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ORIGINAL CONTRIBUTION

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Kinetics of sodium dodecyl benzene sulfonate adsorption on hematite and its interaction with polyacrylamide

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Abstract This article describes the adsorption of sodium dodecyl benzene sulfonate, an anionic surfactant, on a hematite surface and that when the surface is preadsorbed with polyacrylamide. The adsorption of surfactant on a hematite surface has been studied through equilibration and during kinetics measurements at three pH levels, viz. 4.0, 7.0, 8.9. The surfactant adsorbs strongly on the hematite surface. The adsorption density at equilibrium as well as the rate of adsorption are dependent on the suspension pH. The maximum adsorption density has been observed at pH 4, which reflects strong adsorption of negatively charged sulfonate ions on the oppositely charged Fe_2O_3 surface (point of zero charge, 6.4). The adsorption density reaches its equilibrium value sooner in the case of an alkaline suspension and later in the case of acidic pH. The polymer surfactant interaction has been noticed in the present study and is also a function of pH. The hematite mineral when preadsorbed with the polymer draws fewer of the surfactant molecules at lower surface coverage (during the initial period of the kinetics measurement) irrespective of the pH. When the adsorption of the surfactant reaches a value which is near the equilibrium one, the pH effect is evident. In the case of acidic pH, the surfactant adsorbs more on the hematite surface when preadsorbed with the polymer compared to the bare surface. In the case of neutral or alkaline pH, however, the density of surfactant adsorption remains lower throughout the kinetics measurement when the surface is preadsorbed with the flocculant compared to the bare surface. The particles also remain flocculated till the end of the experiment, whereas at pH 4 the particles are deflocculated. In addition to pH, the electrostatic nature of the adsorbent and the presence of anionic surfactant have an influence on the flocculation–deflocculation phenomena. The polymer–surfactant interaction has been schematically represented. The surfactant is bound with polymeric chains as a combination of its monomeric form as well as in the form of association in the case of acidic media and in competition with polymer in the case of alkaline media.

Key words Flotation · Surfactant · Hematite · Adsorption · Kinetics

Introduction

The flotation of minerals is largely controlled by the adsorption of surfactant at the mineral–water interface. A close correlation has been established between the flotation recovery and the adsorption of collector molecules on the mineral surface [1, 2]. A study on polymer–surfactant interaction is important with a view to develop new and effective methods to enrich and utilize fine particles [3–6]. In the Tilden mine, for example, starch is added to selectively flocculate hematite from silica in the desliming stage prior to flotation [7]. Selective dispersion of hematite by polyacrylamide has also been reported in the flotation of a hematite–quartz mixture [8].

The interaction between the surfactant and the polymer during adsorption has been reviewed earlier [5, 9]. There are several pieces of evidence that the ionic surfactant interacts with nonionic polymer by hydrophobic bonding. Such interaction depends on the physicochemical properties of the polymer and the surfactant as well as on the medium in which they are dissolved [10] and it increases with increasing hydrophobic chain length [11]. Sontum et al. [12] have found that the stability of colloidal iron oxide particles is a function of poly(sodium styrene sulfonate) concentration when it is adsorbed on the surface. It is reported that the presence of preadsorbed poly(ethylene oxide) draws sodium dodecyl sulfonate to the silica/water interface: the phenomenon is referred to as binding by complex formation [6]. Gebhardt and Furestenau [13] observed that flotation of hematite particles is improved by forming flocs of primary particles with a low dose of poly(acrylic acid) before the addition of sodium dodecyl benzene sulfonate (NaDBS) collector. Tadros [14, 15] and more recently Szczypa and Chibowski [16] have observed synergism in adsorption due to the formation of a polymer–surfactant complex. However, there are reports that depending on the conditions the adsorption could be competitive where inhibition by either the surfactant or the polymer could also occur [11, 17]. Meguro et al. [18] have observed that adsorption of anionic and cationic surfactants on particles in multiple layers depending on their orientation results in dispersion or flocculation. Aixing [19] has studied the role of polymers and surfactants in the flocculation and dispersion of aqueous suspensions.

Most of the work reported so far has been confined to the simultaneous adsorption of polymer and surfactant on the solid surface from aqueous solution. The results are different depending on the system being studied and, therefore, signify the role of the properties of both the polymer and the surfactant as well as the nature of the medium and the adsorbent. When polyacrylamide-type flocculant is added prior to the flotation of hematite, the surface is preadsorbed with the polymer and it is important to study the polymer–surfactant interaction; however, the literature seems to be scant in this regard.

Experimental procedure

Materials

Hematite powder (99.9%) was procured from M/s Ventron, Karlsruhe, Germany. Its Brunauer–Emmett–Teller surface area, determined using an AUTOSORB model AS-1 from Quanta Chrome Corporation, N.Y., using nitrogen as the adsorbate, was 9.064 m^2/g. The isoelectric point of the hematite sample corresponds to pH 7.8, which is in agreement with the previous results [20, 21]. The point of zero charge (PZC) of the sample, determined through acid–base titration was 6.4 [22].

NaDBS having the chemical formula $C_nH_{2n+1}C_6H_4SO_3Na$ was used. The high-performance liquid chromatography chromatogram of the NaDBS sample shows that the hydrocarbon chain is mostly composed of C_{11} and C_{12} isomers. Its aqueous solution was found to be UV-sensitive, with the highest absorbance peak at 220 nm. The absorbance data follow Lambert–Beer's law up to a surfactant concentration of 1.2×10^{-4} mol/dm^3, where the absorbance is directly proportional to the concentration. This is in agreement with previous finding [5]. The surface tension of aqueous NaDBS solution at different concentrations was measured using a Kruss K_{10} digital tensiometer under isothermal conditions (temperature maintained at 20 °C). Its critical micelle concentration (cmc) at neutral pH was found to be 1.2×10^{-3} mol/dm^3, which is in agreement with that reported in the literature [23, 24].

The polyacrylamide sample used was supplied by BASF (SEDIPUR AF 404). It was a high-molecular-weight anionic polymer. The Brookefield viscosity of a 0.1% aqueous solution, as provided by the manufacturer, was 230 mPas.

Double-distilled water was used in all the experiments.

Methods

Approximately 1 g hematite powder, weighed accurately, was transferred to each of the flasks having 100 ml aqueous NaDBS solution of different initial concentrations. The flasks were shaken in a water bath maintained at 20 ± 0.5 °C for 6 h, followed by equilibration for another 18 h. The supernatant was withdrawn and centrifuged. Its concentration after appropriate dilution was measured spectrophotometrically at 220 nm against pure water with an absorbance of zero. The adsorption density was computed from the residual concentration data.

The kinetics of the surfactant adsorption was determined by continuous monitoring of the residual concentration of the surfactant using a Colora-Hitachi model U-2000 spectrophotometer at 220 nm. A 300-ml solution of 10^{-4} mol/dm^3 concentration was poured into a flask and the solution was stirred under isothermal condition. Hematite powder (3 g), weighed accurately, was poured into the flask. The solution was pumped to the spectrophotometer at a rate of 6 ml/min at a pressure of 10 bar by a model 250 liquid-chromatography pump supplied by Perkin Elmer Corporation, USA. The absorbance values before and after the addition of hematite were noted as a function of time. The surfactant solution passes through a filter of 5-μm porosity before reaching the spectrophotometer and subsequently through another (in-built) filter of 0.5-μm porosity in order to capture all the hematite particles. It was confirmed through a series of blank experiments that hematite particles do not reach the spectrophotometer from the suspension (the absorbance remains the same as that of pure water).

In order to study the polymer–surfactant interaction, a flocculated sample was used in place of bare hematite. For this 3 g hematite sample was equilibrated with 100 ml 50 ppm aqueous polymer solution and then transferred to the flask. It was established that the presence of polyacrylamide in the NaDBS solution did not affect its absorbance value.

The adsorption density of NaDBS on Fe_2O_3 under isothermal condition was measured as a function of time for three different initial pH values. It was observed that the pH of the suspension changed as the adsorption proceeded. These values were noted periodically. The initial concentration of NaDBS in the solution was kept at 10^{-4} mol/dm^3. Since the spectrophotometer had the limitation as regards corrosion in the system at higher pH (10) the kinetics could be studied up to an initial pH of 8.90.

Results and discussion

Equilibrium adsorption: hematite/NaDBS system

A plot of the magnitude of the adsorption of the surfactant at equilibrium on the hematite surface versus its residual concentration at different initial pH levels of the suspension is shown in Fig. 1 on a log–log scale. The adsorption increases linearly with increasing concentration/adsorption density up to a value which lies between 0.6×10^{-4} and 2×10^{-4} mol/dm^3 depending upon the initial pH of the suspension from acidic (pH 4) to basic (pH 10). Beyond this level the slope decreases and the isotherm becomes almost flat, indicating that the adsorption is independent of concentration. The figure also shows that the adsorption attains a plateau adsorption value which is in agreement with the theoretical adsorption model as well as with the predicted value [25]. Above the cmc the pseudo-phase-separation model [26] predicts that the monomer concentration is constant and that the concentration of the micelles increases linearly with total surfactant concentration.

From Fig. 1 it is apparent that at constant surfactant concentration the adsorption increases with decreasing pH. For hematite H^+ and OH^- are potential-determining ions; therefore, the surface potential increases as the pH is decreased [21]. The increased adsorption magnitude at pH 4 reflects the strong adsorption of anionic sulfonate on the oppositely charged sites of Fe_2O_3. Similar findings have been reported for the ionic surfactants and oxide minerals, such as sodium dodecyl sulfonate–alumina, oleic acid–hematite [27, 28], oleic acid–rutile [29] and ^{14}C-tagged oleic acid–hematite [30] systems.

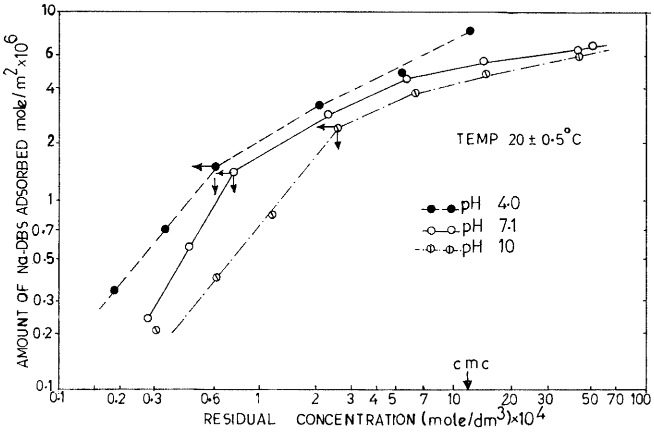

Fig. 1 Equilibrium adsorption isotherms pertaining to the sodium dodecyl benzene sulfonate (*NaDBS*)–Fe_2O_3 system at different pH

Kinetics of NaDBS adsorption on Fe_2O_3

The equilibrium adsorption density at different pH values and the adsorption densities at different time intervals when expressed as a percentage of the former value are shown in Table 1.

From Table 1 it is apparent that the adsorption of NaDBS on hematite reaches 77–83% of the corresponding equilibrium values, depending upon pH, after 10 min. The adsorption density reaches its equilibrium values sooner in the case of an alkaline suspension and conversely later in the case of acidic pH. The surfactant adsorption at the mineral/solution interface is affected by the pH [27, 31–34] because it affects the electrical nature of the interface as well as the distribution of the surfactant species in solution if the surface-active reagent is a weak acid or base. After 150 min the adsorption is above 90% of the equilibrium values in all cases.

The kinetics data for adsorption of the surfactant on the Fe_2O_3 surface when it is preadsorbed with polyacrylamide are compared with those for adsorption on the bare surface in Figs. 2, 3 and 4. These figures show that at any pH level the rate of adsorption (slope) is highest initially; the slope decreases as with time and finally becomes zero, indicating that the adsorption has reached equilibrium. The adsorption of the surfactant is less on the surface preadsorbed with polymer compared to the bare surface. This phenomenon is observed at lower surface coverage (during the initial period of the kinetics measurement) and for all three pH values studied. This may be attributed to the fact that the availability of surface sites for the adsorption by the surfactant is reduced by the presence of polyacrylamide molecules on hematite. Besides, the electrostatic interaction between the sulfonate ions and the positively

Table 1 Adsorption densities in the sodium dodecyl benzene sulfonate and hematite system

pH	Equilibrium adsorption density (mol/m^2 × 10^6)	Adsorption densities at different time intervals expressed as a percentage of the equilibrium value				
		2 min	10 min	50 min	100 min	150 min
4.0 ± 0.1	0.712	22.9	77.2	89.2	91.6	92.3
7.2 ± 0.1	0.580	37.9	79.4	94.9	97.5	99.2
8.9 ± 0.2	0.492	50.8	83.3	97.6	98.5	99.6

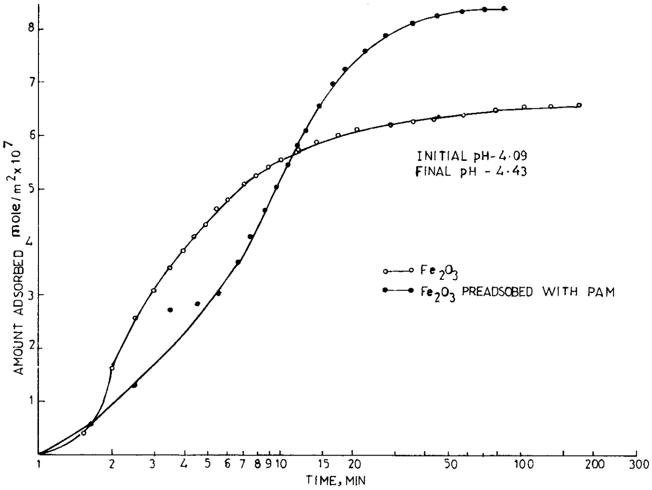

Fig. 2 Kinetics of NaDBS adsorption on bare and preadsorbed Fe_2O_3 surfaces at pH 4 (20 ± 0.5 °C)

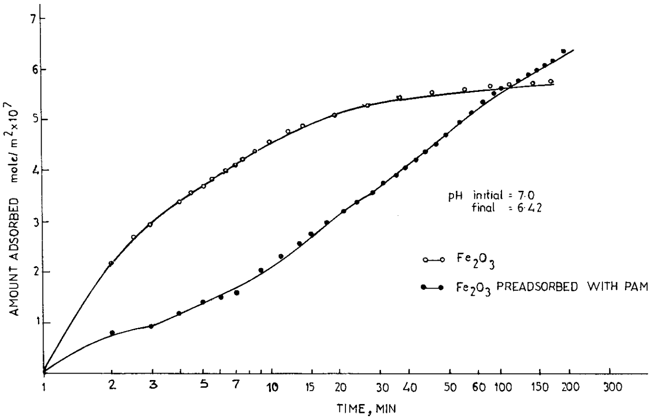

Fig. 3 Kinetics of NaDBS adsorption on bare and preadsorbed Fe_2O_3 surfaces at pH 7 (20 ± 0.5 °C)

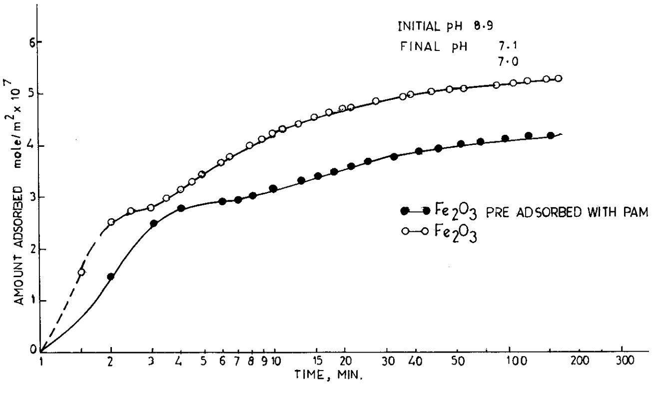

Fig. 4 Kinetics of NaDBS adsorption on bare and preadsorbed Fe_2O_3 surfaces at pH 8.9 (20 ± 0.5 °C)

charged hematite surface at acidic and neutral pH is partly obscured when the polymer is preadsorbed on the surface. A comparison of Figs. 2, 3 and 4 reveals that the difference in adsorption density values in the case of the bare hematite surface and the preadsorbed (by polymer) surface is higher over a considerable period of the kinetics measurement in the case of neutral pH compared to those in the case of acidic or alkaline pH. The fact that larger and a good number of flocs were observed in the case of neutral pH provides a good correlation between the extent of flocculation due to adsorption of the polymer on the hematite surface and the reduction in adsorption density of the surface by virtue of fewer surface sites being available to the molecule for adsorption.

At an adsorption density which is near the equilibrium one, the pH effect is evident. In the case of alkaline (8.9) pH the adsorption density remains lower throughout the kinetics measurement when the surface is preadsorbed with polyacrylamide compared to the bare surface (Fig. 4). It was also observed that the particles remain flocculated till the end of the experiment. Apparently, the available surface area for the adsorption by the surfactant is reduced owing to the presence of polymer molecules on the solid surface. In the case of acidic pH (4) the surfactant adsorbs more on the hematite surface preadsorbed with polyacrylamide compared to the bare surface. The greater adsorption of the surfactant in this case is attributed to binding adsorption. The present result is in agreement with that of Szczypa and Chibowski [16], who observed that the adsorption of sodium dodecyl sulfate (SDS) molecules of flocculated $CaCO_3$ involves interaction of SDS with polymer molecules and is a function of pH and SDS concentration. At reduced pH the formation of hemimicelles is shifted to higher adsorption density [25, 32] and the surfactant molecules should bind both the polymer and the hematite surface (at higher adsorption density) by a combination of electrostatic and hydrophobic interactions, resulting in complex formation between the polymer chain and micelles or premicellar aggregates [5].

The flocculation/deflocculation phenomenon observed in the present case is attributed to the change in conformation of the polymeric chain with the pH of the medium, the electrostatic nature of the adsorbent (with changing pH) as well as the presence of anionic surfactant. Under alkaline conditions, polyacrylamide hydrolyzes at low temperature, whereas generally higher temperatures are required to hydrolyze under neutral or acidic conditions [35]. ^{13}C NMR studies have shown that the sequence distributions of carboxyl and amide upon hydrolysis is a function of pH; while at low pH blocks of carboxyl groups are obtained, at high pH carboxyl groups are more randomly distributed [36–38]. A schematic description of the effect of pH on the

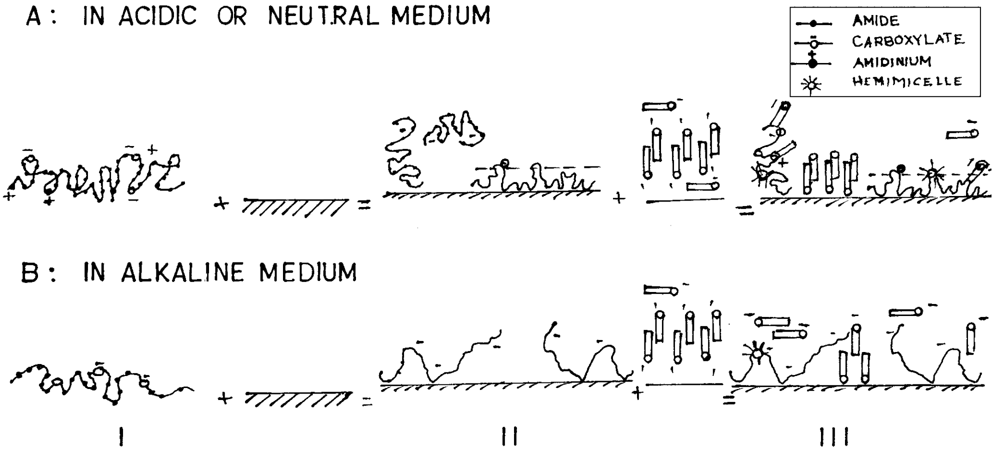

Fig. 5 Schematic diagram showing the effect of pH on the conformations of polyacrylamide molecules in solution (*I*) and at the hematite surface (*II*); the binding adsorption of NaDBS with polymer at pH 4 and competitive adsorption at pH 8.9 (*III*)

configuration of anionic polyacrylamide in the bulk and when adsorbed on the surface at constant ionic strength is shown in FIg. 5. In the case of alkaline media the mildly hydrolyzed polymer has suitably extended chains as a result of intermolecular repulsive interactions [39] and when adsorbed under these conditions on a slightly negatively charged hematite surface they provide good flocculation. It is also more likely that (at alkaline pH) the negatively charged surfactant interacts with polyelectrolyte having more OH^- ions, which results in a more expanded coil than in case of acidic pH. In the case of acidic media, on the other hand, the polymeric chains are tightly coiled and are adsorbed mainly in trains owing to the lack of repulsion with the surface and this results in poor flocculation [40].

The polymer–surfactant interaction with changing pH has been proposed through the schematic representation which is also shown in Fig. 5. The surfactant is bound with polymeric chains in the case of acidic media and is in competition with polymer in the case of alkaline media. In the former case the surfactant is bound with polymer chains through hydrophobic bonding as a combination of its monomeric form resulting in association between the hydrophobic tail of the surfactant and similar areas on the polymer as well as in the form of association which may result in the formation of hemimicelles along the polymer chains [41–43]. In the latter case, the available surface area for the adsorption by the surfactant was reduced owing to the presence of polymer molecules on the solid surface.

Conclusions

NaDBS adsorbs strongly on a Fe_2O_3 surface. The isotherms reach saturation at a concentration which is beyond the cmc. The surfactant adsorption decreases with an increase in pH and vice versa. The phenomenon is understandable since at lower pH the Fe_2O_3 surface becomes positively charged, favoring attraction of the negatively charged sulfonate ions. The adsorption density reaches its equilibrium value sooner in the case of an alkaline suspension and conversely later in the case of acidic pH.

The polymer–surfactant interaction is influenced by the suspension pH. The hematite mineral when preadsorbed with the polymer draws fewer of the surfactant molecules at lower surface coverage (during the initial period of the kinetics measurement) irrespective of the pH. When the adsorption of the surfactant reaches a value which is near the equilibrium one, the pH effect is evident as follows.

- At pH 4.0 the surfactant adsorbs more on the hematite surface when preadsorbed with the polymer compared to the bare surface and the particles are subsequently deflocculated.
- In the case of neutral or alkaline pH (the PZC of hematite is 6.4) the density of surfactant adsorption remains lower throughout the kinetics measurement when the surface is preadsorbed with the flocculant compared to that in the case of the bare surface. The particles also remain flocculated till the end of the experiment.

The flocculation–deflocculation phenomena have been explained in terms of the suspension pH, the electrostatic nature of the adsorbent as well as the presence of anionic surfactant. The polymer–surfactant interaction has been schematically represented. The surfactant is bound with polymeric chains as a combination of its monomeric form as well as in the form of association by virtue of hydrophobic bonding in the case of acidic media and in competition with polymer in case of alkaline media.

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