Research paper

Organization of amphiphiles, Part VIII: Role of polyoxyethylated alkylphenols in optimizing the beneficiation of hydrophilic mineral

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Abstract

The floatability of silica has been determined by adsorbing various concentrations of a series of polyoxyethylated nonyl and octyl alkyl phenols of varying oxyethylene units (10–40 units) to investigate the role of adsorbed layer. It is seen that the floatability of silica increases with increase in concentration till a maximum of ∼ 90% in premicellar region and then decrease to minimum of 40–45% in all cases in spite of the significant differences in adsorption densities. Zeta potential measurement reveals that a thin oxyethylene layer is formed at silica–water interface masking silica surface (Pramila K. Misra, P. Somasundaran, J. Surf. Deterg., Vol. 7, 2004, 373). This layer with oxyethylene units lying on silica surface and alkyl chain dangling to the bulk solution provides the same extent of hydrophobicity. The decrease in flotation recovery has been attributed to increase in the solvent hydrophobicity due to formation of premicellar aggregates and micelles.
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1. Introduction

Due to the increasing demand for pure, fine and ultrafine minerals from different industrial organizations and research laboratories, the development of different separation techniques has received much attention at present. The minerals can be purified by methods such as flotation, flocculation, the feasibility of which is controlled by the properties of the mineral surface. Modification of the surface charge, the surface hydrophobicity, and the structure of the solvent molecules, in the interfacial region are all important characteristics which play key roles on flotation (Hanna and Somasundaran, 1976). The basic requirement for flotation of a mineral is to have regions of significant hydrophobicity. Surface chemical alterations resulting from adsorption or surface precipitation of flotation reagents and the orientation of such species at the solid–liquid interface determine the hydrophobicity of the mineral surface. The flotation is dependent on the extent of adsorption (Somasundaran and Ananthapadmanavan, 1979) and the orientation (Somasundaran and Lee, 1981; Moudgil et al., 1987) of the surfactants at the solid–liquid interface. Nonionic surfactants and nonpolar oils are often used for coadsorption with ionic surfactants at the solid–liquid interface thereby increasing the hydrophobicity (Soto and Iwasaki, 1986) and hence the floatability. Nonionic surfactants along with acrylamide are found to affect the flotability of silicate and mineral flotation (Aliferova et al., 2005). Excess of adsorption of surfactants at high concentration form

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bilayer with the polar head towards the bulk solution leading thereby decrease in the mineral hydrophobicity and thus its flotation (Somasundaran et al., 1983; Ceik and Somasundaran, 1980). In general, both anionic and cationic surfactants like carboxylates, alkyl sulphonates, alkyl sulfates and chelating agents such as xanthates and oximes are used in flotation (Somasundaran et al., 1991). The flotation behaviour of quartz and microcline by different types of nonionic surfactants (Brij-56, Brij-58) have been studied. Increasing quartz recovery, when oxyethylinic length of surfactant increases has been observed (ElSalmawy et al., 2000).

The objective of this work is to study the role of adsorbed layer of polyoxyethylated alkyl phenols on flotation recovery of silica. These surfactants are chosen because of their strong affinity for silica surface in comparison to other minerals (Patryka et al., 1984; Lawrence, 1987).

2. Experimental

2.1. Materials

Polyoxyethylated *p*-octyl and *p*-nonyl phenols were obtained from Nikko chemicals, Japan under the product name OP-*X* (1a, *X*=10, 30) and NP-*X* (1b, *X*=10, 15, 20) respectively where *X* represents the number of poly (oxyethylene) group present in the surfactants. Polyoxyethylated (40) nonyl phenol was obtained from GAF corporation under the product name Igepal CO890. Throughout the paper we have referred to it as NP-40 for convenience. These surfactants were used as received. The absence of a minimum in the surface tension–concentration curve confirmed the high purity [>99%] of these surfactants (Sahoo et al., 2002b: Okano et al., 2000; Jun-Fu et al., 2001).

R—⟨◯⟩—O(CH₂CH₂O)ₙ—H
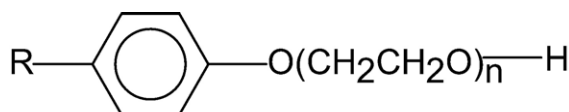
1a: R= Octyl, n= 10 and 30
1b: R= Nonyl, n=10,15,20 and 40

Sodium chloride (Fisher Scientific Co., USA, purity>99.9%) was used for maintaining a constant ionic strength.

2.2. Methods

2.2.1. Adsorption studies

Silica (2 g) was mixed with 100 ml of 0.01 M NaCl in a capped glass vial and was shaken for 3 h in an orbital shaker. This pre-conditioned silica was then treated with 100 ml of surfactant solution of desired concentration. The solution with silica was shaken for 12–15 h at (23 ± 0.2) °C. The experimental pH found was 5.0 ± 0.2. The adsorption density is not affected within the pH range from 2 to7 (Misra et al., 2005). The equilibrium concentration of the surfactant in supernatant was determined by UV analysis at 223 nm (λ_{max} for both OP and NP series) using Shzimadzu-1201A UV–Visible spectrophotometer. The effect of porosity on the adsorption of the surfactant has been neglected since the pore size (1200 $A^{\circ 2}$) was much larger than the size of the surfactant ($\sim$200 $A^{\circ 2}$). The solid was separated at the end of the equilibrium by centrifuging the sample for 40 min at a speed 300 c/s (30,000 g). The adsorption density has been calculated using Eq. (1).

$$\text{Adsorption Density}(\Gamma) = \frac{(C_i - C_r) \times V}{1000 \times X \times A} \text{Moles cm}^{-2} \qquad (1)$$

Where

C_i Initial concentration of surfactant in mole dm^{-3}
C_r Equilibrium concentration in mole dm^{-3} of surfactant (after adsorption)

V Volume of the aliquot in cm^3, X=mass of the adsorbent in gm
A Surface area of the adsorbent in cm^2/gm

2.2.2. Floatability measurement

Slurry from the adsorption studies was transferred to a modified Hallimond tube and flotation was measured by passing nitrogen at a flow rate of 10 cm^3/min for 5 min. The particles that are made hydrophobic through adsorption of surfactants rise to the top of the tube on collision with nitrogen bubbles. The float and the sink were collected separately. The percentage of float was calculated as

$$\% \text{ of ..Float} = \frac{\text{Weight of the Float}}{\text{Weight of Float} + \text{Weight of Sink} + \text{Weight of adsorbed surfactant}} \times 100 \qquad (2)$$

The reproducibility of the flotation test was determined by repeating the experiments and the error was found to be within 2%.

3. Results and discussion

The flotation of a mineral primarily depends on the hydrophobic nature of its surface. The surface of silica is not naturally hydrophobic due to its surface charge. The predominating mechanism of surface charge generation in the case of silica is hydrolysis of surface species followed by the pH dependent dissociation of surface hydroxyl groups (Somasundaran, 1975: Scheme 1). The pH at which the surface charge is zero is referred to as point of zero charge (PZC). The PZC of spherosil silica under investigation is 2.0 (Misra et al., 2005; Koksal et al., 1990). As the pH of the solution is increased, the surface becomes more and more hydrophilic due to the dissociation of silanol groups. The flotation recovery of this silica is found to be ∼ 1%. For appreciable flotation, the surface of hydrophilic minerals like silica, are to be made hydrophobic by the adsorption of surface active species. In this study we have used a series of polyoxyethylated alkyl phenols with varying hydrophobic chain (alkyl chain) and hydrophilic chain (polyoxyethylene chain) length as collectors. From past surface tension measurements (Sahoo et al., 2002b) it is seen that the surfactant hydrophobicity decreases with increase in number of polyoxyethylene groups and decrease in alkyl chain length. In order to float silica the surfactant molecules have to adsorb at solid–liquid interface with polar head group oriented towards mineral surface and the hydrophobic tail pointing towards the solution thereby masking the mineral surface hydrophilicity. The adsorption isotherms of NP- and OP-series are shown in Figs. 1 and 2. For surfactants with lower number of oxyethylene groups (NP-10, NP-15, NP-20, OP-10) an S shaped adsorption isotherms characteristics of electrostatic, hemimicellar forces controlling surfactant adsorption is obtained. In the beginning of adsorption isotherm the adsorption is proposed to be through the H-bonding between the ethereal linkage of the surfactants and silanols and therefore the surfactants with more number of oxyethylene units would adsorb strongly. At a certain residual concentration, there is a sharp increase in adsorption density due to the association of hydrophobic chains of the adsorbed surfactant forming two dimensional surface aggregates similar to the formation of micelles in solution. This surfactant concentration where such strong association occurs on solid phase is referred to as the critical hemimicellization concentration (CHMC). The CHMC is analogous to the solutions' critical micelle concentration, but typically found at lower concentrations (Becraft and Richmond, 2005; Besio et al., 1998; Fuersteanau, 2002). Fluorescence and ESR spectroscopic work (Somasundaran and Krishnakumar, 1994) reinforces the mechanism of formation of
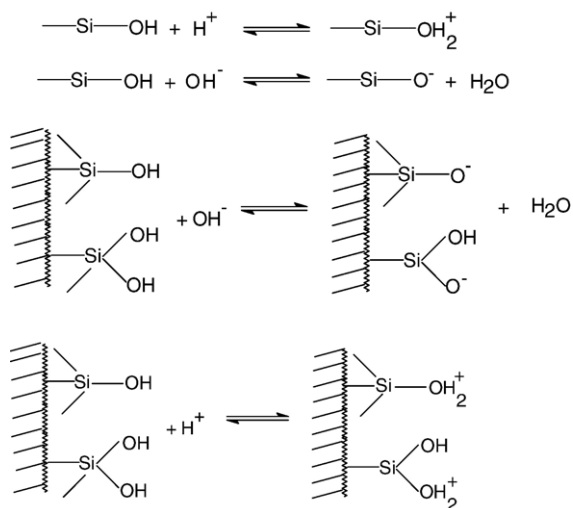
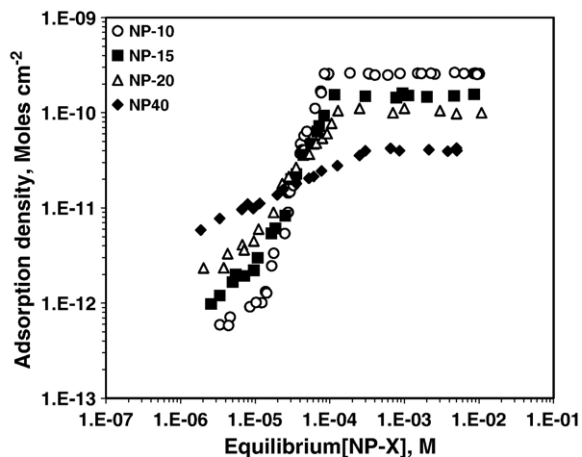Scheme 1. Behavior of silica surface with change of pH.

Fig. 1. Adsorption isotherm of NP series [pH=5.2, I=0.01 M NaCl, temp=$(23\pm0.2$ °C)].

aggregates. From adsorption and fluorescence studies we have seen that NP-10, NP-15, NP-20 and OP-10 form hemimicelles at silica–water interface (Somasundaran, 1975; Misra et al., 2003), whereas OP-30 and NP-40 adsorb as surfactant monomers throughout the adsorption isotherm (Figs. 3 and 4). The CHMC is found to be elevated as the number of oxyethylene group increases.

The onset of plateau coincides with the CMC (Table 1) of the surfactant as determined by surface tension measurement (Sahoo et al., 2002b). The appearance of adsorption plateau is due to the formation of micelles which limits the monomer activity (Sarangi et al., 1999). It has also been suggested by many workers that the adsorption of surfactants involves surfactant monomer rather than micelles (Kolbel and Horig, 1959; Griffith and Alexander, 1967). The reduced plateau adsorption density as the number oxyethylene group increases is due to the interaction of the oxyethylene groups with the surface and the bulky hydrated ethoxyl groups preventing closer packing of alkyl chain. The adsorption isotherms of all surfactants crosses through a common point (isoadsorptive point) below which the adsorption density increases with the increase in number of the oxyethylene units and above this the trend is reversed (Figs. 1 and 2).

The flotability of silica is shown as a function of the equilibrium concentration of the surfactants in Figs. 5–10. It is seen that with increase in adsorption the flotation increases and attains a maximum value in the premicellar region. At a surfactant concentration of 3×10^{-5} M, the order of floatability is NP-40>NP-20>NP-15>NP-10 in NP series and OP-30>OP-10

in OP series (Figs. 11 and 12). In the premicellar region at around 4×10^{-5} M, the flotability of silica attains the maximum value of $\sim90\%$ with all the surfactants. The point corresponds to the *isoadsorptive point*, where the adsorption densities of all surfactants are the same. With further increase in the surfactant concentration the flotation of silica declines till it reaches a minimum value of about ~40–45%. It is interesting to note that even though the adsorption densities are significantly different for different surfactants the percentage of floation is almost the same in all cases above CMC.

The above phenomenon can be explained by considering the possible way in which surfactant adsorbs. At low concentration, the surfactant molecules adsorb due to the possibility of hydrogen bonding between ethoxyl oxygen atoms with silanol group with the polyoxyethylene group lying flat on the silica surface and the alkyl chain pointing towards the bulk solution (Fig. 13: Misra and Somasundaran, 2004). With the same alkyl chain length of the surfactant, with greater number of oxyethylene groups the more will be the coverage of the surface and the greater will be the reduction of surface charge and the surface hydrophilicity. This has been supported by the zeta potential measurement along the adsorption isotherm (Misra and Somasundaran, 2004). Below CMC the negative zeta potential of silica decreases more for surfactants containing the larger number of polyoxyethylene groups (Fig. 14: Misra and Somasundaran, 2004). The surface also becomes more hydrophobic with large number of aliphatic CH_2 group in the hydrocarbon chain (Xiao et al., 1990). Thus the flotation percentage decreases in the
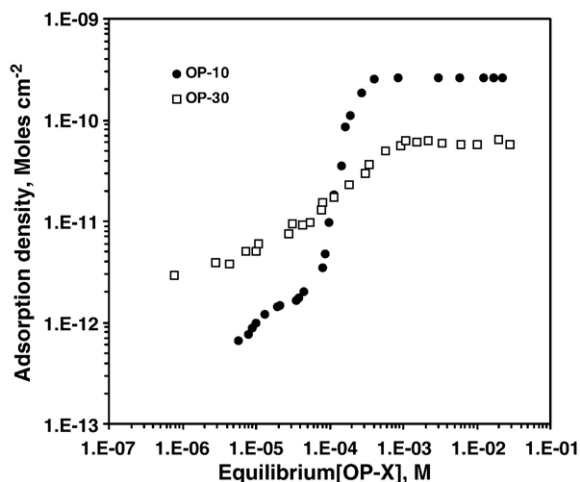

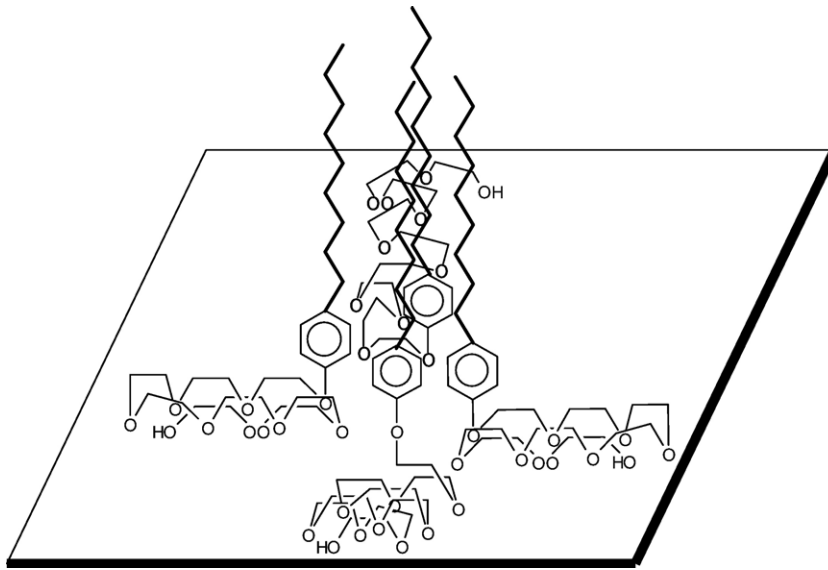Fig. 2. Adsorption isotherm of OP series [pH=5.2, I=0.01 M NaCl, temp=$(23\pm0.2$ °C)].

Fig. 3. Schematic representation of NP-10 hemimicelle at silica–water interface.

order NP-40 > NP-20 > NP-15 > NP-10 in NP series and OP-30 > OP-10 in OP series (Figs. 5–12). Further increase in adsorbed surfactant increases the surface hydrophobicity attaining a maximum flotation of ∼90% recovery around 4×10^{-5} M in all cases.

The decrease in flotation above CMC (Table 1) is usually attributed to the formation of a bilayer through hydrophobic interaction of the hydrocarbon

tail with polyoxyethylene units oriented towards the bulk solution (Somasundaran and Lee, 1981). The molecular parking areas of all surfactants have been calculated from the adsorption density value at the plateau assuming monolayer adsorption (Misra et al., 2003). A linear plot with a correlation coefficient 0.997 is obtained when the molecular parking area of the NP series surfactants is plotted against their
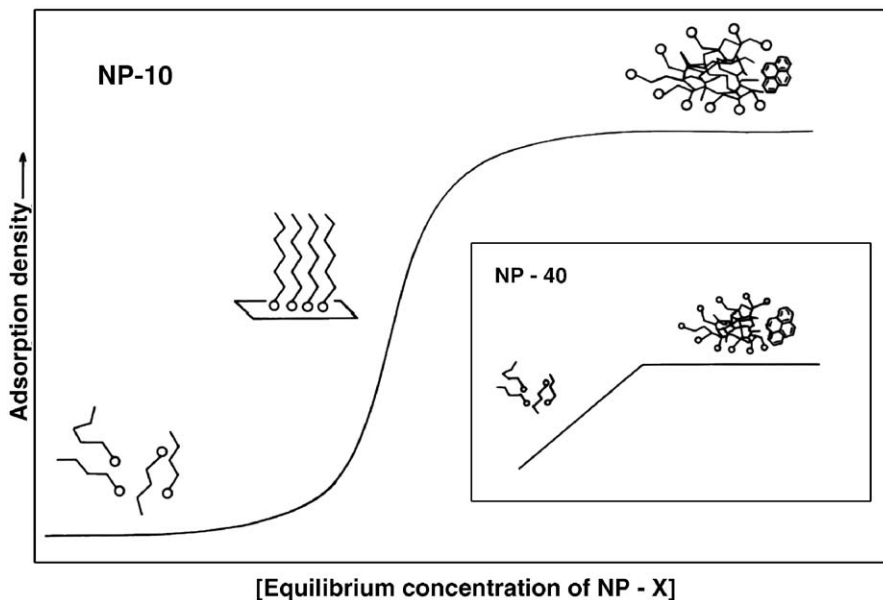

Fig. 4. Schematic diagram of surfactant-adsorption on silica surface as monomer, hemimicelle, and at surfactant concentration above CMC where pyrene is bound to micelle.

Table 1
CMC for NP and OP-series

Surfactants	No. of oxyethylene units	CMC $\times 10^5$ M
NP-10	10	8.00
NP-15	15	10.00
NP-20	20	12.34
NP-40	40	30.00
OP-10	10	40.00
OP-30	30	100.00

number of oxyethylene units. The molecular parking areas of both OP-10 and OP-30 fit on the same plot of NP series which suggests that the surfactant molecules anchor on the surface with oxyethylene group lying flat and alkyl chain away from silica surface and is thus independent of the length of the hydrophobe. The linear plot of oxyethylene unit versus molecular parking area derived by assuming monolayer adsorption precludes the formation of bilayer and is therefore the decrease in flotation beyond CMC cannot be attributed to the bilayer formation in the present case.

The decrease of adsorption density at the plateau with increase in oxyethylene unit suggests that at maximum adsorption the packing of these surfactants is governed, to a large extent, by the number of oxyethylene units. The higher the number of oxyethylene unit, the larger is the area occupied by the surfactant molecule. The number of molecules with more polyoxyethylene groups will therefore be less for the monolayer packing than that with less number of polyoxyethylene units and hence the decrease in the adsorption density (in moles/cm^2
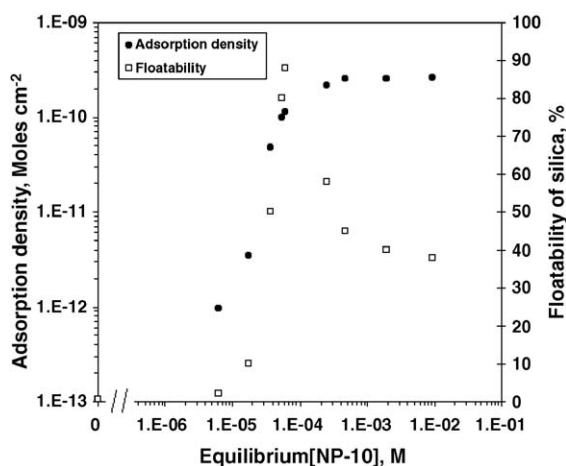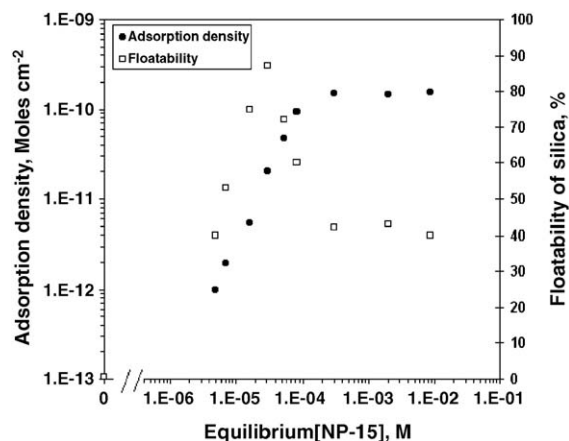

Fig. 6. Flotation recovery % of NP-15 along its adsorption isotherm [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].

unit). But at maximum adsorption the percentage of the silanols groups connected to the surfactants through H-bonding is same in all cases. This has been corroborated by zeta potential measurements (Misra and Somasundaran, 2004). The zeta potential of silica is −5.5 mV in the plateau of all isotherms irrespective of the marked difference in adsorption densities. The surfactants form an ethylene layer in between the bulk solution and the silica surface masking a constant fraction of the surface charge of silica decreasing zeta potential from −20 mV to −5.5 mV. Basing on the zeta potential data the flotation recovery would be expected to continuously increase till a constant value is reached at the plateau. But the flotation decreases above CMC. This
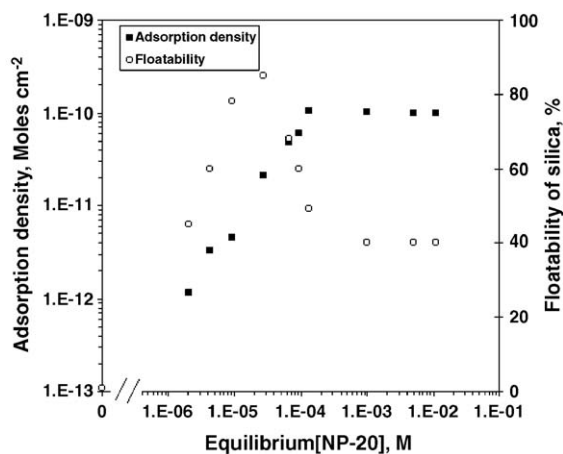

Fig. 5. Flotation recovery % of NP-10 along its adsorption isotherm [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].

Fig. 7. Flotation recovery % of NP-20 along its adsorption isotherm [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].
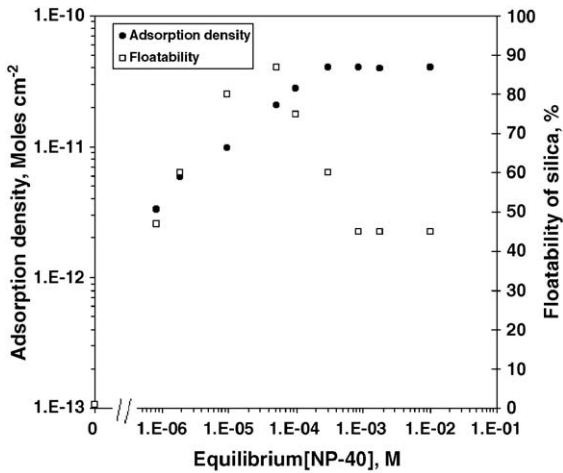
Fig. 8. Flotation recovery % of NP-40 along its adsorption isotherm [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].

could be understood considering the influence of solvent of the surrounding bulk solution since the effect of surrounding medium on different processes cannot be ignored (Reichardt, 1994). The polarity of the bulk solution decreases due to the formation of micelle as indicated by the emission characteristics of pyrene in the presence of NP surfactant micelles (Sahoo and Misra, 2001). The emission spectrum of pyrene consists of five peaks out of which the relative intensity of the first (I_1) and third (I_3) shows greater solvent dependency (Sahoo et al., 2002a; Thomas, 1984). Qualitatively the ratio (I_3/I_1) decreases with solvent polarity (e.g. 1.65 for hexane and 0.6 for water: Thomas, 1984) and increases with
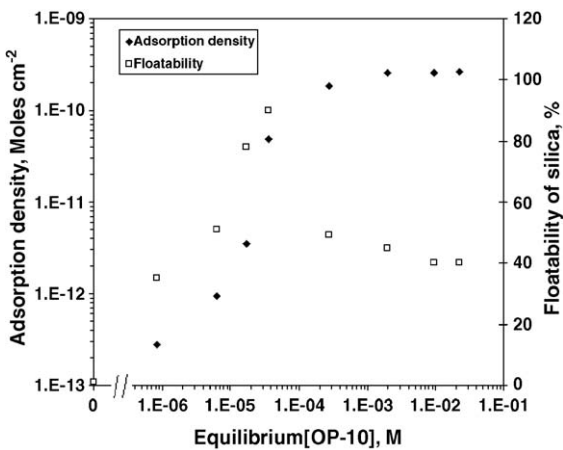
the formation of micelles (Sahoo et al., 2002a; Thomas, 1984). In water the I_3/I_1 value is 0.59 but changes to 0.74–0.85 with the formation of micelles. This I_3/I_1 value correlates well to solvent polarity, E_T (30) values (Misra et al., 2003; Taft, 1981; Kosower, 1981) of surfactant solution. Thus with the formation micellar aggregates, the solvent hydrophobicity of the bulk solution increases which may hold the silica particles through favorable hydrophobic interactions. This is also supported by considering the flotation at the plateau. It is seen that the decrease of flotation recovery due to the presence of OP-30, and NP-40 is about 45% whereas in the presence of the rest of the surfactants it is 40%. In NP-series all three surfactants except NP-40 micelles have I_3/I_1 yield around 0.85–0.9 whereas in the case of NP-40 and

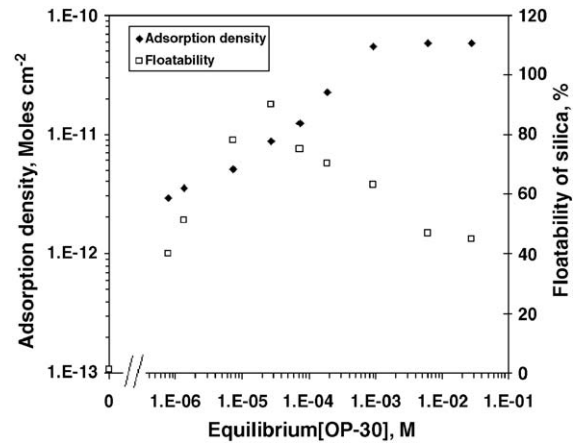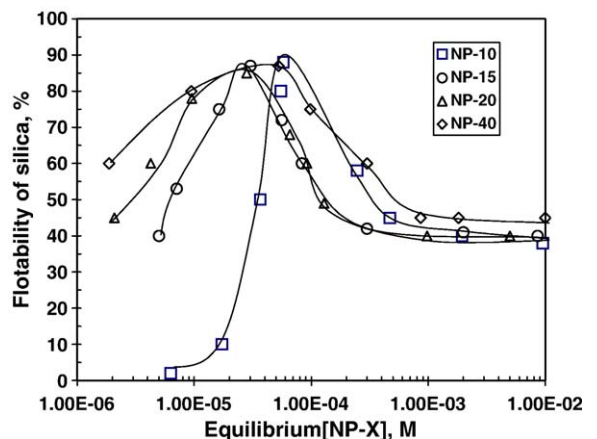Fig. 10. Flotation recovery % of OP-30 along its adsorption isotherm [pH=5.2, I=0.01 M NaCl, Temp=(23±0.2 °C)].

Fig. 9. Flotation recovery % of OP-10 along its adsorption isotherm [pH=5.2, I=0.01 M NaCl, Temp=(23±0.2 °C)].

Fig. 11. Flotation recovery % with change in equilibrium concentration of NP series [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].

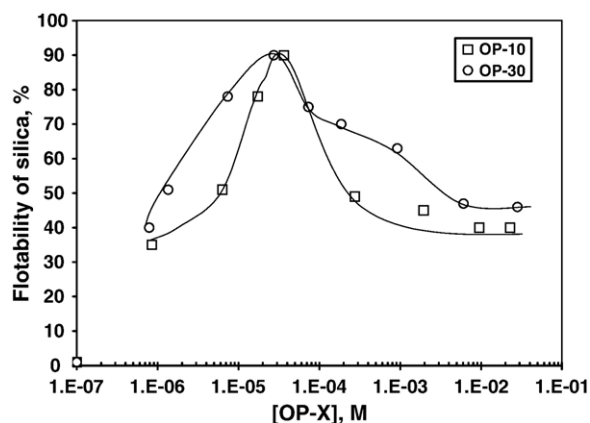Fig. 12. Flotation recovery % with change in equilibrium concentration of OP series [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].

Fig. 14. Comparison of zeta potential of NP-10 and NP-40 [pH=5.2, I=0.01 M NaCl, temp=(23±0.2 °C)].

OP-30 micelles the values are 0.74 and 0.78 respectively. The variation of I_3/I_1 of pyrene with change in concentration of NP-10 is shown in Fig. 15. Fluorescence spectroscopic analysis shows that usually polyoxyethylated nonionic surfactants aggregate to form micelles in step-wise manner (Sahoo et al., 2002a). Due to the large number of polyoxyethylene units in OP-30 and NP-40, their loosely packed micelles and premicelles have substantial penetration of water thereby increasing the micropolarity of the micelle. Flotation recovery can

increase as long as solvent polarity is water-like. In premicellar region the silica surfaces are packed with hemimicelles and isolated monomers from the bulk solution which renders hydrophobicity to the surface. Around the *isoadsorptive point* the hydrophobicity of all surfactants as determined by the hydrophobic chain length, hemimicelles and number of $-CH_2$ group, is maximum for all surfactants. Above *isoadsorptive point* the decrease in flotation may be due to the formation of micellar aggregates which decreases the solvent polarity of the bulk solution.

In conclusion the flotation of silica is increased due to the increase in surface hydrophobicity of silica due to formation of hemimicelles and accumulation of $-CH_2$ on its surface. Decrease of solvent polarity of bulk solution due to the formation of micelles in it is a major constraint of good flotation recovery above CMC.
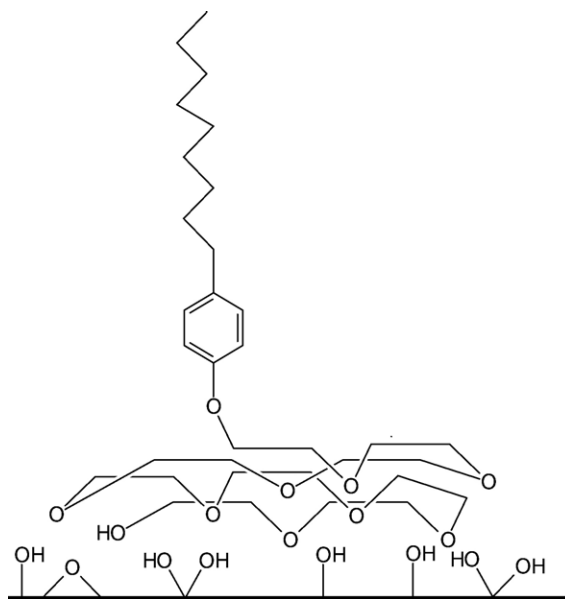

Fig. 13. Schematic diagram of the orientation of NP-10 at silica–water interface. The silica surface has ethereal linkage, gem-OH group, and Silanol-OH group.
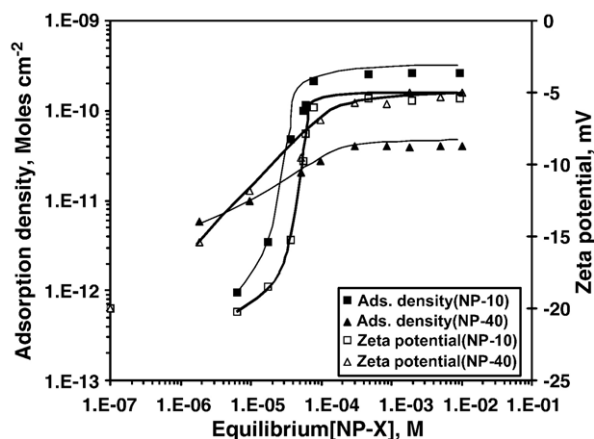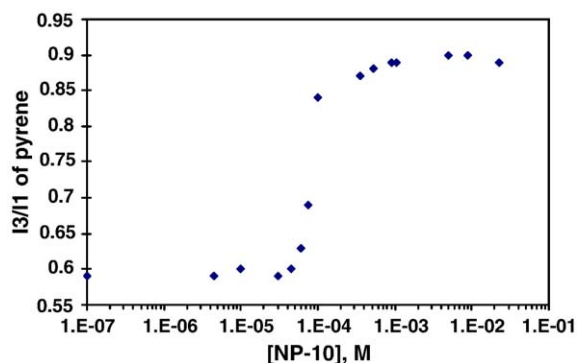

Fig. 15. Variation of polarity parameter(I_3/I_1) of pyrene in presence of various concentration of pyrene I=0.01 M NaCl, temp=(23±0.2 °C)].

Acknowledgement

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