THERMODYNAMIC STUDIES OF ADSORPTION AND MICELLIZATION
OF ALKYL XYLENE SULFONATES

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Adsorption of surfactants has important applications in many industrial processes such as enhanced oil recovery, detergency and flotation. Among the different factors that influence surfactant adsorption, surfactant structure plays a major role. The purity of the surfactant is critical in adsorption studies because impurities even in small amounts can mask the effect of structural variations on adsorption. In this study, effect of position of sulfonate and methyl groups on the benzene ring on the adsorption of alkyl xylene sulfonates on alumina was investigated using isomerically pure surfactants. Charge in charge characteristics of the mineral due to the surfactant adsorption was investigated by measuring the zeta potential. Microlcalorimetry was used to measure the enthalpies of adsorption and micellization of the surfactants. Position of the functional groups on the ring showed a marked influence on the adsorption and this is explained on the basis of electrostatic and steric effects that are dependent on the relative positions of the groups. The studies also showed that at low adsorption densities enthalpy was the governing factor, while at higher coverages, entropy was the main driving force.

INTRODUCTION

Surfactants are used in a number of industrial processes such as enhanced oil recovery, detergency, flotation and microelectronics. In addition, surfactant aggregates such as micelles and hemimicelles have potential applications in novel separation and reaction schemes such as catalysis and solar energy conversion. The feasibility of many of the applications resides largely in the ability of these microstructures to function as microscopic reaction media that enable encapsulation and compartmentalization of key ingredients necessary for the catalysts and manipulation of reactions. Therefore, a full understanding of the mechanisms of surfactant adsorption and of phenomena controlling hemimicellization and micellization is important for improving the efficiency of the above processes.

Studies on surfactant adsorption have shown the phenomenon to be highly complex and to depend on a number of factors such as pH, ionic strength, temperature and surfactant structure. Surfactant adsorption is very sensitive to changes in surfactant structure as is evident from the literature.
The effect of different structural modifications such as change in alkyl chain length, branching of the alkyl chain and addition of functional groups such as ethoxyl and methyl groups on surfactant adsorption has been investigated in detail. An important variation in surfactant structure is the position of functional groups. However, systematic studies on the effect of the position of functional groups on adsorption are lacking. In this work, the effect of position of methyl and sulfonate groups on the benzene ring on the adsorption and micellization of alkyl xylene sulfonates has been investigated using microcalorimetry, electrokinetics and surface tension. Calorimetry provides accurate thermodynamic data and these data are helpful for elucidating the mechanisms of micellization and adsorption. Calorimetry has been extensively used to measure the enthalpies of micellization of single surfactants and also the excess enthalpy of mixing of surfactant mixtures. Extension of calorimetric work to study adsorption at solid/liquid interface has been limited. The emphasis in most of the work has been on the establishment of the technique to study adsorption and studies show the potential of this technique to understand the adsorption mechanisms.

EXPERIMENTAL

Materials

Surfactants: The two alkyl xylene sulfonates used in this study were obtained from ARCO Exploration and Technology Company. The surfactants were specified to be at least 97% isomerically pure. Their structures are given below. The para xylene sulfonate (sulfonate in the para position) will be referred to as Para S and the meta xylene sulfonate as Meta S.

<table>
<thead>
<tr>
<th>Meta S</th>
<th>Para S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina: High purity Linde A alumina purchased from Union Carbide was used as substrate. The specific surface area was determined by nitrogen adsorption to be 15 m²/g.</td>
<td></td>
</tr>
</tbody>
</table>

Experimental Conditions

All the experiments were carried out at 43.3°C and at a constant ionic strength of 3 × 10⁻² kmol/m³ NaCl.

Methods

Surface Tension: Surface tension was measured using water-jacketed ring tensiometer set to the test temperature.

Adsorption: For adsorption on alumina, a gram was conditioned with 0.03 kmol/m³ NaCl for 2 hours. Then, 5 ml of surfactant solution of desired concentration in 0.03 kmol/l NaCl was added and the slurry was centrifuged and the supernatant analyzed for concentration.

Surfactant Analysis: The surfactant concentration was analyzed using DU-8 UV-Vis spectrophotometer at a wavelength of 254 nm.

Microcalorimetry: Calorimetric experiments were performed using a differential microcalorimeter system. The calorimeter consists of a rotating cell placed inside an air bath maintained at a constant temperature. The block contains sample cell and a reference cell. Each cell has two compartments. Mixing of the reactants is achieved by rotating the block. The temperature difference is then measured using thermocouples attached to each cell. The outputs of the thermocouples are read.
The adsorption isotherms obtained for the two surfactants on alumina are given in fig. 1. The shape of the isotherms is typical of that of ionic surfactant adsorption on oppositely charged oxide minerals, with the adsorption at low surfactant concentration due to electrostatic attraction between the surfactant species and the charged surface sites and at high concentrations being in addition due to the associated interactions between the hydrocarbon chains to form hemimicelles. When the particle charge is neutralized by the oppositely charged surfactant species, additional adsorption takes place with electrostatic repulsion between the particles and the species holding up till the critical micelle concentration. The adsorption of Para S is higher than that of Meta S in the premicellar region but is the same in the plateau region. The lower adsorption of Meta S could possibly be due to its lower hydrophobicity and to the increased steric constraints arising from the position of the methyl groups to the packing of the surfactant molecules in the hemimicelles. Reverse phase high performance liquid chromatography was used to obtain a measure of the relative hydrophobicity of the two surfactants. The stationary phase used was a 75/25 mixture of octadecyl and tetrabutylammoniumphosphate. The retention time of the para xylene sulfonate was 8.2 minutes and that of the meta xylene sulfonate was 7 minutes. The higher retention time of Para S shows that it is indeed more hydrophobic than Meta S.

Surface Tension

Surface tension data are useful for interpreting the adsorption data on solids, since they do provide complementary information on adsorption at the liquid/air interface and also information on surfactant interactions in solution. Surface tension results obtained for the two surfactants are given in fig. 2. Absence of a minimum in the two curves indicates that the surfactants are sufficiently pure. From the data it can be seen that Para S is more surface active than Meta S. Also, the CMC of Para S is 35 x 10^{-4} kmol/m^3, which is higher than that of Para S (3.5 x 10^{-4} kmol/m^3). These results indicate that the behavior of the two surfactants is similar at all the interfaces.
Figure 1. Adsorption of alkyl xylene sulfonates on alumina.

Figure 2. Surface tension of alkyl xylene sulfonate solutions.
Enthalpy of Micellization of Para S

The heat of dilution data for premicellar and micellar Para S solutions are given in Tables I and II, respectively.

<table>
<thead>
<tr>
<th>C_{init} (kmol/m³)</th>
<th>C_{fin} (kmol/m³)</th>
<th>ΔH_{dil} (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.11 x 10⁻⁴</td>
<td>2.02 x 10⁻⁴</td>
<td>-120</td>
</tr>
<tr>
<td>3.11 x 10⁻⁴</td>
<td>2.56 x 10⁻⁴</td>
<td>-116</td>
</tr>
<tr>
<td>3.11 x 10⁻⁴</td>
<td>2.10 x 10⁻⁴</td>
<td>-118</td>
</tr>
</tbody>
</table>

Average: -118

Table II. Heat of Dilution of Micellar Solutions.

<table>
<thead>
<tr>
<th>C_{init} (kmol/m³)</th>
<th>C_{fin} (kmol/m³)</th>
<th>9_{dil} (cal)</th>
<th>ΔH_{m} (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.77 x 10⁻⁴</td>
<td>2.80 x 10⁻⁴</td>
<td>3.93 x 10⁻⁴</td>
<td>-1041</td>
</tr>
<tr>
<td>8.92 x 10⁻⁴</td>
<td>2.86 x 10⁻⁴</td>
<td>5.04 x 10⁻⁴</td>
<td>-1084</td>
</tr>
<tr>
<td>1.13 x 10⁻³</td>
<td>2.58 x 10⁻⁴</td>
<td>4.67 x 10⁻⁴</td>
<td>-1148</td>
</tr>
</tbody>
</table>

Average: -1091

The dilution of premicellar solutions results in an exothermic change of -118 cal/mol, and is due to dilution of sulfonate monomers. For the dilution of micellar solutions, demicellization accounts for the bulk of the heat change, which for Para S is exothermic. The ΔH_{m} values are given in column 4 of Table II and show excellent consistency with a mean value of -1091 cal/mol. Since, the standard state of micelles is defined to be the state of infinite dilution, i.e. CMC, and the dilution measurements are carried out in the region of the CMC, the value of -1091 cal/mol is approximately the standard enthalpy of micellization, ΔH^{0}_{m}.

Enthalpy of Micellization of Meta S

The heat of dilution results for premicellar and micellar Meta S solutions are given in Tables III and IV, respectively.

<table>
<thead>
<tr>
<th>C_{init} (kmol/m³)</th>
<th>C_{fin} (kmol/m³)</th>
<th>ΔH_{dil} (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.22 x 10⁻⁴</td>
<td>4.96 x 10⁻⁴</td>
<td>-33</td>
</tr>
<tr>
<td>6.22 x 10⁻⁴</td>
<td>4.97 x 10⁻⁴</td>
<td>-39</td>
</tr>
</tbody>
</table>

Average: -36

<table>
<thead>
<tr>
<th>C_{init} (kmol/m³)</th>
<th>C_{fin} (kmol/m³)</th>
<th>9_{dil} (cal)</th>
<th>ΔH_{m} (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.96 x 10⁻⁴</td>
<td>3.57 x 10⁻⁴</td>
<td>4.94 x 10⁻⁴</td>
<td>-745</td>
</tr>
<tr>
<td>5.96 x 10⁻⁴</td>
<td>3.86 x 10⁻⁴</td>
<td>4.74 x 10⁻⁴</td>
<td>-720</td>
</tr>
<tr>
<td>1.20 x 10⁻³</td>
<td>6.01 x 10⁻⁴</td>
<td>9.31 x 10⁻⁴</td>
<td>-858</td>
</tr>
</tbody>
</table>

Average: -774

sulfonates on alumina.

cene sulfonate solutions.
The mean heat of monomer dilution is -36 cal/mol, which is significantly smaller than that for Para S dilution. Applying this correction to data obtained with demicellized solutions and using a CMC of $6.3 \times 10^{-3}$ kmol/m$^3$, the above data yield a mean $\Delta H^\circ_m$ of -774 cal/mol.

The standard free energy of micellization according to the phase separation model\textsuperscript{20} is given by

$$\Delta G^\circ = 2RT\ln(CMC)$$

where CMC is the critical micelle concentration expressed as a mole fraction.

The standard entropy of micellization is then calculated from the following equation

$$\Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T$$

The values for the thermodynamic parameters of micellization for the two surfactants are tabulated below:

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ$ (cal/mol)</th>
<th>$\Delta G^\circ$ (cal/mol)</th>
<th>$\Delta S^\circ$ (cal/deg mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Para S</td>
<td>-1091</td>
<td>-15,226</td>
<td>45</td>
</tr>
<tr>
<td>Meta S</td>
<td>-774</td>
<td>-14,407</td>
<td>43</td>
</tr>
</tbody>
</table>

The main contribution to the free energy change of micellization comes from the entropy change arising from the removal of water molecules from around the hydrocarbon chain. Both the enthalpic and entropic changes for the Para S are more favorable than that for Meta S.

**Enthalpy of Adsorption**

The differential adsorption enthalpy of the two surfactants as a function of the adsorption density is shown in figure 3. The enthalpy of adsorption of the two surfactants is exothermic at all adsorption densities and decreases rapidly with the formation of surfactant aggregates through hemimicellization. This indicates that, like the formation of micelles, the formation of hemimicelles is also entropy driven. The enthalpy of adsorption of Para S is higher than that of Meta S at low adsorption densities indicating greater attraction to the mineral which results in its higher adsorption in region I as seen from figure 1. This greater attraction to the mineral could be due to Para S being more negatively charged than Meta S. This was tested by measuring the electrokinetic potential after adsorption of the two surfactants and this will be discussed later. Once hemimicelles form, the enthalpy of adsorption of the two surfactants is the same. The free energy of hemimicellization of Para S is higher than that of Meta S as is evident from its greater adsorption. Since, the enthalpy of hemimicellization is the same, the entropy of hemimicellization is higher for Para S than for Meta S. The entropy can be considered to result from two contributions: a negative contribution due to ordering of the surfactant in the aggregate and a positive and major contribution from the release of the water molecules structures around the hydrocarbon tail upon its association. Thus, the releasing of the molecules in the aggregates, the more will be the release of water molecules and higher will be the entropy. Thus, the higher entropy of hemimicellization of Para S indicates tighter packing of the molecules which was proposed earlier as the reason for its higher adsorption.

**Electrokinetic Potential of Alumina**

The zeta potential of alumina after the adsorption of the two surfactants is shown in figure 4 as a function of the adsorption density. The zeta potential is the same for the
6 cal/mol, which is significantly higher than the data obtained with 0.4 kmol/m³. The above data yield a value of 15.226 kcal/mol for the enthalpy of adsorption of the two surfactants at low adsorption densities. This indicates that the charge characteristics of the two surfactants are the same or that the technique is not sensitive to small changes in the charge of the surfactant, and this does not explain the greater enthalpy of adsorption of Para S to the mineral at low concentrations. One possible reason could be that the water molecules near the alumina surface being structured, the interfacial region is relatively less hydrophilic and Para S due to its greater hydrophobicity (as measured by HPLC) is drawn more to the interface than Meta S.

![Figure 3. Enthalpy of adsorption of alkyl xylene sulfonates on alumina.](image)

![Figure 4. Zeta potential of alumina after surfactant adsorption.](image)
Mixed Micelle Format

Surface tension was also used to measure the CMC of the mixtures of these two surfactants and the results are given in Fig. 5. Also, the theoretical CMC values for the different mixtures calculated using the ideal solution and regular solution theories are shown in this figure. The system shows a negative deviation from the ideal behavior which is not normally expected for mixtures of similar surfactants. Regular solution theory fits the data well with an interaction parameter \( (W) \) of -0.32. The deviations from ideality can be attributed to the difficulty in packing of the molecules in the mixed micelles. However, prior to applying the regular solution theory to model the data, it is necessary to verify the validity of the thermodynamic assumptions of the theory as applied to the system under investigation. Regular solution theory is based on the assumption that the excess Gibbs free energy of mixing is given by

\[ \Delta G_{\text{mix}} = X_1 X_2 W R \]  

where \( X_1 \) and \( X_2 \) are the mole fractions of the two surfactants in the mixed micelle and \( W \) is the interaction parameter. Regular solution theory also assumes that the excess entropy and volume of mixing are zero and hence

\[ H_{\text{mix}} = X_1 X_2 W R \]  

Recently, \( H_{\text{mix}} \) and Scamehorn\(^{36,37}\) have measured enthalpy of mixing that the assumptions are valid for our system.

The excess enthalpy of mixing of the two surfactants in this study was measured using microcalorimetry and is shown in Figure 6. The interaction parameter obtained by fitting the excess enthalpy data was -0.32. This value is very close to -0.32 obtained from the surface tension data, indicating that the assumptions are valid for our system.

Figure 5  CMC of mixture of para xylene sulfonate and meta xylene sulfonate
the CMC of the mixtures of these two surfactants. The deviations from the theoretical CMC values for the ion and regular solution theories are due to the small changes in the surfactant structure. Regular solution theory (W) of -0.32. The deviations from the ideal behavior of the molecules in the mixed solution theory to model the data, it is evident from this work that the small changes in the surfactant structure, such as change in the position of sulfonate and methyl groups on alkyl xylene sulfonates can have a marked effect on the adsorption characteristics. The Para S adsorbed to a greater extent than the Meta S on alumina. The lower adsorption of Meta S is attributed to its lower hydrophobicity and increased steric hindrance to the packing of the molecules in the hemimicelles. Microcalorimetry is sensitive to such small changes in structure and is an excellent tool to study mechanism of surfactant adsorption. The studies indicate that at low adsorption densities, enthalpy is the driving force while at higher concentrations, the adsorption is governed by entropic changes due to micelle formation. It helped confirm the steric hindrance to the packing of the molecules as the reason for the difference in the adsorption of the two surfactants. Surprisingly, mixed micellization of the two surfactants is non-ideal and regular solution theory fits the data well. Microcalorimetry shows that the thermodynamic assumptions of the theory are valid for the surfactant mixtures.

CONCLUSION

It is evident from this work that the small changes in the surfactant structure, such as change in the position of sulfonate and methyl groups on alkyl xylene sulfonates can have a marked effect on the adsorption characteristics. The Para S adsorbed to a greater extent than the Meta S on alumina. The lower adsorption of Meta S is attributed to its lower hydrophobicity and increased steric hindrance to the packing of the molecules in the hemimicelles. Microcalorimetry is sensitive to such small changes in structure and is an excellent tool to study mechanism of surfactant adsorption. The studies indicate that at low adsorption densities, enthalpy is the driving force while at higher concentrations, the adsorption is governed by entropic changes due to micelle formation. It helped confirm the steric hindrance to the packing of the molecules as the reason for the difference in the adsorption of the two surfactants. Surprisingly, mixed micellization of the two surfactants is non-ideal and regular solution theory fits the data well. Microcalorimetry shows that the thermodynamic assumptions of the theory are valid for the surfactant mixtures.

ACKNOWLEDGEMENTS

The authors (A.S. and P.S.) wish to thank the National Science Foundation (CBT-86-15524), Department of Energy (DE-FG22-89BC14432), ARCO Oil and Gas Company, BP-America and New York Mining and Minerals Resources Research Institute (NYMRRRI) for funding of this work.

REFERENCES


THICKENING OR DEWATERING OF SLOW-SETTLING MINERAL SUSPENSIONS

Invited lecture by P. Somasundara:
Henry Krumb School of Mines, Columbia University, New York, USA

INTRODUCTION

The processing of slow-settling mineral suspensions called slimes or sludges is an industrial problem of great magnitude. A typical example of this problem is the one facing the phosphate mining industry in the southern United States. There, just an hour's drive from the fantasy land of Walt Disney, a piece of colossal machinery bearing whimsical names such as Super Scooper, mine for phosphate rock. This operation, while yielding about 30% of the world phosphate required for meeting the fertilizer need for ever-increasing food production, also produces in its wake slimes that has to be thickened or dewatered. This slime is currently being held in lakes covering thousands of acres of land and since it is slow-settling, the land that it covers remains unused and the billions of gallons of water that it contains remain immobilized. Similar slimes and sludges are also generated in other industries, some

operations the clays are liberated from the matrix. It is mainly this clay which, when present along with other minerals, appears to be responsible for the slow-settling behavior of slimes. The role of clays has been investigated recently by Naqaraj, McAllister and Somasundaran \[12\] who studied the sedimentation behavior of suspensions of various combinations of major mineral components of phosphatic slime or morphologically similar materials.

The systems investigated were essentially composed of kaolinite or montmorillonite, quartz and a fibrous mineral (attapulgite, chrysotile or amphibole). Table 1 lists various the mineral systems that were studied. It was stipulated that a system should simulate the following settling characteristics of typical slow-settling slimes: (a) an initial period of gelling; (b) slow overall subsidence with a continuously changing settling rate that is typical of a network structure; (c) absence of significant segregation of mineral constituents during sedimentation; (d) a clear supernatant and a sharp slurry/supernatant interface; (e) a bulky sediment; (f) presence of tears and channels in the sedimenting structure, and (g) water exiting as microvolcanoes. A system exhibiting such characteristics can also be used as a model system for controlled studies on slow settling. The study of Naqaraj et al. \[12\] showed that none of the constituent minerals themselves or their binaries resembled industrial slime with respect to the above characteristics.

From the various combinations of kaolinite, montmorillonite attapulgite, quartz, chrysotile, and amphibole studied, the montmorillonite-attapulgite-kaolinite ternary and the montmorillonite-attapulgite-kaolinite-quartz quarternary were found to
### TABLE 1

**Mineral Systems Studied**

<table>
<thead>
<tr>
<th>Single Minerals:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>Quartz</td>
</tr>
<tr>
<td>Kaolin</td>
<td>Chrysotile</td>
</tr>
<tr>
<td>Attapulgite</td>
<td>Amphibole</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Binary Systems:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin-Chrysotile 1:1</td>
<td>Attapulgite-Montmorillonite 4:1 and 6:1</td>
</tr>
<tr>
<td>Kaolin-Attapulgite 1:4 and 1:1</td>
<td>Amphibole-Montmorillonite 4:1, 5:1 and 6:1</td>
</tr>
<tr>
<td>Kaolin-Amphibole 1:1</td>
<td>Chrysotile-Montmorillonite 4:1</td>
</tr>
<tr>
<td>Kaolin-Quartz 1:2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ternary Systems:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite-Attapulgite-Kaolin</td>
<td></td>
</tr>
<tr>
<td>Montmorillonite-Attapulgite-Quartz</td>
<td></td>
</tr>
<tr>
<td>Kaolin-Attapulgite-Quartz</td>
<td></td>
</tr>
</tbody>
</table>

**Quaternary System:**

*Montmorillonite-Attapulgite-Kaolin-Quartz*

behave very similarly to the industrial slime. The study using these systems also enabled us to determine the role of each constituent. The clay minerals, montmorillonite and attapulgite, were found to be responsible for the slow sedimentation rate, possibly to their peculiar morphology and swelling properties. For example, whereas montmorillonite-attapulgite-kaolinite-quartz behaved similarly to industrial slime, the ternary system kaolinite-attapulgite-quartz showed no similarity - suggesting that montmorillonite does play a major role in determining the settling behavior of slimes. Similarly, systems without attapulgite or other fibrous-type mineral were also found to settle differently from typical slimes.
The earth supernatant can be mineralized by large art. The era component in the pH of all we observed till obtain supernatan

IMENATA

other are not shown: study spending the part.
study the mening the sol.
pu: the impo with trea
imary In use: be strength so:
study is major conceal the pan: the can then thinner we
ser: hang in the strata: the fun time bat with
This usual sensed the tai: in be enemy the supernatan
im: per int: on mod ha: been till laran and
3) and spect view an:
imp sediment: produced by susi
act: aqua ti
cen: to the cas: bat
se: act: by in: gh: vs
an: se
period". It is easily analysed along the lines of the modified Kozeny model for flow through porous media [14]. Here settling ends abruptly with little further decrease in height; such material is said to be incompressible.

![Fig. 1. Typical batch sedimentation curve.](image)

On the other hand, when the system contains particles of different sizes, one can obtain multiple interfaces [15-17]. Davies [18] has shown that the existence of such multiple interfaces can be seen up to a critical solid concentration of about 30 to 35 vol.%. The appearance of multiple interfaces is attributed to the faster settling of the larger spheres. Above the critical concentration, this differential settling is prevented by interparticle distances that are smaller than the diameter of the smaller particles.

In contrast to the above cases, the sedimentation curves of dilute suspensions of clay-type materials display a reverse S-shape such as the one shown in Fig. 2, which is in fact so
TABLE 2

Major Criteria in Dewatering

- Solid concentration of sediment
- Volume of sediment
- Settling rate
- Supernatant clarity
- Cake yield strength
- Cake moisture

Fig. 2. Reverse S-shape sedimentation curve.
Figure 3. Sedimentation curves for slurries of various solid
concentrations [24].

Each solid concentration region shown in Fig. 3.

three different types of settling curves are obtained, one for
tended three-dimensional network, on the basis of this model,
ters called aggregates, and the aggregates in turn form an ex-
tect particle, as low shear rates, the flocc group into large clus-
ters of particles called a floc, rather than the indidual
cluster. In the Michaels-Bolger model, the basic flow unit in the floccs-forming model is a small
structure of the floccs and the properties of the surrounding medium.

intended the settling rate of flocculated particles to the matrix-
study in this area is that of Michaels and Bolger [24], who ex-
tray, qualitative, and quantitative [20-23]. A number of investigations have been studied
The sedimentation of such clay suspensions has been studied.

time period, suggesting that the material is compressible.
In this case, an ever-decreasing rate over an extremely long
start settling rate period [19]. Moreover, settling continues
curved that no region could be described as exhibiting a con-
the work, provided that
the boundary between
the two areas is clearly
indicated in the any-
cameras. For
the under
area, it,
the
boundary be-
tween
the
two
areas is
clearly
indicated
in the
any-cama-
ras.
suggest that the container diameter has a negligible effect on the settling of flocculated slurries. The effect of container diameter on the settling of a phosphatic clay suspension examined by us [26], however, showed that the diameter has a definite effect on the settling rate (Fig. 4). An increase in diameter caused a decrease in the settling rate for diameters up to about 8 cm and above that, a slight increase. This observation can, however, be explained with the help of a phenomenological model that we have developed.

![Fig. 4. Diagram illustrating the effect of container diameter on the height of phosphate slime-supernatant interface; initial solids concentration, 2.6% -37 μm slime; no additives, height of the slime column, 17.8 cm, time of settling, 8 h [26].](image-url)
Our model is based on the actual visual observation of the settling systems and the formulation of the simplest plausible equations for the settling curves which display an S-shape with no region exhibiting a constant settling rate period and settling continuing at an ever-increasing rate over an extremely long time period. In fact it is in this respect, i.e., where constant settling rate period is absent, that these systems fail to be satisfactorily represented by the previous models of Kynch, Richardson-Zaki, etc.

Figure 5 illustrates the observed sequence of the settling. In the first one or two seconds after one stops mixing the slurry, the rotational movement of the suspension ceases due to gelling. The gelling process itself appears to be complete over a period of several minutes, and then due to the downward movement of coarser particles and the upward movement of micro air bubbles through the structure, fissures and tears begin to form. Water seeps up through these tears and when the water meets resistance to its continued transport, lenses of water are formed. Further seepage occurs when channels open up between tears, with water finally exiting at the slurry-supernatant interface in the form of microvolcanoes. At this point one can clearly see the interface settling down quickly and water along with entrained particles can be seen spouting through the center of the domes of the volcanoes. Water also seeps along the walls of the container, folding the slurry away from the wall at the interface. The observed effect of the container diameter on the rate of settling is in fact attributed to this seepage..
SEDIMENTATION PROCESSES FOR BATCH CONDITIONS

Fig. 5. Sedimentation processes for batch conditions [26].
2.6% phosphatic slimes, 0.5 g coarse graphite tracer.
Observations: 0 min, suspension gels almost immediately following mixing and the rotational movement terminates; ~10 min, rising air bubbles and descending particles create vertical tears; ~13 min to ~35 min, water concentrates into lenses around the tears; ~2 h, channeling and microvolcanoes enhance dewatering process; ~4 h, water filaments depleted, channels begin to close and no further significant sedimentation.
along the walls. The advantages of using a thickener with an inclined wall is very well known. On the whole, the sediment settles as a bulky compressible mass, leaving a clear supernatant. Finally the continuous removal of water causes the contraction of the channels and as a result further subsidence becomes difficult.

If the movement of either the particles or micro air bubbles through the slurry structure is responsible for dewatering, then the addition of coarse particles to the slurry or the generation of micro-bubbles in it should enhance its sedimentation. The effect of particles and micro-bubbles have been tested and the results are discussed below.

**Effect of Coarse Particle Additives**

As shown in Fig. 6, the addition of different amounts of sand tailings to slime was indeed found to increase the settling rate by as much as fifty-fold. The reason for the effect of additives was investigated by conducting settling tests using particles with a wide range of specific gravities, surface properties, sizes and shapes. The effect of varying the density of the additives was studied primarily to test the possibility that the effect of coarse particles might be due to an increase in the weight of the slurry network when they are trapped in it. If the effect of the coarse particles was due to such an increase in the weight of the network, denser particles should be better additives. Results given in Fig. 7, however, show that an increase in the density of the additive produced no enhancement in settling; this suggested that the observed effects were not
due to any increase in the weight of the network. It is inter-
resting to note here that cassiterite, the heaviest mineral,
produced no effect on settling. A careful examination of the
settling suspensions showed that the heavy cassiterite parti-
cles had broken through the slurry before the slurry had a
chance to gel and trap them. Apparently, since the particles
had thus already left the slurry, it could produce no effect
on subsequent settling. Hydrophobic silicon-coated glass beads.

Fig. 6. Diagram illustrating the effect of addition of
quartz flotation tailings on the settling of 2.6%
-37 μm phosphatic slime, vertical bars indicate
range when larger than the symbol [26].
which also broke through the slurry too early, similarly failed to produce any effect on settling. In contrast, uncoated (and thus hydrophilic) glass beads and quartz particles of the same size did get trapped in the slurry and were effective in enhancing the settling. Thus various hydrophilic and partially hydrophilic minerals had approximately the same effect on the subsidence, while totally hydrophobic silicone coated glass beads did not have much effect. This finding suggested that some polar interactions with the aqueous medium is necessary.
to hold and trap the coarse particles in the slurry during gel-
ning in order that there can be subsequent movements in the
slurry for the creation of tears.

In this regard, it appears that addition of certain polymers
to the whole slurry or treatment of the coarse additives with
polymers under certain conditions might be beneficial to settl-
ing. The effect of polymers could possibly be due to the en-
hanced bridging of particles to clay and resultant better trap-
ning of particles by the slurry. Whether such bridging occurs
or not, results of La Mer et al. [28] given in Fig. 8 do show
that addition of polymers can produce significant effects on
settling. It is to be noted, however, that while polymers may
increase the initial settling rate, the final solid content can
even be lower than where there is no such increase, often due

![Diagram](image)

**Fig. 8.** Sedimentation in the absence (curve I) and in the
presence (curve II) of polymer [28].
to almost permanent entrapment of large quantities of water inside the bulky flocs that may form in the presence of polymers. In this respect, the correct choice of polymers and the proper conditioning of the slurry with it, is important.

Recently a polyethylene oxide polymer has been successfully used by the U.S. Bureau of Mines for the dewatering of Florida phosphatic clay wastes both in batch tests and in a continuous test with a trommel [29].

Effect of Air Bubbles

The experiments conducted to determine the effect of air bubbles consisted of the application of suction above a suspension of the slurry. The results obtained are shown in Fig.

![Diagram](image)

Fig. 9. Diagram illustrating the effect of air bubbles generated by suction on the settling of phosphatic slime [12].
It can be seen from the results given in Fig. 10 that the generation of bubbles enhances subsidence significantly. Like the microbubbles that are ordinarily present in slime, these bubbles are also found to act by altering the physical features of the slurry such that water seepage becomes possible through more channels. It can also be seen that suction has no effect on settling during the initial ten to twenty minutes. Also, once the solids settle to a volume of 25 to 26%, mild suction above the suspension even for long periods produces no measurable effect. A stronger suction was found to merely disperse the sediment. The above observations suggest that generation
Reticular Stage $H(t_1)$ to $H(t_2)$

we have continuous diffusion through the channel interface in
the aggregate with the incoming impingement
of the aggregate interface has

\[ \frac{\Delta a}{\Delta t} \]

The water through the aggregate interface has
shaped the very supernatant inner liquid

\[ \exp \cdot \text{on the less} \]

Vermicular Stage $H(t_2)$ to $H(t_3)$

In bridging the liquid lamellae to narrow vermiqustructur
ealed in the channel water in
is further expanded into the channel

be the q
parameters than in the reticular stage. A better fit for the
dewatering rate has been found to be given by the exponential
relation (9) and it represents a moderating rate of interaggregate
water expulsion as compared with that during the reticular
stage.

\[
\frac{dW_a}{dt} = -k \exp (-W_a)
\]  

(9)

This Equation also can be rewritten to relate the descent of
the interface to settling time in the form given below:

\[
H(t) = H(t_2) - b \ln(t/t_2)
\]  

(10)

Floccular Stage \(H(t_3) \to H(\infty)\)

When all the water in the macrochannels between aggregates
has been expelled, the end of the vermicular stage is reached
and further dewatering can take place due to the consolidation
of individual flocs. Water removal at this stage, called the
floccular stage, can take place due to two processes: relatively
fast expulsion of interfloc water in the microchannels
between flocs and relatively slow expulsion of intrafloc water
from within the flocs. The forces involved are gravitational
and opposing viscous forces. Each of these processes follow
first-order kinetics:

\[
\frac{dW_f}{dt} = -kW_f
\]  

(11)

where \(W_f\) is now the fraction of inter- and intra-floc water.
Asymptotic Stage  \( E, \infty \), to \( E(\infty) \):

The solution can proceed through an asymptotic stage. The graph shows the asymptotic value as \( E(\infty) \).

Test of the Phenomenological Mode

To refine the phenomenological model, the appropriate equations tested and verified with the experimental data are compared. The agreement between the experimental values and the theoretical data in the observed phenomena are essential. The results have been provided in the chemical context.
CONCLUDING REMARKS

A detailed description of behavior of slow-settling suspensions has been given here along with the mechanism by which dewatering occurs and the mechanisms by which additives help the dewatering process. The role of certain major factors such as vessel diameter and the properties of additives has also been discussed. Furthermore a phenomenological settling model that satisfactorily represents the observed behavior of slime has been reviewed. The problem of dewatering is very important as it can be a very costly operation (Table 3). Depending on the technique used, it can cost anywhere up to $50 per dry ton and this range of expense is indeed prohibitively high.
Obviously there is a great need to develop new technology and to achieve this, there is also an equal need to fully advance our scientific understanding of these systems. Much more research certainly needs to be done before we can claim such a full understanding. Detailed and systematic experimental studies in the areas discussed above, physical and chemical alike, are in dire need of the proper formulation of settling models and of full understanding of the settling behavior of slow-settling slimes and sludges, the processing of which is steadily gaining in importance every day.

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REFERENCES


ABSTRACT

Properties of slow-settling suspensions have been described and it was shown that clays when present along with other minerals appear to be responsible for the slow-settling behaviour of slimes.

The mechanism by which additives help the dewatering process has been discussed. A phenomenological settling model that satisfactorily represents the observed phenomena has been reviewed.

RÉSUMÉ

On a décrit les propriétés des suspensions à sédimentation lente et on a montré que les argiles en présence d'autres minéraux sont responsables de la sédimentation lente des bones.

On a discuté le mécanisme grâce auquel les additifs aident les processus de déshydratation. On a passé en revue les travaux sur le modèle phénoménologique de sédimentation qui décrit d'une manière suffisante le comportement observé des bones.

ZUSAMMENFASSUNG

Die Eigenschaften der langsäm sedimentierenden Suspensionen werden erörtert und gleichzeitig wird gezeigt, daß der Ton in Anwesenheit von anderen Mineralien ein langsames Absetzen der Schlümmen verursacht.

Diskutiert wird der Mechanismus, infolge dessen die Beimengen den Entwässerungsprozeß unterstützen. Es wird ein Überblick der Arbeiten zum Thema des phänomenologischen Modells des Absetzvorganges gegeben, daß das beobachtete Verhalten der Schlämme vollständig beschreibt.
РЕЗЮМЕ

Описаны свойства медленно седиментирующих взвесей и показано, что глины в присутствии других минералов влияют решительным образом на медленное осаждение суспензий. Обсужден механизм, вызывающий вспомогательное действие добавок в процессе обезвоживания. Произведен обзор работ на тему феноменологической модели осаждения, которая полностью описывает наблюдаемое поведение илов.