ρ = density of crystals, g/ml
σ = surface energy, erg/cm^2
τ = residence time, min

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The Mechanisms of Transfer of Hydrophobic Coated Mineral Matter Particles from a Hydrocarbon to an Aqueous Phase

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A solid/liquid separation process based on the transfer of hydrophobic coated mineral particles from a hydrocarbon to an aqueous phase is described. This process could be used, for example, to remove mineral matter from coal derived liquids in order to meet fuel specifications. A model system which involves hydrophobic, asphaltic, coated mineral matter particles in a model liquid, xylene, was used in conjunction with the mechanistic studies. The mineral matter distribution coefficient to the aqueous phase decreases rather than increases with time in batch experiments. Five asymptotic models based on the fate of the surface active chemical at long time are investigated. Included were adsorption on the mineral matter particle, adsorption at the oil/water interface, distribution of the surfactant to the aqueous phase, complete detergency, and partial detergency. Experimental data on the influence of surfactant concentration, contact time, water/oil ratio, and shear are consistent only with the partial detergency model.

SCOPE

An extractive method is presented for the transfer of solid particles from one liquid stream to another. The process is based on the surface characteristics of the particle. Albertsson (1958, 1971) and Raghavan and Fuerstenau (1975) have previously demonstrated this process. This paper deals with the case where the particles are naturally wet by the original stream due to an acquired carbonaceous matter coating.

An experimental system consisting of an oil phase (xylene), an aqueous phase (pH adjusted water), and composite particles is studied. A composite particle consists of a mineral matter core which is surrounded by a hydrophobic layer. The composite particles are obtained from a coal derived liquid. Particle removal from coal derived liquids is a potential application of this process.

A surface active agent is used in order to promote particle transfer from the oil phase to the aqueous phase. The surfactant can function either by adsorbing onto the particle surface, making it hydrophilic, or by removing the hydrophobic coating (detergency), thereby exposing the more hydrophilic mineral matter surface. The liquid phases have been chosen so that the surface properties of the composite particles will dominate the experimental system.

Five mechanistic models based on the fate of surfactant at long time are proposed. These include adsorption onto the composite particle, adsorption at the oil/water interface, distribution of the surfactant to the aqueous phase, complete detergency of the hydrophobic layer, and partial detergency. These models are compared with data from batch experiments in which mixing time, mixing speed, surfactant concentration, and water/oil ratio are varied. The asymptotic models permit an unambiguous interpretation of the qualitative parameter dependences.

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CONCLUSIONS AND SIGNIFICANCE

A decrease in the distribution coefficient of mineral matter from the hydrocarbon phase to the aqueous phase with mixing time is observed. This result is unusual in that more conventional mechanistic models of flotation (Sutherland and Wark, 1955) predict an increase in the amount of material transferred with an increase in the mixing time. A long time distribution coefficient, independent of the initial surfactant concentration, was observed. The experimental results indicate increasing particle transfer at high shear (oil/water contacting) and short time.

The partial detergency model is presented. This mechanistic model explains all of the parameter dependences observed in the experimental system. Parameters studied in relation to the equilibrium value of the distribution coefficient include mixing speed, initial surfactant concentration, and water/oil ratio. The short time (nonequilibrium) distribution coefficient was studied as a function of mixing time.

The partial detergency model includes several phenomena. The surfactant adsorbs onto the hydrophobic carbonaceous coating, making the composite particle hydrophilic. The distribution coefficient increases. The surfactant is then lost from the surface and the distribution process through the solubilization of the hydrophobic coating. More hydrophobic coating is exposed, and less surfactant is available for adsorption. Therefore, the distribution coefficient decreases.

Several other mechanistic models for particle transfer are presented and discussed. They are eliminated from consideration in our system because they predict parameter dependences which are contrary to those observed experimentally.

The distribution coefficient is found to be a function of the *p*H of the aqueous phase. A sharp increase in the amount of material distributed is observed at *p*H's above 8.5. This observation, as well as the observations of Henry and Jacques (1977), tends to confirm that the adsorbed hydrophobic layer consists of asphaltic fractions from coal derived liquids.

This work has possible applications to the removal of mineral matter from coal derived liquids and other solid/liquid separations, where the particles are dominated by a surface layer which is not wet by the receiving liquid. Other applications in addition to particle distribution, such as the liquid bridging of particles, have been reviewed by Jacques et al. (1977). The wetting kinetics which have been observed may be analogous to processes which occur in conjunction with the surfactant flooding of oil wet reservoirs.

PROCESS CONCEPT

The preferential wetting of composite particles from one fluid phase to another appears to be a liquid-liquid extraction. The process is, however, more closely related to flotation than to extraction. The surface characteristics of the particles dominate the behavior of the system instead of a concentration related chemical potential difference. Liquid-liquid systems important in the process industries would normally consist of a hydrocarbon phase and an aqueous phase. A composite particle can be characterized as a hydrophilic mineral matter core surrounded by a hydrophobic coating. The use of surface active agents either to remove this hydrophobic coating (detergency) or to adsorb as a new hydrophilic coating over the hydrophobic layer (adsorption) would facilitate interphase transfer. An additional emulsion breaking step might be necessary if the liquid-liquid contacting resulted in a stable emulsion. Albertsson (1958, 1971) and Raghavan and Fuerstenau (1975) have presented examples of liquid-liquid-particle transfer.

An example of the above process would be the removal of mineral matter particles from coal derived liquids. Many of the minerals found in coal derived liquids (clays and silicates) are hydrophilic in nature. These particles have obtained a hydrophobic carbonaceous matter coating due to the severity of the coal liquefaction process (high temperature and pressure). It is believed that this coating consists of the asphaltene and preasphaltene fractions of the coal liquid. Briggs and Smith (1976) have shown that the asphaltene fraction exhibits surface active characteristics. Henry and Jacques (1977) have presented evidence to the effect that this coating is composed of asphaltenes by showing that the coated particles and the asphaltenes are both positively charged in the presence of a hydrogen donor solvent such as is present in solvent refined coal (SRC) filter feed.

PREVIOUS WORK

Young in 1805 presented the basic equations governing the transfer of a particle from one phase to another in the absence of body forces [Equation (1)]. Using an equilibrium force balance, he developed

$$\gamma_{so} = \gamma_{sw} + \gamma_{ow} \cos\theta \tag{1}$$

a set of inequalities which expressed whether or not a particle could (because of interfacial forces) transfer from one phase to another. Young's results show that the contact angle θ is the governing factor in the distribution process. The contact angle measured through the water phase is zero when the particle is totally water wet and 180 deg when it is totally oil wet. This observation leads to the following criteria for distribution in the absence of body forces. Equation (2) represents the case where total water wetting occurs, and the particles are in the water phase. Equation (3) describes the condition of total oil wetting where all the particles are in the oil phase. Nonpreferential wetting is represented by Equation (4). The particles so described are situated in the interface:

$$\frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} > 1 \tag{2}$$

$$\frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} < -1 \tag{3}$$

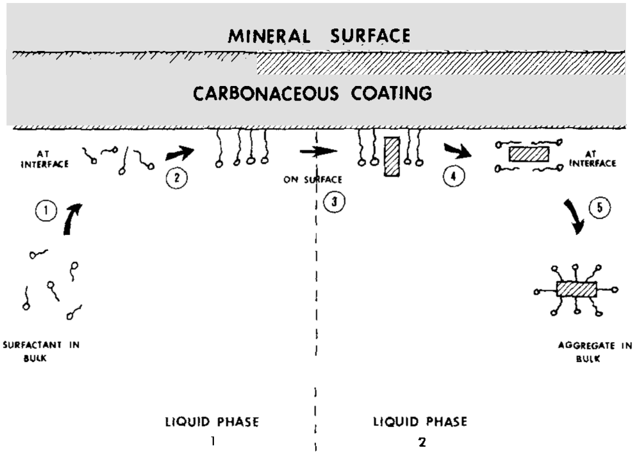

Fig. 1. Phenomenological model of solubilization detergency: 1. diffusion of the surfactant from the bulk liquid to the particle surface, 2. adsorption of the surfactant onto the surface, 3. surface reaction, 4. desorption of the surfactant-carbonaceous matter aggregate from the surface, 5. diffusion of the surfactant-carbonaceous matter aggregate into the bulk liquid phase.

$$\left|\frac{\gamma_{so}-\gamma_{sw}}{\gamma_{ow}}\right| \leqq 1 \qquad (4)$$

It should be remembered that these are equilibrium equations and that they do not say how the particle initially comes into contact with the interface. A body force is usually required in order to initiate this contact.

Additional work has been done by Maru et al. (1971), Winitzer (1973), Huh and Mason (1974), and Rapacchietta and Neumann (1977) which incorporates body forces into the force balance. The body forces normally included are buoyancy, gravitational forces, and hydrostatic pressure differences. The distribution criteria in these cases include the densities of the two fluid phases and the solid, along with the particle size. The pressure difference across the interface must be included in cases where the interface is nonplanar. Jacques et al. (1977) have applied force balances in the case of spherical particles at spherical interfaces. Their work is applicable to systems where no body forces are present and where the radius of the fluid droplet is much greater than the radius of the solid sphere. The experimental system under study has fixed densities and a fixed distribution of particle sizes. Therefore, the contact angle is the most important variable in determining the amount of particle transfer in this system.

Since the contact angle is naturally unfavorable to particle distribution due to the presence of the hydrophobic coating, it must be altered by the addition of a surface active agent. A surface active agent will alter (lower) an interfacial tension by adsorbing onto the surface and creating an excess surface concentration of surfactant. The surfactant will most likely change the interfacial tensions of all the interfaces present in the system. The most favorable alteration occurs when the surfactant increases the numerator of Equation (2) ($\gamma_{so} - \gamma_{sw}$). This will be accomplished by adsorbing the surfactant onto the surface of the particle with its hydrophobic end oriented in toward the solid and its hydrophilic end oriented out into the bulk liquid. This will cause the solid surface to become increasingly more hydrophilic with an increased amount of surfactant adsorbed. A limit will be reached, depending upon the characteristics of the system, where a maximum hydrophilic character (minimum contact angle through the water) exists. The adsorption of additional surfactant beyond this point will not improve the surface characteristics of the particle.

Detergency, the removal of the hydrophobic surface by the surfactant and surface shear, can also occur in the liquid-liquid-particle system. Chan et al. (1976) have recently developed a phenomenological model for the solubilization mechanism of detergency. They have postulated a five-step mechanism for solubilization detergency (Figure 1). The steps include diffusion of the surfactant from the bulk liquid to the particle surface, adsorption of the surfactant onto the surface, surface reaction, desorption of the surfactant-carbonaceous matter aggregate, and diffusion of the surfactant-carbonaceous matter aggregate into the bulk liquid phase. (Note: Figure 1 has been altered slightly from the Chan figure so that it can be used in conjunction with the discussion of wetting for the xylene, water, mineral matter system. In the Chan model, both liquid phases 1 and 2 are the same aqueous detergent solution.) The removal of these aggregates and their actual formation is aided by the mechanical energy supplied to the surface by agitating the system.

Removal of the carbonaceous matter could result in the lowering of the three-phase contact angle (increased distribution) in the case where hydrophilic mineral matter surface is exposed. However, its removal could also result in an increase in the contact angle (decreased distribution) if the carbonaceous matter layer is sufficiently thick that only additional carbonaceous matter is exposed. In this case, the surfactant-carbonaceous matter aggregate would serve merely to remove surfactant from the surface. This surfactant would otherwise be used to make the particle surface more hydrophilic.

The above discussion illustrates that there can be several final locations for the surfactant in the system.

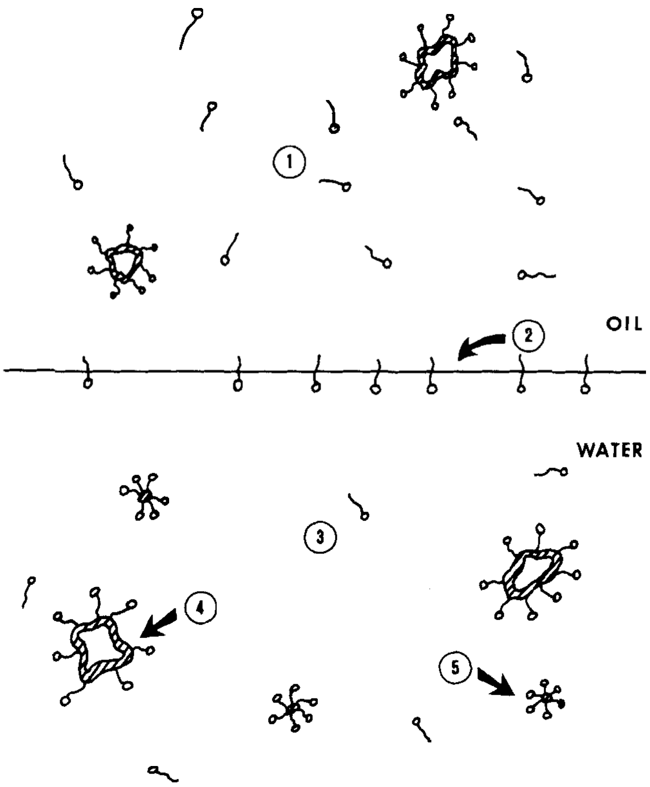

Fig. 2. Possible locations for surfactant in the liquid-liquid-particle system: 1. bulk oil phase, 2. adsorbed at the oil/water interface, 3. bulk water phase, 4. adsorbed onto the composite particle making it hydrophilic, 5. tied up in a surfactant-carbonaceous coating aggregate.

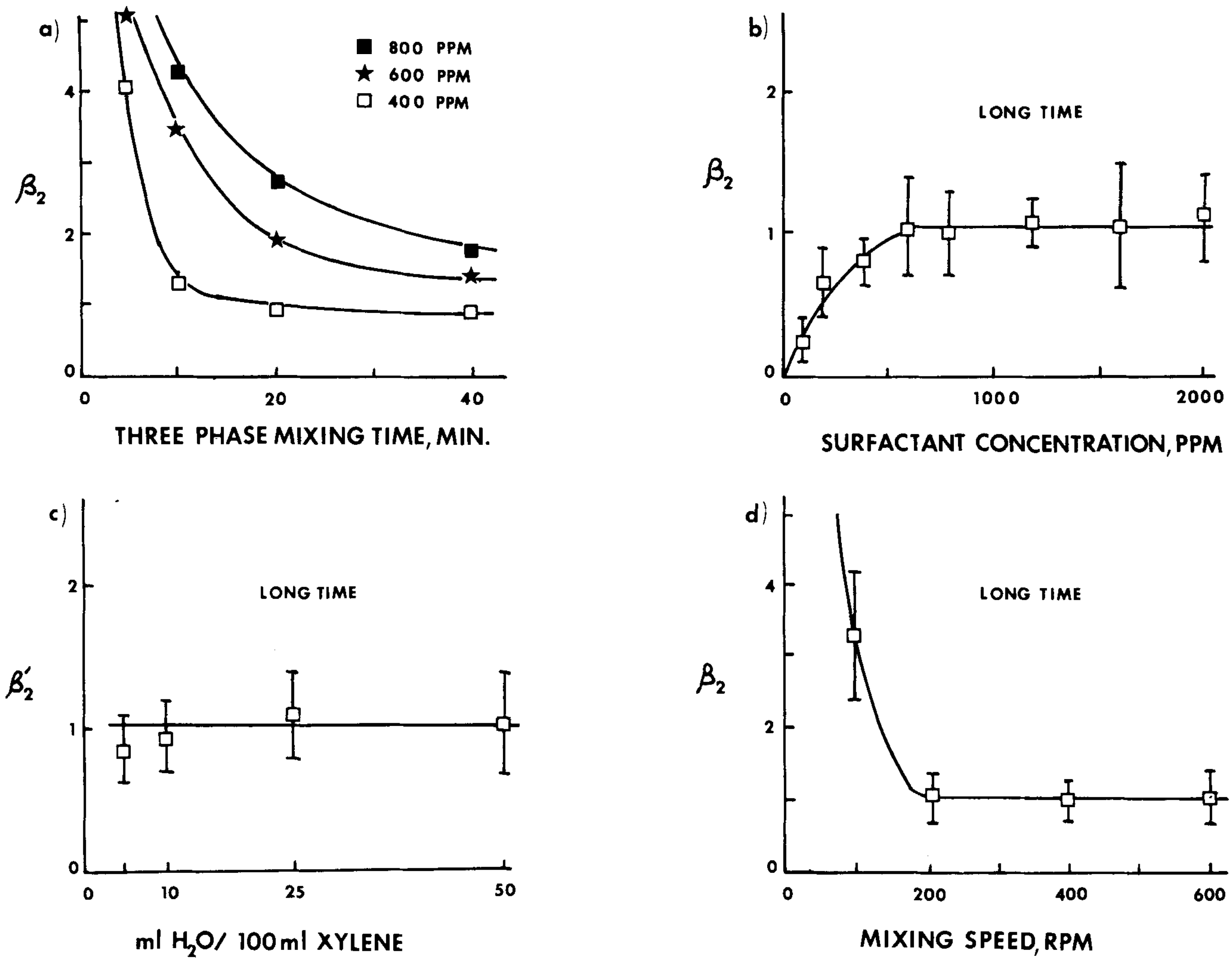

Fig. 3. Experimental results: effect of system parameters on the distribution coefficient β_2.

These locations are shown in Figure 2. The surfactant can adsorb either to the solid/liquid or liquid/liquid interfaces. Additionally, the surfactant can be in solution in both bulk phases as well as being tied up in the formation of surfactant-carbonaceous matter aggregates such as mixed micelles or liquid crystals. The most likely location and function of the surfactant is the subject of the mechanistic modeling.

Mechanistic modeling can be useful in a system such as that described above in order to identify the dominant effects. Once the important mechanisms have been identified, a more detailed mathematical model can be developed. This type of reasoning is especially important in cases where widely varying models can be considered. A group of asymptotic mechanistic models will be presented in a later section in order to explain the wetting behavior of the experimental system.

EXPERIMENTS

Liquid-Liquid-Particle-Surfactant System

A liquid-liquid-particle system consisting of xylene and pH adjusted water as the liquid phases and benzene washed Synthoil (coal liquid) mineral matter as the composite particle was chosen as the experimental system. The choice of Synthoil mineral matter as the composite particle was prompted by the fact that mineral matter removal from coal derived liquids is a possible application of this work. The benzene washing removed the adhering Synthoil liquid from the particles. The hydrophobic coating on the particles was left intact. Low temperature ashing caused a 20% weight loss. The average diameter (by volume) of the particles was 5.5 μ. Preliminary data on ash plugs show that the contact angle through the water phase is 130 to 150 deg.

Xylene was chosen as the hydrocarbon phase because of its relative safety (as compared to benzene) and because it was desired to run low temperature experiments in well-defined systems to facilitate a visual interpretation of the results. It was also desired to assure that the solid surface characteristics control in this set of experiments. Studies are presently underway to alter the model liquid to more closely approximate the chemical functionality of a coal liquid.

A proprietary nonionic ethoxylate was used in this work as the surface active agent. It was chosen on the basis of its ability to cause particle transfer in the experimental system.

Procedure

A predetermined amount of surfactant was added to 100 ml of xylene. The xylene was then mixed at 600 rev/min in a 250 ml cylindrical glass container for 10 min to insure the complete dissolution of the surfactant. The mineral matter (0.2 g) was added to the xylene-surfactant system and mixed at 600 rev/min for 15 min to allow the surfactant to adsorb onto the particle surface. It has been experimentally determined that the 15 min mixing time is long enough so that an increase in mixing time will cause no additional particle transfer.

The pH adjusted aqueous phase was then added to the container, and the resultant mixture was agitated for a predetermined time. All experiments were buffered to $p\text{H} = 7.0$ using a 0.05 M potassium phosphate monobasic-sodium hydroxide buf-

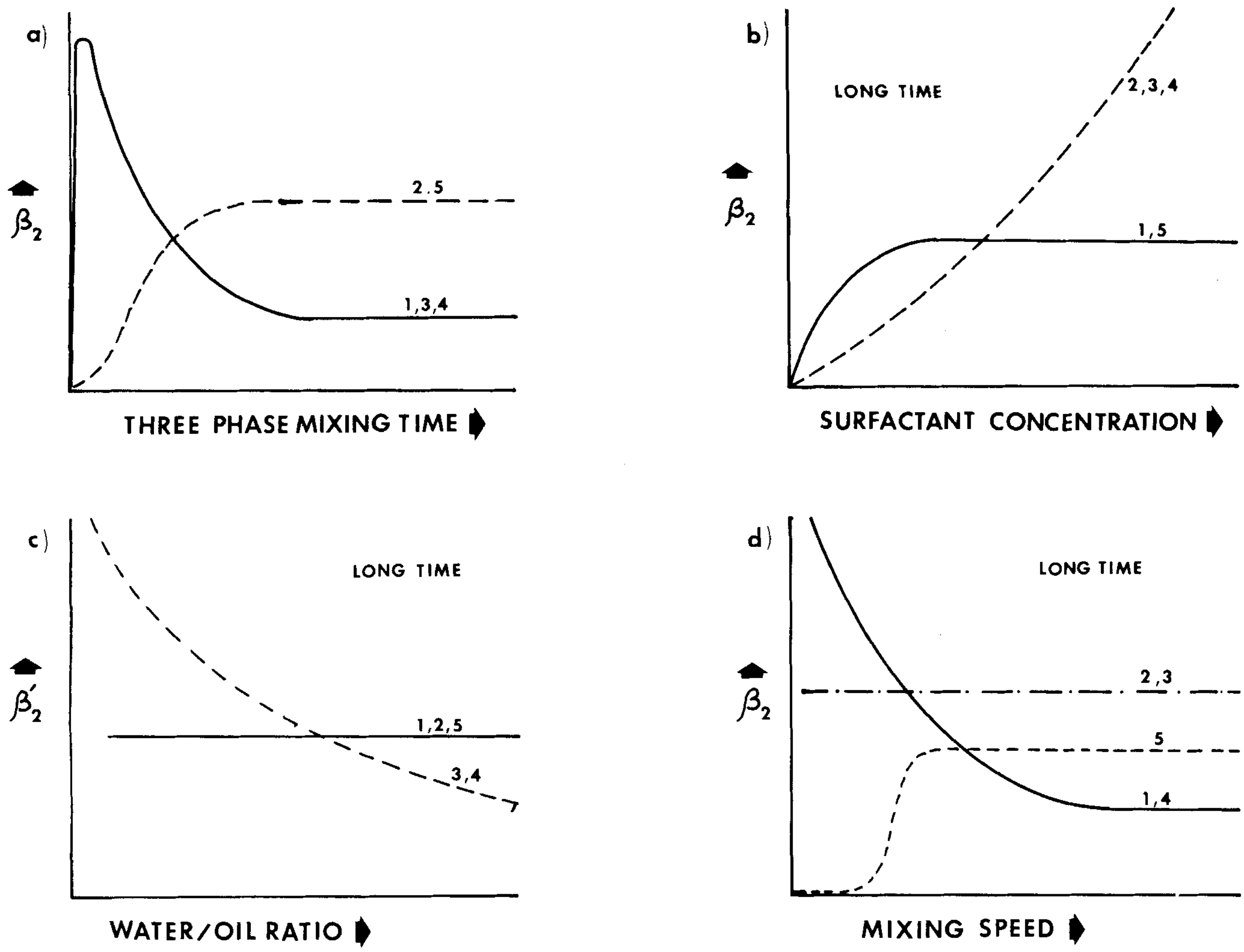

Fig. 4. Parameter dependences predicted by mechanistic modeling: 1. partial detergency model, 2. particle surface adsorption model. 3. water phase soluble model, 4. oil/water interface adsorption model, 5. complete detergency model.

fer with the exception of the experiments presented in Figure 5. Appropriate buffers were used in these cases. Upon completion of the three-phase mixing, the mixture was introduced into a 250 ml teflon separatory funnel. A teflon funnel was used because the particles tend to stick to glass surfaces. The emulsion was then allowed to resolve. The resolution times were on the order of 2 to 10 s. The funnel was then lightly shaken to insure that all of the loose mineral matter particles had fallen from the oil/water interface. Three fractions were then drawn from the funnel: the aqueous phase, the interface, and the oil phase. These fractions were then filtered through a 0.45 μ millipore filter, dryed, and weighed.

Care was taken to keep the cross contamination between experiments at a minimum since small changes in the surfactant concentration can cause large changes in the amount of material transferred. The entire apparatus was washed with acetone between experiments, and all glass surfaces were further cleaned using a chromic acid solution. The final resolved oil/water interfacial area was also important since there was a slight dependence between this area and the amount of material transferred. This area was held constant at 16.5 cm^2 from run to run. All experiments were run batch.

Parameters

The system parameters which have been varied are three-phase mixing time, mixing speed, surfactant concentration, water/oil ratio, and aqueous phase *p*H. The understanding of the effects of these variables is necessary to understand which mechanistic model best describes the system. Three-phase mixing time varies, of course, with time in the system. The other variables, even though they have definite effects on the rate of change in the amount of material transferred with time, are best studied at their long time or equilibrium values. These long time values are determined such that additional three-phase mixing time does not influence the amount of material transferred.

The amount of material transferred is described by the distribution coefficient β_2 defined as the concentration of material in the aqueous phase divided by the concentration of material in the oil phase. The interfacial material is assigned to the oil phase. (Note: in some cases, this stable interfacial material represents 35% of the total mineral matter in the system.) A traditional distribution coefficient defined in terms of particle concentration is used even though the long time distribution coefficients are not directly dependent on particle concentrations. This does not imply that if the concentration of particles is doubled without doubling the concentration of the surfactant, the β_2's will remain constant. In this case, less surfactant would be adsorbed per particle, and the distribution coefficient would decrease. When the water/oil ratio varies, an artificial distribution coefficient β_2' is used. β_2' is calculated as if the base of 50 ml water still applies. It should be remembered that the β_2 distribution coefficients are equilibrium properties only when reported as long time values. The short time values of β_2 are merely measures of the degree of particle transfer.

MECHANISTIC MODELING AND RESULTS

The experimental results in terms of β_2 and β_2' are shown in Figure 3. Contrary to an expected increase in the distribution coefficient with mixing time, a decrease in β_2 with time was observed. The purpose of this section is to explain the observed decrease in β_2.

The long time points represent at least four different experiments. A confidence interval of 90% around the mean is represented by the bars. These confidence intervals are not shown on the three-phase mixing time curve to avoid crowding. The results, Figure 3, as well as the predicted curves for the mechanistic models (Figure 4) are presented as plots of β_2 vs. three-phase mixing time, long time β_2 vs. initial surfactant concentration, long time β_2 vs. water/oil ratio, and long time β_2 vs. mixing speed. Figure 4 is merely an aid for comparison between the models. Its intent is to show the general trends (increase, decrease, no change) predicted by the models. (Note: even though one curve may be labeled with the name of more than one model, it is not claimed that the exact same values of the distribution coefficient apply to all the models. It is only implied that the same qualitative parameter dependences exist.) The data presentation in this form illustrates the reasoning behind the modeling and permits convenient comparison of the experimental results with the predicted model curve shapes. The solid lines in Figure 4 represent the parameter dependences observed experimentally.

The mechanistic models are presented in order to explain the behavior of the experimental system. The models presented below are asymptotic in nature and are named in relation to the final fate or location of the surfactant. The path by which the surfactant attains this final location determines the qualitative parameter dependences of the model. Comparing the experimental dependences of the distribution coefficient with the predicted trends enables unambiguous differention among the conceptual models. It should be remembered in the analysis of the time dependent three-phase mixing time curve that the surfactant has already been adsorbed onto the particle surface at zero time. The mechanistic modeling-curve shape comparison makes the following additional assumptions:

1. The hydrophobic coating on the particle is homogeneous.
2. The surfactant adsorptions and solubilities can be represented by distribution coefficients.
3. Surfactant adsorption onto the surface of the particle is reversible.
4. The final location of the composite particle is primarily a function of its surface characteristics.

Partial Detergency Model

The only model which explains the experimental results in terms of all the system parameters is the partial detergency model (Figures 3 and 4). The model can be described as follows:

1. The surfactant is adsorbed onto the hydrophobic coating making the composite particle hydrophilic.
2. Water is added, and collisions between the particles and the water droplets result in transfer. β_2 increases.
3. Detergency, the removal or solubilization of the hydrophobic coating in the form of surfactant-carbonaceous matter aggregates, begins. The rate of increase of β_2 decreases, and eventually β_2 declines.
4. A long time value of β_2 is reached which is dependent only upon the work of detergency and not upon the initial surfactant concentration.

The partial detergency model assumes that the hydrophobic coating is sufficiently thick so that the mineral matter surface is not exposed in the detergent process. The removal of an onion skin of hydrophobic material from the particle surface serves only to create a sink for the surfactant; that is, the surfactant involved in the surfactant-carbonaceous matter aggregates is no longer available for adsorption on the composite particle to produce particle transfer. This decrease in the amount of surfactant adsorbed on the surface results in a decrease in the distribution coefficient with three-phase mixing time (see Figure 3*a*).

An increase in the initial surfactant concentration does not affect the long time value of β_2 in the partial detergency model (Figure 3*b*). This is due to the fact that a certain amount of work, called the work of detergency [Equation (5)], is necessary to remove a unit of hydrophobic coating

$$W_d = \gamma_{hw} + \gamma_{sw} - \gamma_{sh} \tag{5}$$

from the composite particle surface. This work of detergency is supplied by the mechanical energy (mixing) input to the system. Detergency will occur only as long as the surface conditions are such that the required work of detergency is less than or equal to the work input into the system. Equation (5) illustrates the fact that as long as additional surfactant is available in the oil phase to adsorb onto the particle and cause detergency, this excess surfactant will eventually be tied up in mixed micelles. Therefore, an increase in initial surfactant concentration only causes an increase in long time mixed micelle concentration. This has little effect on the system owing to the small micelle activity coefficient. The surface condition at which the work of detergency equals the work input into the system determines the constant long time value of β_2.

The above argument also explains the expected decrease in long time β_2 with increasing mixing speed (Figure 3*d*). An increased mixing speed corresponds to an increased work input. Equation (5) shows that this allows a smaller amount of surfactant to be adsorbed onto the surface at the point where the work input equals the work of detergency. This implies a smaller distribution coefficient.

Changing the water/oil ratio has no effect on the final value of β_2' (Figure 3*c*). This is because the partial detergency model assumes that the amount of surfactant dissolved in the water phase and adsorbed in the oil/water interface is negligible.

A more detailed description of the partial detergency model can be made in a matter analogous to that of Chan. This treatment also makes use of Figure 1. However, the surfactant diffusion to the surface and adsorption occur during the fraction of time $(1 - f)$ that the particle surface is in contact with the oil phase (liquid phase 1). The surface reaction, the surfactant-carbonaceous matter aggregate desorption, and aggegate diffusion into the aqueous phase (liquid phase 2), occur during the fraction of time f that the particle surface is in contact with the aqueous phase. The functional dependences of f become important in this case. Alterations in the Chan model also must allow for the variable surfactant concentrations and the work of detergency effect. This modeling approach is presently under study. Experimental methods, such as the spinning disk, used in Chan's analysis are not applicable to this work owing to the two liquid phases present in the experimental system.

It can be seen by comparing Figures 3 and 4 that the partial detergency model explains the changes in the distribution coefficient with respect to all the system parameters. The initial increase in β_2 can not be observed by our experimental methods because this change occurs too quickly. It is obvious that at zero three-phase mixing time, the amount of material transferred to the water phase is zero since no particle-water droplet collisions have taken place. The following discussions show why the more conventional mechanistic models of particle transfer are not satisfactory in explaining the experimental observations.

Particle Surface Adsorption Model

The particle surface adsorption model assumes that the surfactant remains primarily on the composite particle and does not desorb to the oil/water interface or go into solution in the aqueous phase. The conceptual model of oil flotation (Sutherland and Wark, 1955) is similar to this model. The model can be explained as follows:

1. The surfactant is adsorbed onto the hydrophobic coating making the composite particle hydrophilic.
2. Water is added, and collisions between the particles and the water droplets result in transfer. β_2 increases.
3. β_2 levels off at a constant value dependent upon the contact angle.

No detergency (mixed micelle formation) or other sinks for surfactant are predicted by the particle surface adsorption model. This results in an increased amount of material transferred with increased initial surfactant concentration and no decrease in the β_2 three-phase mixing time curve (Figure 4*a*). This increase in β_2 with increased surfactant concentration exists also in the long time values of β_2 (Figure 4*b*). Both of these predictions are contrary to the experimental observations shown in Figure 3. This illustrates the distribution coefficient concept of the surfactant between the oil phase and the solid surface, that is, the more surfactant available, the more adsorbed. This increased adsorption causes a decrease in the contact angle which in turn results in increased particle transfer.

Changes in the water/oil ratio (Figure 4*c*) and the mixing speed (Figure 4*d*) do not cause a change in the amount of surfactant available to cause distribution and therefore do not cause any change in the long time values of the distribution coefficient. The predictions represented by Figure 4*d* are inconsistent with the experimental results.

Water Phase Soluble Model

The water phase soluble model introduces the water phase as a sink for the surfactant. Mechanistic models which include a sink for the surfactant are of particular interest because they will predict a decrease in β_2 with increased three-phase mixing time. The model proceeds as follows:

1. The surfactant is adsorbed onto the hydrophobic coating making the composite particle hydrophilic.
2. Water is added, and collisions between the particles and the water droplets result in transfer. β_2 increases.
3. Surfactant desorbs from the particle surface and goes into solution in the water phase. β_2 decreases.

Long time values of the distribution coefficient increase with increased initial surfactant concentration (Figure 4*b*). This can be attributed to the assumption that surfactant distribution coefficients exist between the oil phase and the particle surface, the water phase and the solid surface, and the oil phase and the water phase. An increase in the initial surfactant concentration therefore results in an increase in the amount of surfactant adsorbed onto the particle surface.

Increasing the water/oil ratio would be expected to decrease the long time value of β_2' (Figure 4*c*). An increase in the amount of water present increases the available sink for surfactant. Therefore, an increase in water/oil ratio decreases the amount of surfactant available to the particle for transfer.

The mixing speed (Figure 4*d*) has no effect on the long time value of β_2 because it in no way affects the amount of surfactant available to the particle surface. All three of the above predicted effects shown in Figures 4*b*, 4*c*, and 4*d* do not agree with the experimental results. It has been determined experimentally that our surfactant is only slightly soluble in water.

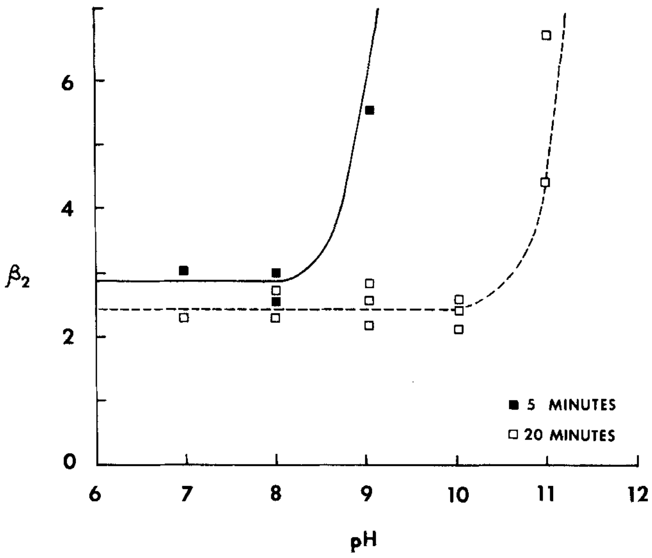

Fig. 5. Effect of pH on the distribution coefficient β_2.

Oil/Water Interface Adsorption Model

The surfactant sink in this model is the oil/water interface.

1. The surfactant is adsorbed onto the hydrophobic coating making the composite particle hydrophilic.
2. Water is added, and collisions between the particles and the water droplets result in transfer. β_2 increases.
3. Surfactant desorbs from the particle surface and adsorbs at the oil/water interface. β_2 decreases.

This model is similar to the water phase soluble model with the water phase surfactant sink being replaced by the oil/water interface. Surfactant distribution coefficients exist between the oil phase and the particle surface, the oil phase and the oil/water interface, and the particle surface and the oil/water interface. These surfactant distribution coefficients are responsible for the increase in the long time distribution coefficient with increased initial surfactant concentration (Figure 4*b*).

An increase in the amount of oil/water interface in the system would also be expected to cause a decrease in the long time distribution coefficient. Increasing the water/oil ratio (Figure 4*c*) and the mixing speed (Figure 4*d*) increases the amount of oil/water interface. Decreases in the amount of surfactant available for particle distribution occurs in both of these cases. A decrease in the long time values of β_2' and β_2 takes place. Experimental evidence contradicts Figure 4*c*.

Complete Detergency Model

The complete detergency model differs from the previous mechanistic models in the fact that the adsorption of the surfactant onto the particle surface does not make the composite particle hydrophilic. Also, unlike the previous three models, detergency and mixed micelle formation are involved. The model sequence follows:

1. Surfactant adsorbs onto the particle surface.
2. The work input into the system results in the formation of mixed micelles. The removal of the hydrophobic coating, instead of exposing more of the hydrophobic coating, exposes the more hydrophilic mineral matter surface. β_2 increases.
3. The entire mineral matter surface is exposed. β_2

levels off to a constant value characteristic of the mineral matter surface.

The long time value of β_2, as predicted by the complete detergency model, is independent of initial surfactant concentration (Figure 4*b*). This occurs because the long time distribution coefficient is dependent only upon the characteristics of the hydrophillic mineral matter surface. The surfactant does not change these characteristics. It is necessary, however, that enough surfactant be available to allow for the removal of the entire hydrophobic coating. Figure 4*a* does not agree with the experimental results.

It is assumed that only a negligible amount of the surface active agent is water soluble or adsorbed at the oil/water interface. Therefore, the long time value of β_2' would not be affected by changes in the water/oil ratio (Figure 4*c*).

Similarly, changes in the mixing speed will not affect the long time value of β_2 (Figure 4*d*). It is necessary, however, that sufficient work (shear) is put into the system to allow complete detergency to take place. This trend also disagrees with experimental evidence.

pH Effects

The *p*H of the aqueous phase was found to have a significant effect on the observed values of β_2. This effect is shown in Figure 5. The distribution coefficient was found to be constant at values of *p*H up to 8.5. The distribution coefficient was then observed to increase markedly in the range of 8.5 to 10. The exact point where this increase occurs is a function of the three-phase mixing time. These data have been obtained by Clay (1976) and Ranson (1977). This supports the hypothesis that the hydrophilic matter adsorbed onto the particle surface is from the asphaltene fraction of the coal liquids. This hypothesis is further supported by the previously cited particle charge work of Henry and Jacques. Bartell and Nederhauser (1949) and Strassner (1967) have shown similar charge characteristics and *p*H dependent wetting effects with petroleum asphaltenes.

DISCUSSION AND CONCLUSIONS

Several asymptotic mechanistic models have been presented to describe the effects of the different functions and final locations of the surfactant on the distribution coefficient. The partial detergency model is the only mechanistic model which successfully explains all of the phenomena that were observed experimentally (Figure 3 and the solid lines in Figure 4). This is important in that this model predicts both a decrease in distribution coefficient with increased mixing time and the fact that the long time value of distribution coefficient is independent of initial surfactant concentration. Both of these observations are opposite to the effects predicted by the conventional particle surface adsorption model of liquid-liquid-particle transfer. It should be remembered that the mechanistic models presented are asymptotic in nature. It is not implied that the partial detergency model is the only mechanistic model which applies to the system but rather that it is the dominant mechanism.

The partial detergency model and its mechanistic concepts can be applied to such areas as the removal of mineral matter particles from coal derived liquids and other solid/liquid separations where particles are dominated by a surface layer which is not wet by the receiving liquid phase (water in the case of coal liquids). It is believed that some of the minerals present, for example, pyrites, are hydrophobic. This does not affect our conclusions because all of the experimental evidence indicates that complete detergency never occurs.

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NOTATION

f = time fraction
W_d = work of detergency
β_2, β_2' = distribution coefficients
γ_{ij} = interfacial tension between phases i and j

Subscripts

h = hydrophobic layer
o = oil phase
s = solid
w = aqueous phase

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