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A REVIEW OF THE FACTORS AFFECTING THE STABILITY OF SOLIDS-STABILIZED EMULSIONS

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ABSTRACT

This paper discusses the main factors that play an important role in the formation and stabilization of emulsions containing finely divided solids. The influence of contact angle, particle size, particle interactions, and surfactants on emulsion behavior is discussed, and the state of the art in experimental techniques and fundamental research work is described.

INTRODUCTION

The production of clean fuel from crude oil, coal-derived liquids, shale oil and tar sands-bitumen generally involves a number of separation steps for the removal of impurities. These impurities include water in the form of water-in-oil emulsions and solid particles that are either freely dispersed or entrained on the surface of emulsion droplets. The demulsification of such emulsions and the removal of fine particles prior to downstream processing is imperative not only to recover clean oil but also to decrease oil viscosity and prevent fouling of processing units.

Solids-stabilized emulsions of water-in-oil (W/O) are formed during petroleum recovery due to the shearing of oil, water, and mineral particles at wellhead chokes and valves. The mineral fines often form strong interfacial films (skins) around the water droplets resulting in extremely stable emulsions. In addition to mineral fines, the emulsions may also be stabilized by wax particles that are precipitated from the oil due to changes in temperature during processing.(1)

In the hot water extraction process for tar sands, the bitumen is leached from the surface of sand particles using a hot caustic solution. During this process, sand and clay particles that are intrinsically present in the system form stabilizing films at the surfaces of bitumen-water emulsion droplets. The solid particles are attached to the bitumen droplets by surfactant molecules and polar moeities present in the oil.(2)

During synfuel production from coal and oil shale, the removal of fine particles from the oil is usually accomplished by dispersing water into the oil in a mixer, thereby forming solids-stabilized emulsions. These emulsions are subsequently separated from the oil by electrocoalescence and sedimentation.(3,4,5) The advantage of such an operation is that fine particles which sediment very slowly are transferred to the surface of water droplets whose sizes are much larger than those of the particles, thereby accelerating the separation process.

In addition to the above examples, solids-stabilized emulsions are also encountered in pharmaceutical formulations, food products such as mayonnaise, pesticides, and inks. In the energy-related industries, these emulsions are usually detrimental to the process and need to be demulsified, whereas in some of the pharmaceutical and food industries, they are desirable and often formed intentionally.

In this paper we discuss some of the factors affecting the stability of solids-stabilized emulsions. For recent reviews on the subject see references (2) and (6).

FACTORS AFFECTING EMULSION STABILITY

The formation and stabilization of a solids-stabilized emulsion occurs in three stages: (1) approach of solid particles to the droplet surface, (2) entrainment of particles at the oil-water (O/W) interface, and (3) interfacial stabilization by forming particulate networks (films). The first stage is a function of particle size, concentration and density, continuous phase viscosity, and mixing energy. The second stage depends mainly on the three-phase contact angle, O/W interfacial tension, interfacial viscosity, surfactant and/or demulsifier type and concentration, and pH. The formation of particulate networks at the interface is dependent on the magnitude of particle interactions, which in turn is a function of some of the above parameters. A brief description of some of the major factors is given below.

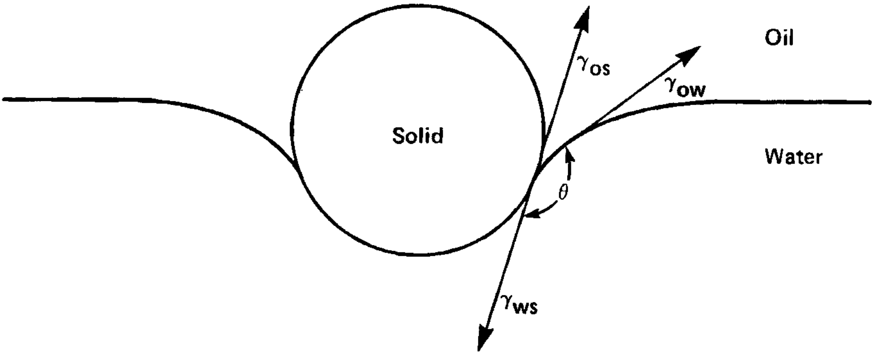

Fig. 1. Definition of the three-phase contact angle.

Contact Angle

While it was known since 1907 (7) that solids preferentially wetted by water tended to stabilize O/W emulsions, it was the experimental work of Schulman and Leja (8) that demonstrated conclusively the effect of contact angle on emulsion type. They measured the contact angle of benzene and water on crystals of barium sulfate in the presence of anionic surfactants. At contact angles greater than 90° (measured through the aqueous phase) emulsions of W/O were stabilized while at contact angles less than 90°, O/W emulsions were favored (see Fig. 1 for definition of contact angle). This relationship between wettability and emulsion type has since been proven experimentally and theoretically by many researchers.(9,10)

The contact angle is a function of the surface energies at the oil/water, oil/solid, and water/solid interfaces. These surface energies, in turn, are dependent on the concentration of surface active species present at the interface. In crude oil-water systems, the wettability is a strong function of the concentration of adsorbed asphaltic species on the particles. Asphaltenes are large polycyclic compounds with a large number of heteroatoms.(11,12) Petroleum asphaltenes have molecular weights in the 5,000 to 6,000 range, while coal and shale asphaltenes have molecular weights that are around 3,000. Asphaltenes adsorb irreversibly onto clay and mineral surfaces and alter their surface character.(4,13) Fig. 2 depicts the change in contact angle of an initially hydrophilic clay due to the adsorption of asphaltenes.(6) The contact angle was measured using the sessile drop goniometric technique on a disk of the particles. This disk was

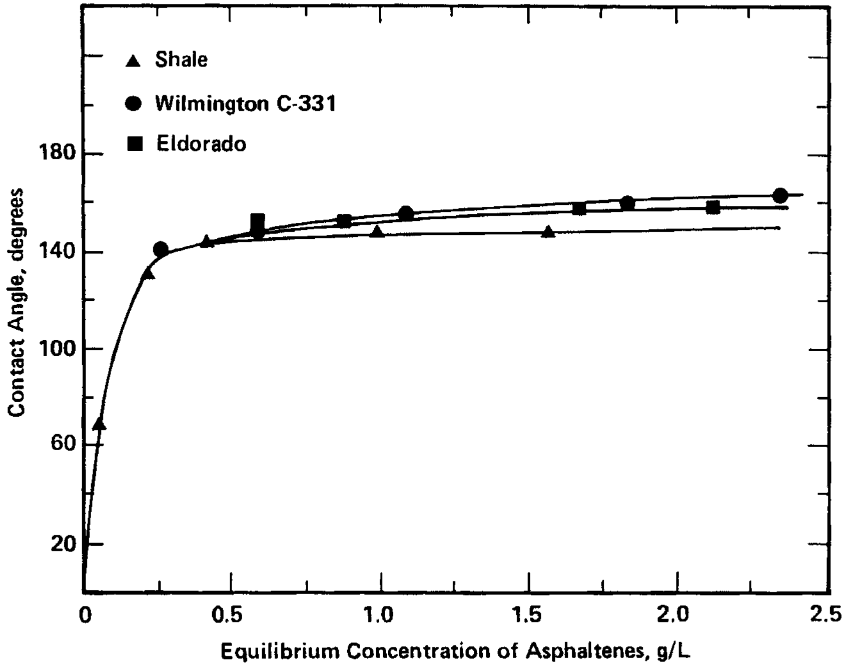

Fig. 2. Effect of petroleum and shale asphaltenes on the contact angle of sodium montmorillonite (6).

prepared in a stainless steel potassium bromide die whose surfaces were finely polished. For details of this technique see Reference (4). The clay, sodium montmorillonite, has been known to stabilize O/W emulsions in the absence of any adsorbed asphaltic layers.(14) The adsorption of asphaltenes renders the clay particles hydrophobic and they stabilize W/O emulsions.(4)

The effect of contact angle on emulsion type can be summarized in the following statement:(15)

> Solid particles wetted by phase A in preference to phase B, will promote and stabilize emulsions of B into A and inhibit or break emulsions of A into B.

The extent of stability generally decreases as the contact angle deviates from 90°.

Particle Size

Bechold, Dede, and Reiner conducted an extensive investigation of the effect of particle size on emulsion stability.(16) They found that a decrease in particle size resulted in an increase in stability until a critical size was attained. Below this size, emulsion stability decreased. Kitchener and Musselwhite showed that it is the relative size of the droplet with respect to that of the particle, and not the absolute particle size, that is important.(17) The absolute size of the particle becomes important only when the particles are so large that sedimentation times are much shorter than the half-life, or when the particles are so small ($< 0.001\ \mu m$) that Brownian motion inhibits particle transfer to the interface.

Thermodynamic analyses of the mechanism of emulsion stabilization have been carried out by many researchers.(2,4,18) While solids-stabilized emulsions are known to be thermodynamically unstable, their shelf life is often of the order of 6 months or more. Hence, these emulsions can be treated as being metastable, and equilibrium thermodynamic arguments can be applied without significant error.(2) The results of such analyses have revealed that the ease of emulsion formation and stability increase with a decrease in the ratio of particle size to droplet size (n). In our analysis we found that the effect of n' on emulsion stability diminished below a value of 0.01.(19)

Solids Concentration

An increase in the concentration of solid particles usually results in an increase in emulsion stability, until the O/W interface becomes covered with particles. It has been reported that in cases where the solids concentration is in excess of that required for complete interfacial coverage, the droplet size decreases so that all the particles can be accommodated at the interface.(20) The diameter at which all particles are accomodated is sometimes referred to as the "limited coalescence diameter."(21) There are practical limitations to the size a liquid droplet can decrease or increase to, hence, the concept of limited coalescence diameter is valid only in certain size regimes. From a study of toluene-water emulsions stabilized by carbon black, Gelot, Friesen, and Hamya concluded that the size of the droplets bears an inverse relationship to the amount of powder added, and the volume of emulsion formed bears a direct relationship with the amount of powder.(20)

The effect of solids concentration on emulsion stability is closely related to particle size and the magnitude of interparticle interactions. The number of particles that can be accommodated at the interface is a function of these two variables. The decrease in free energy associated with the transfer of particles from the continuous phase to the droplet surface is proportional

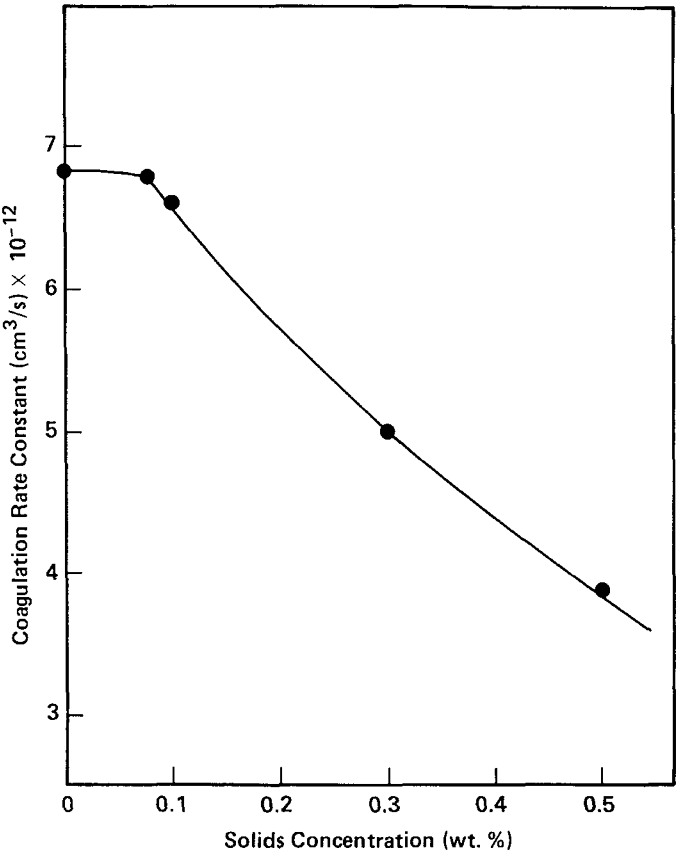

Fig. 3. Variation of coagulation rate constant with solids concentration for a water-in-shale oil emulsion (3).

to the number of particles. This also implies that the magnitude of the free energy barrier for coalescence is proportional to the solids concentration.(6,22) Fig. 3 shows the change in coagulation rate constant of a water-in-shale oil emulsion with an increase in the solids concentration in the system. The solids were hydrophobic shale dust particles with an average diameter of 4 μm. The rate of coagulation decreased by a factor of two, for an increase in solids concentration from 0.1 percent to 0.5 percent of the oil phase.

As the interfacial solids concentration approaches that corresponding to monolayer coverage, the energy required to locate an additional particle at the interface becomes large and the net free energy change becomes positive. At this stage, two events can occur; the larger droplets can break up into smaller ones leading to an increase in interfacial area thereby allowing additional particles to adsorb, or the excess number of particles can form a dispersion in the continuous phase. Experimental evidence suggests that both these mechanisms occur.

Particle Interactions

As discussed in the previous section, the number of particles that can be accommodated at the droplet surface is dependent on the particle interaction energy. The strength of interfacial films observed on droplets of solids-stabilized emulsions is a consequence of the particulate network that is formed at the interface. Such networks have been observed in O/W and W/O emulsions. Tsugita et al. observed that networks of sodium montmorillonite formed on the surface of O/W emulsions considerably enhanced emulsion stability.(14) The networks were stabilized by complexation reactions with the aqueous phase as well as by an interplay of attractive and repulsive forces between individual particles. In studies of W/O emulsions, we observed the formation of periodic colloid structures of clay particles on the surface of water droplets.(23) These ordered structures normally form as a result of long-range electrostatic interactions between particles.

We conducted single drop coalescence experiments with a planar O/W interface that was covered with different concentrations of fine particles.(6) For spherical glass beads coated with asphaltenes (diameter = 4 μm, contact angle = 150°), the particle interaction energy attained its maximum (repulsive) value at an interfacial solids concentration that approached monolayer coverage. Fig. 4 shows the variation in total interaction energy for an ensemble of particles at an O/W interface with change in solids concentration. The interaction energy was calculated from measurements of interfacial tensions of the clean and solids-covered O/W interface. Details of the experimental technique are provided elsewhere.(6)

Electrostatic interactions between particles is a major contributor to the overall particle interaction energy because of the presence of ionic surfactants in almost all the systems of industrial interest. In petroleum and synthetic fuel systems, the particles are of clay or mineral origin. Hence they possess surface charges that can be of the order of ± 10-60 mV. The surface charge is also a strong function of the surface active species adsorbed on the surface. For example, asphaltene adsorption on clay surfaces increases the surface charge (or zeta potential) due to the presence of ionic groups present on the asphaltene moieties. Fig. 5 shows the variation in zeta potential for illite

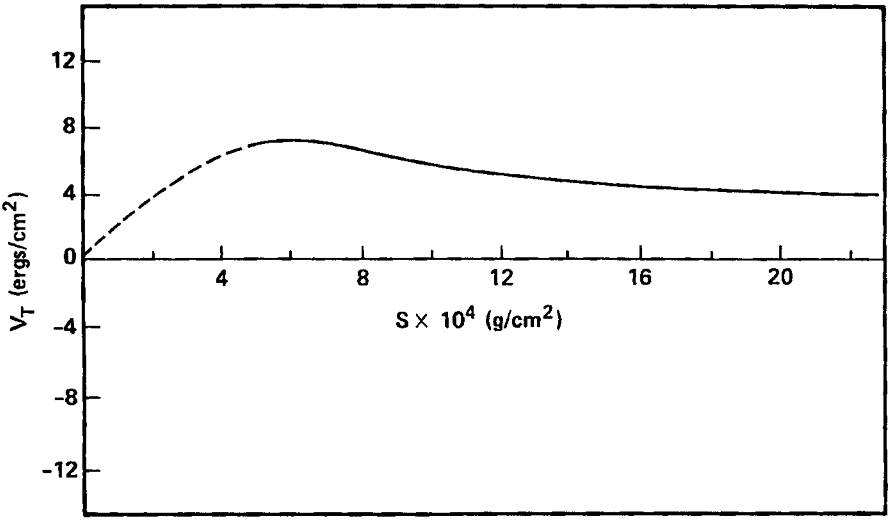

Fig. 4. Effect of interfacial solids concentration of asphaltene-coated glass beads on particle interaction energy (24).

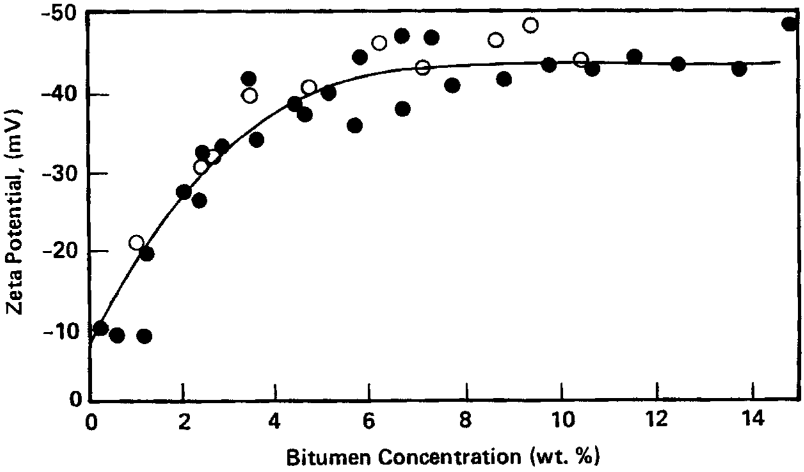

Fig. 5. Zeta potentials of illite in bitumen/toluene solutions. (●) calculated from streaming potentials; (○) calculated from electrophoresis data (25).

particles as a function of bitumen concentration.(25) The magnitude of zeta potential values increases with increasing bitumen concentration and levels off at high concentrations, presumably because of saturation of surface sites on the clay. A similar trend has also been observed for the zeta potential of asphaltene-coated montmorillonite particles.(26)

In addition to electrostatic interactions, van der Waals, capillary and steric interactions also contribute to the total energy. Approximate estimates of the magnitudes of each of these components for particles at an O/W interface have been made by Levine, Bowen, and Partridge.(27) Their calculations suggest that the depth of the energy well into which particles are deposited at the interface is two to three orders of magnitude higher than the contributions from particle interaction energy. From experimental measurements of particle interaction energy at an O/W interface, we obtained values that were of the same order as the depth of the energy well. The strength of the interfacial skin will depend on the charge and magnitude of these interaction energies as well as on the chemical interactions that occur between the particles and the two liquids.

Surface Active Species

Factors such as contact angle and particle interaction energy are dependent to a great degree on the specific chemical functional groups that are present at the interface. Asphaltenes represent the major natural surface active species present in most petroleum crudes and synfuels. They possess a predominantly aromatic structure with hydrophilic sections housing the oxygen, sulfur, and nitrogen molecules. The asphaltenes stabilize emulsions either by adsorbing at the O/W interface directly, or by adsorbing on mineral or clay particles which in turn stabilize the interface.

Eley, Hoy, and Lee have studied the rheological properties of O/W interfaces containing adsorbed asphaltene films.(28) The creep curves were found to exhibit dilatancy, with the shape of the curve depending on the concentration of asphaltenes at the interface. They attribute some of the creep profiles to the presence of flocculated asphaltene particles at the O/W interface.

The three types of natural anionic surfactants present in bitumen are sulfonates, sulfates, and carboxylates. The dissociation of each of these species is a strong function of the pH, as is the dissociation of ionic sites on clay and mineral particles. Hence, there is a tendency for such solid particles to form complexes with the organic species in the oil. Taubman and Koretskii attribute complexation reactions to be one of the major causes of emulsion stabilization.(29) Tsugita et al. also attribute reactions between sites on the clay and OH^- groups present at the O/W interface to contribute to network formation.(14)

The destabilization of solids-stabilized emulsions is usually accomplished by adding demulsifiers to the system and/or changing the aqueous phase pH. The demulsifier molecules either displace the stabilizing species from the interface due to their superior surface activity or adsorb onto the particles and change their wettability or ionic nature. Svitova, Spirodonova, and Tolystaya used water-soluble polymers to break W/O emulsions stabilized by asphaltic layers.(30) They found that demulsification occurred as a consequence of wettability alteration due to the adsorption of polymer molecules on the asphaltene particles. Gelot, Friesen, and Hamza evaluated the effect of a cationic demulsifier on W/O emulsions stabilized by ionic particles such as calcium bentonite and calcium kaolinite.(20) They report that the mechanism of demulsification appears to be due to the adsorption of the cationic sites of the demulsifier onto the negatively charged clay surfaces, thereby changing their wettability or state of aggregation.

Displacement of asphaltene fractions from the interface due to the greater surface activity of demulsifier molecules was observed by Eley, Hey, and Lee.[28] They observed a direct correlation between decrease in surface tension due to the presence of demulsifier and increase in asphaltene displacement. In single drop coalescence experiments conducted with shale dust particles at a planar O/W interface, we found that an anionic demulsifier modified both the O/W interfacial tension and the particle interaction energy.(6) This implies that some of the demulsifier molecules displace other surface active species from the O/W interface while others adsorb on the solid particles and alter their surface characteristics. The specific mechanism by which demulsification of solids-stabilized emulsions occurs is as yet unclear.

Summary

This paper discusses some of the factors affecting the formation and stability of emulsions stabilized by finely divided solid particles. The current state of research in this field is referenced and the merits and drawbacks of some of the existing approaches are delineated. This paper is meant to complement two other review articles on this subject (2,6) and has attempted to address areas that have not been discussed in detail in the earlier work. Factors such as contact angle, particle size, particle interactions, and the presence of surfactants play an important role in determining the formation and stability of such emulsions. Of these, contact the effects of angle and surfactants has been known for a long time, but it is only in recent years that the significance of particle interaction energy is being realized.

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