987) 31.