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Sangobtip Pondstabodee; John F. Scamehorn; Sumaeth Chavedej; Jeffrey H. Harwell

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Cleanup of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation

SANGOBTIP PONDSTABODEE
THE PETROLEUM AND PETROCHEMICAL COLLEGE
CHULALONGKORN UNIVERSITY
BANGKOK, THAILAND

JOHN F. SCAMEHORN*
INSTITUTE FOR APPLIED SURFACTANT RESEARCH
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019, USA

SUMAETH CHAVEDEJ
THE PETROLEUM AND PETROCHEMICAL COLLEGE
CHULALONGKORN UNIVERSITY
BANGKOK, THAILAND

JEFFREY H. HARWELL
INSTITUTE FOR APPLIED SURFACTANT RESEARCH
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019, USA

ABSTRACT

This study showed that the efficiency of removal of σ-dichlorobenzene from water by batch froth flotation increases as changes in salinity cause the system to vary from a Winsor Type I microemulsion to a Winsor Type III microemulsion. The cationic surfactant studied is more effective than either the monosulfate or the disulfonate anionic surfactants studied. The oil flotation efficiency increases as the initial surfactant concentration increases, as the salinity increases (causing a Winsor Type I to III transition for these systems), and as the oil/water ratio decreases.

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* To whom correspondence should be addressed.

INTRODUCTION

Chlorobenzene and its derivatives are classified as hazardous substances. However, they are widely used in applications such as solvents in paints, a raw material in the manufacture of phenol and aniline, an insecticide for termites, a degreasing agent for metals, and as a heat transfer medium (1). Due to their versatility, they are commonly found in industrial wastewaters.

Froth flotation is a separation technique which can be used to remove oils (either dissolved or as oil droplets) from water (e.g., cleaning up oily wastewaters) and is illustrated in Fig. 1. In froth flotation a surfactant is usually introduced into the wastewater to enhance the flotation of oil. Air is introduced into the system through a sparger which produces fine bubbles. The surfactant tends to concentrate at the air/water interface with hydrophobic groups (water insoluble) in the air and the hydrophilic or head groups in the water. The oil attaches to the air bubbles as they rise through solution and is highly concentrated in the foam layer called froth at the top of the flotation cell which is skimmed off. Many factors are considered to have an effect on oil removal such as air flow rate, size

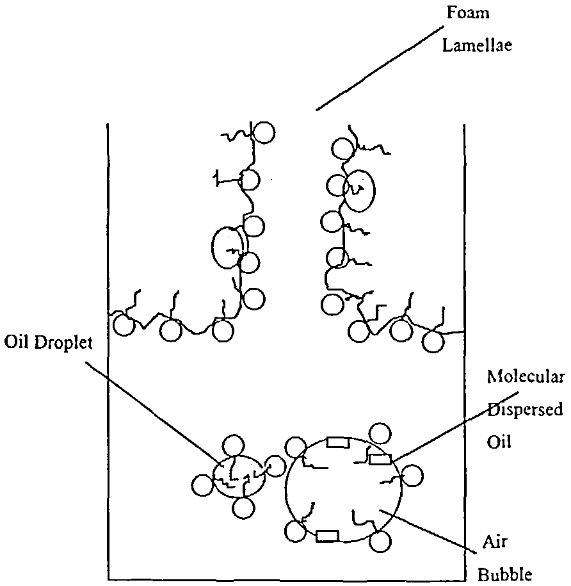
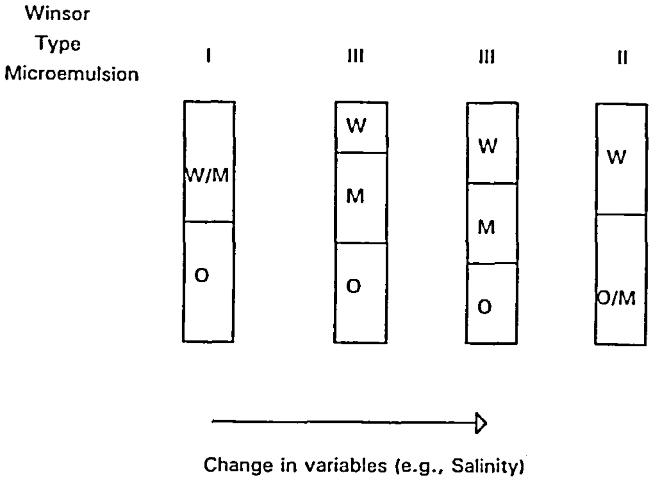


FIG. 1 Schematic of the froth flotation removal of oil from water.

of gas bubbles and oil droplet, zeta potential of oil droplets and bubbles, oil density, and concentration of added polyelectrolyte (2–5).

When water-soluble surfactant is added to water under the proper conditions and above the critical micelle concentration (CMC), the surfactant forms aggregates called micelles which dissolve or solubilize oil and can result in an increase in oil solubility in the aqueous phase. This aqueous phase in equilibrium with excess oil is also known as a Winsor Type I microemulsion (6). Under the proper conditions, as some variable (e.g., salinity, temperature) is changed, this oil/water/surfactant system can change from the two phases which compose a Winsor Type I microemulsion and its excess oil phase into a three phase system, as shown in Fig. 2. The three phases consist of an excess oil phase, an excess water phase (both containing little surfactant), and a Winsor Type III microemulsion phase containing high levels of both water and oil, along with most of the surfactant in the system (7). Ultralow interfacial tensions (e.g., $< 10^{-4}$ mN/m) between the excess oil and the microemulsion phase, between the



O = oil phase

W = water phase

M = microemulsion phase

FIG. 2 Demonstration of microemulsion phase behavior for a model system with oil denser than water.

excess water and the microemulsion phase, and between the excess oil and excess water in the Winsor Type III system can be attained in this manner (8). The condition corresponding to equal volumes of oil and water being transferred from the excess phases to form the Winsor Type III or middle phase microemulsion approximately corresponds to the minimum interfacial tensions between the oil and the water which compose the excess phases (9, 10). This is referred to in the enhanced oil recovery literature as the optimal condition (e.g., optimal salinity when salt concentration is the variable being altered). This is the condition which is desirable for mobilization of trapped oil in enhanced oil recovery (11, 12) using surfactants. As the adjustable variable is changed further, the system becomes two phases again, now with the surfactant predominately in the oil phase (Winsor Type II microemulsion) in equilibrium with an excess water phase as also shown in Figure 2. For the oil used in this study and that shown in Fig. 2, the oil is more dense than water, so the oil phase is on the bottom and the water phase is on the top. This is the opposite of the much studied hydrocarbon/water systems, so the appearance of the phase behavior of those light oil systems are different from the heavy oil studied here.

Altering the variables in a froth flotation process using surfactants to remove oil droplets from water affects a number of separate but interacting phenomena: e.g., oil droplet size and hydrophilicity of droplet surface, air bubble size and nature of the air/water interface, and froth characteristics and stability.

In a previous study we systematically investigated the effect of surfactant type on the efficiency of removal of a dissolved organic solute from water (13). In the current study we have investigated the froth flotation of oil greatly in excess of its saturation concentration. In particular, the effects of surfactant type and salinity (causing a Winsor Type I to Type III microemulsion transition) on flotation efficiency were investigated here.

EXPERIMENTAL SECTION

Materials

The oil used was *ortho*-dichlorobenzene (ODCB) from Fisher Scientific Co., (99.9% purity). Three types of surfactants were used. Sodium dodecyl sulfate (SDS), commercial grade with 90% purity, was obtained from Henkel Co. The sodium salt of mono- and dihexadecyldiphenyloxidedisulfonate (DADS), 36% by weight, was supplied in liquid form by Dow Chemical Co. (trade name of DOWFAX 8390). Cetylpyridinium chloride or *n*-hexadecylpyridinium chloride (CPC), with a purity of greater than 99.9%, was obtained from Pfaltz & Bauer. Sodium chloride (NaCl), analytical purity grade, was obtained from Aldrich Chemical Co. Triple distilled water was used in all of the experiments.

Methods

In both the phase behavior and the froth flotation experiments, the surfactant concentration and salinity were expressed as weight percent of the overall system (including the water, oil, surfactant, and salt). All experiments were at 30°C.

In the study of equilibrium phase behavior, aqueous solutions were prepared at various surfactant and sodium chloride concentrations. The 5 mL solution was prepared in a vial, heated to 40°C, and mixed vigorously with an autoshaker. An equal volume of σ-dichlorobenzene was pipetted and allowed to contact the solution, and the system was then heated to 40°C again. The sample was then allowed to equilibrate at a constant

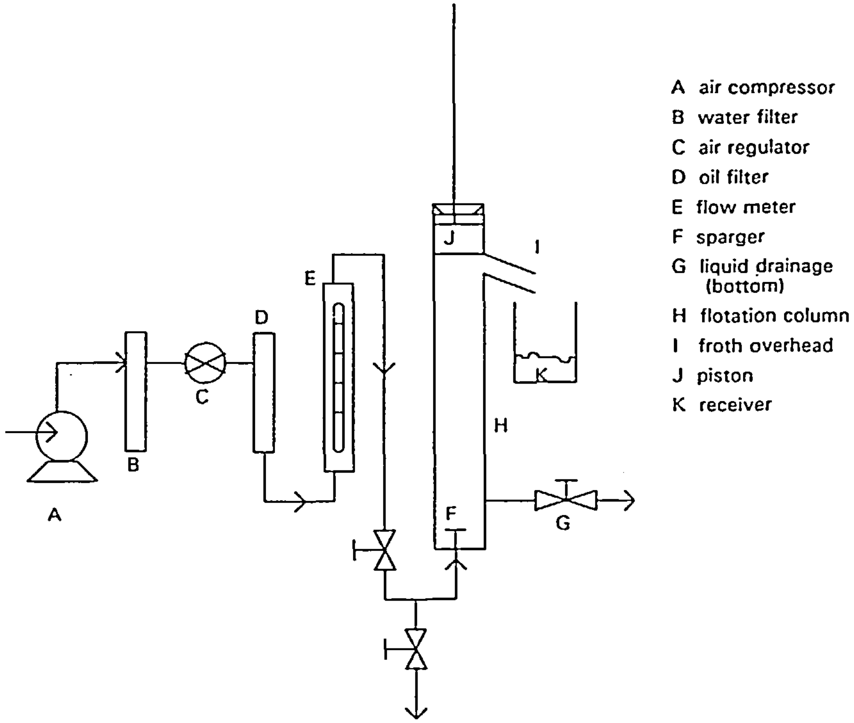


FIG. 3 Experimental froth flotation apparatus.

temperature of 30°C in an environmental room. Equilibrium was assumed to have been achieved when the volumes and the appearance of the different phases did not change with time. The height and therefore volume of each of the phases present was measured using a polarized light screen (PLS).

A schematic diagram of the froth flotation unit used in this study is shown in Fig. 3. A glass cylindrical column with 5 cm internal diameter and 60 cm height was used as the flotation column. A 1-L equilibrated microemulsion sample prepared as described in the previous paragraph was transferred to the froth flotation column by slowly pouring and letting it set undisturbed for 10 minutes. Filtered air was introduced into the bottom of the column through a sintered glass disk, having a pore size diameter of 16–40 μm. The froth from the top of the column was collected into the receiver over a period of 300 seconds. The froth was broken by freezing followed by thawing. The concentrations of ODCB, CPC, and DADS were analyzed by using HPLC with a UV detector; a HPLC with a refractive index detector was used to measure the SDS concentration.

RESULTS AND DISCUSSION

Equilibrium Phase Behavior

Figures 4 to 11 illustrate the effect of salinity on the phase behavior with an oil/water initial volumetric ratio of 1/1 for different surfactant types and concentrations. The 1/1 ratio is used here for the phase behavior

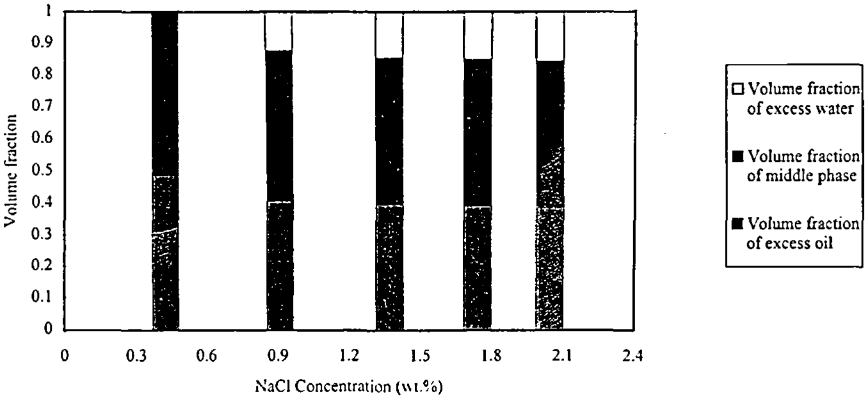


FIG. 4 Phase volume of microemulsion system with SDS concentration = 1 wt%, initial oil/water volume ratio = 1/1.

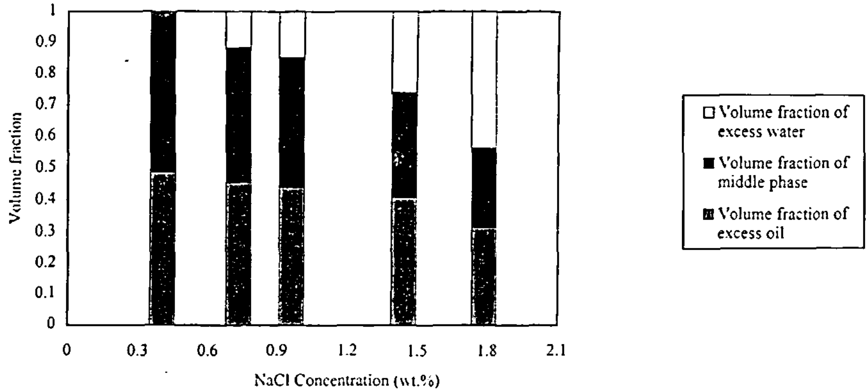


FIG. 5 Phase volume of microemulsion system with SDS concentration = 2.5 wt%, initial oil/water volume ratio = 1/1.

and flotation experiments because this is the traditional condition for microemulsion phase studies of this kind, so results from this work can be compared to other systems in the literature. In the systems without salt, the oil and the water phase each exhibit negligible volume change and very little oil solubilizes in the water phase and very little water in the

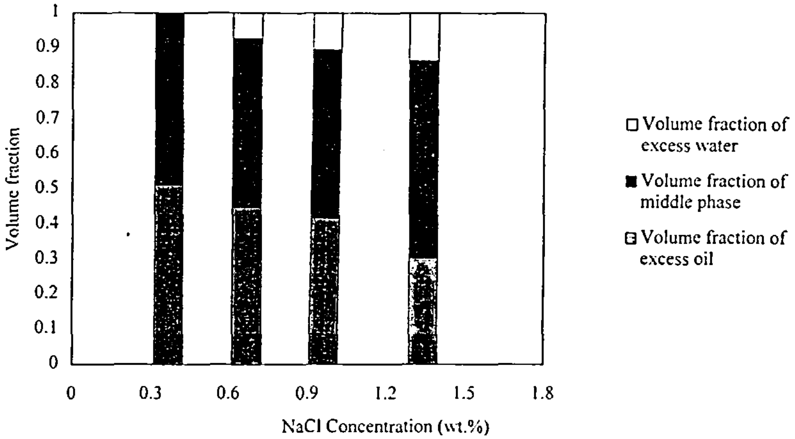


FIG. 6 Phase volume of microemulsion system with SDS concentration = 3.5 wt%, initial oil/water volume ratio = 1/1.

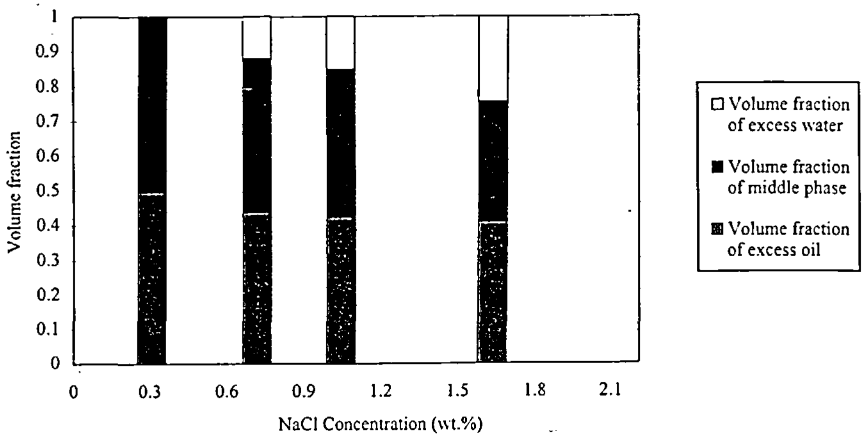


FIG. 7 Phase volume of microemulsion system with CPC concentration = 0.5 wt%, initial oil/water volume ratio = 1/1.

oil phase. Increasing salinity causes the phase primarily containing the surfactant (microemulsion phase) to undergo the transition of upper phase (oil in water microemulsion where water is the continuous phase) to a middle phase microemulsion. It is important to remember that ODCB is

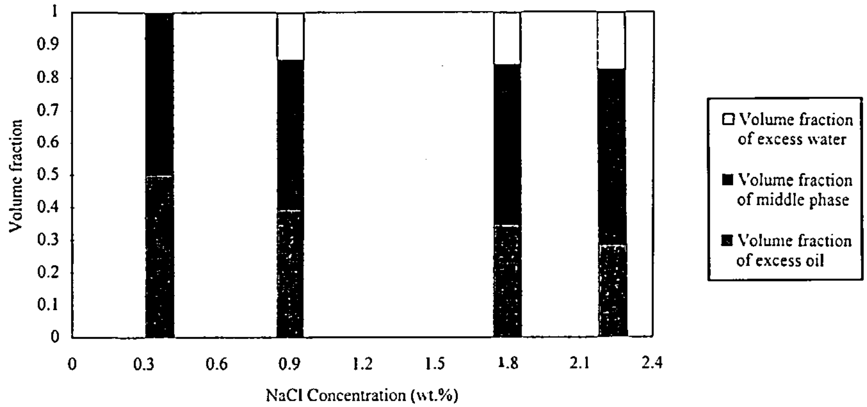


FIG. 8 Phase volume of microemulsion system with CPC concentration = 3.5 wt%, initial oil/water volume ratio = 1/1.

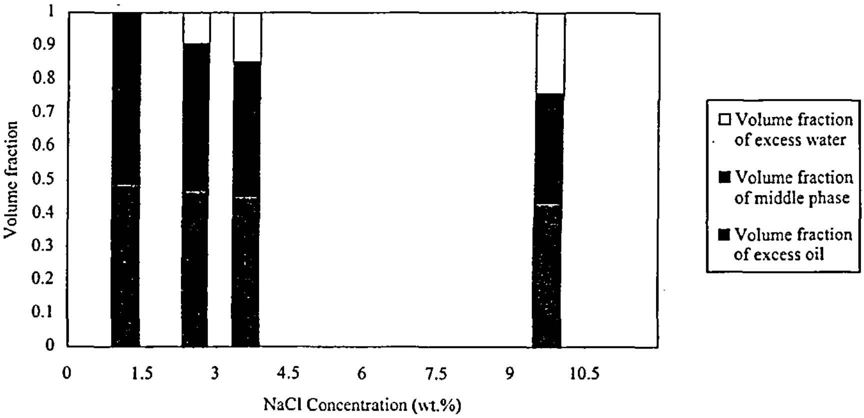


FIG. 9 Phase volume of microemulsion system with DADS concentration = 1 wt%, initial oil/water volume ratio = 1/1.

heavier than water so the transitions observed here appear to be different than in studies related to enhanced oil recovery where the oil is less dense than water. The middle phase microemulsion is in equilibrium with an excess water phase and an excess oil phase, neither of which contain

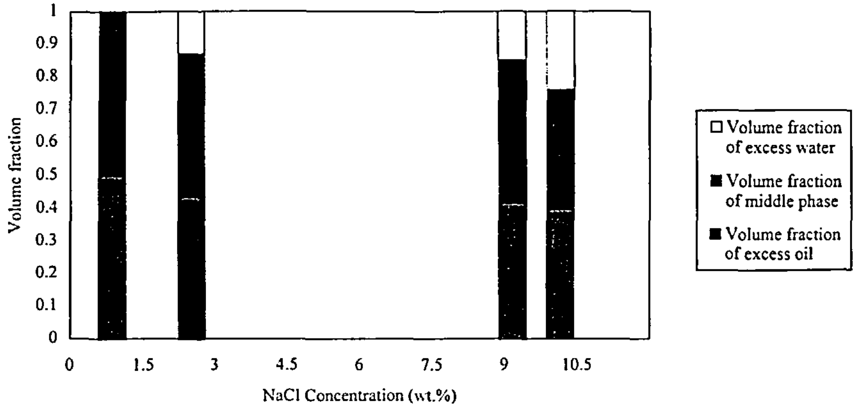


FIG. 10 Phase volume of microemulsion system with DADS concentration = 3.5 wt%, initial oil/water volume ratio = 1/1.

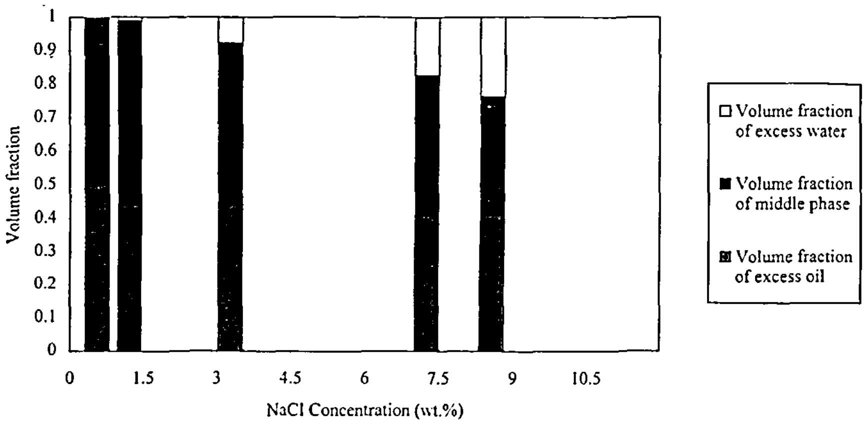


FIG. 11 Phase volume of microemulsion system with DADS concentration = 10 wt%, initial oil/water volume ratio = 1/1.

substantial surfactant concentrations. This is the Winsor Type III microemulsion system with the microemulsion phase containing substantial concentrations of both oil and water. Using SDS as a surfactant, the phase volume of excess oil decreases while the phase volume of excess water increases with increasing salinity. The same trends were also obtained for CPC and DADS. The direction of phase transitions shows that adding an electrolyte to the system causes the surfactant solubility in the aqueous phase to decrease (14). None of the systems studied here showed the Winsor Type II microemulsion behavior illustrated in Fig. 2 over the range of salinities studied here. At NaCl concentrations of 2.3 wt% and higher, precipitation and gel formation occur for both SDS and CPC; DADS systems do not exhibit precipitation over the salinity range studied. As a result, the optimal salinity was only reached for the DADS surfactant system with no cosurfactant.

As can be seen from Fig. 9 to 11, the minimum salinity causing the middle phase microemulsion decreases with increasing surfactant concentration for DADS. A lens at the aqueous–oil interface was observed when using low surfactant concentration without salt for all three surfactants. A dependence of phase behavior and interfacial tension on surfactant concentration has been reported for a complex mixture of anionic surfactants (15). Previous work has shown that for sufficiently high surfactant concentrations, the interfacial layer attains a constant composition (considered to be comprised only of those surfactant molecules adsorbed at the oil/

water interface) and phase transitions between Winsor Type I, III to II may not occur (16). Not enough salinities were studied to reach a conclusion about the minimum surfactant concentration required for middle phase (Winsor Type III) microemulsion formation for SDS or CPC.

At a low oil-to-water volume ratio of less than 0.09 for SDS, less than 0.07 for CPC, and less than 0.3 for DADS, what appears to be a liquid crystalline phase was observed as illustrated in Fig. 12. Changing the oil-to-water ratio to very large or very small values may lead to the formation of liquid crystalline or other nonisotropic phases (17–19).

Froth Flotation

The effect of NaCl concentration on ODCB removal and on surfactant removal can be seen in Fig. 13 through 18 and Fig. 19 to 24, respectively. Also shown in the figures is the approximate salinity at which the equilibrium phase behavior showed the Winsor Type I to Type III transition as inferred from the phase boundary measurements. The removal of oil increases with increasing salinity, decreasing oil/water ratio, and increasing surfactant concentration. As the salinity increases in the Winsor Type III region, the interfacial tension between the microemulsion (middle) phase and the excess water and excess oil phases decreases until optimal salinity is attained (20). The salinity did not reach the optimal salinity in the flotation experiments reported here due to the aforementioned surfactant

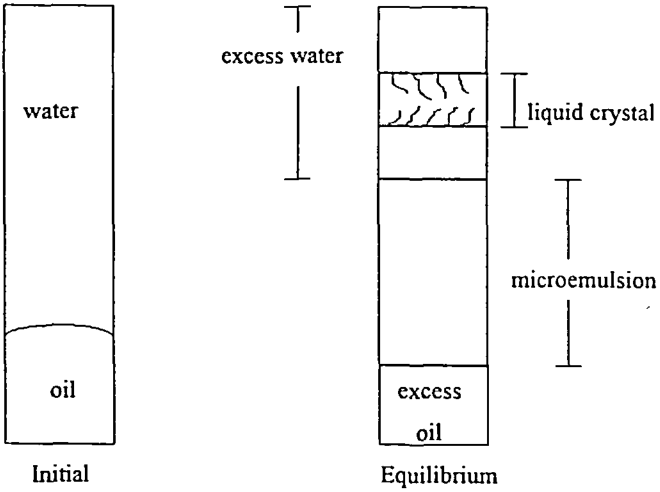


FIG. 12 Illustration of apparent liquid crystal formation at low oil/water ratio.

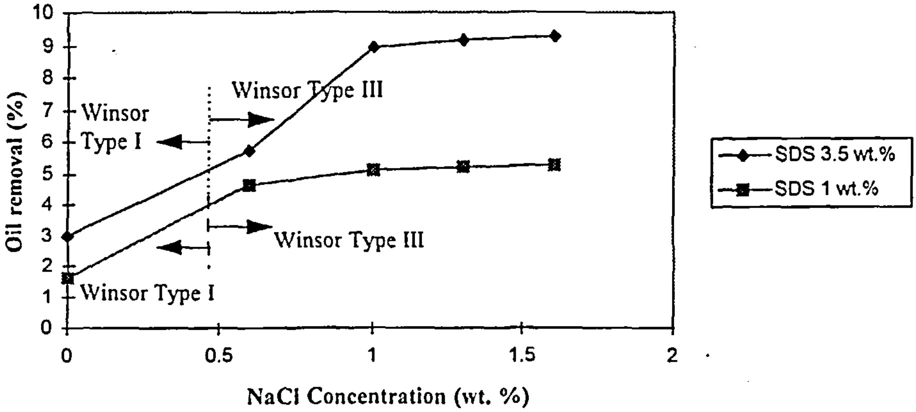


FIG. 13 Effect of SDS and NaCl concentration on oil removal with SDS concentration = 1.0 and 3.5 wt%, initial oil/water volume ratio = 1/1.

precipitation problems. As the oil/water ratio decreases or surfactant concentration increases, a higher fraction of the ODCB is present in the microemulsion instead of the excess oil phase. The results reported here would imply that when the oil is in microemulsion form, the flotation efficiency is greater than when the oil exists as an excess phase. DADS is a poor foamer, and the froth lifetime is too short for the foam to rise

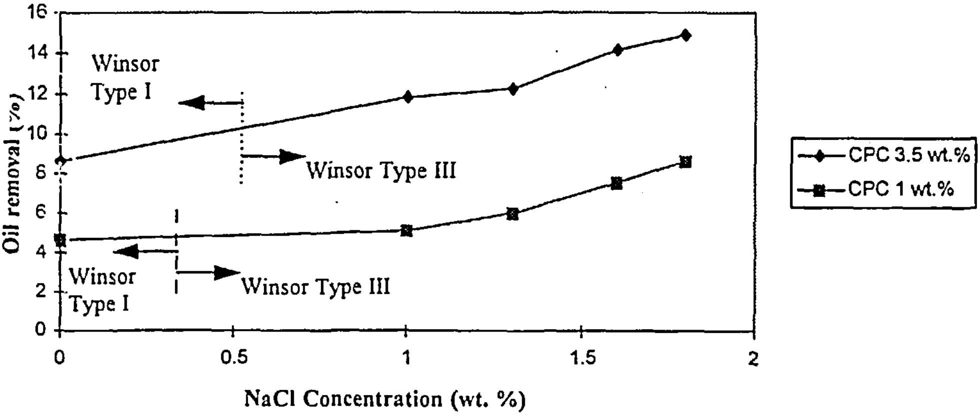


FIG. 14 Effect of CPC and NaCl concentration on oil removal with CPC concentration = 1.0 and 3.5 wt%, initial oil/water volume ratio = 1/1.

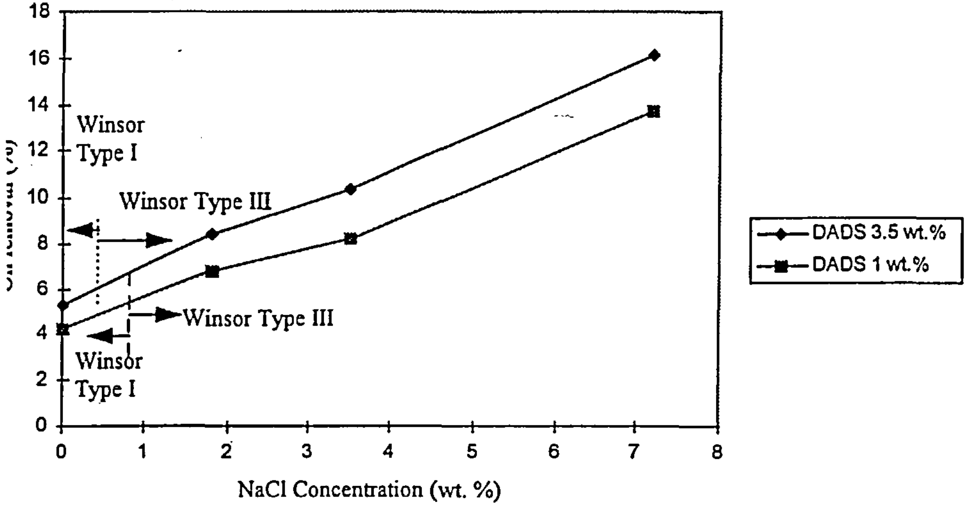


FIG. 15 Effect of DADS and NaCl concentration on oil removal with DADS concentration = 1.0 and 3.5 wt%, initial oil/water volume ratio = 1/1.

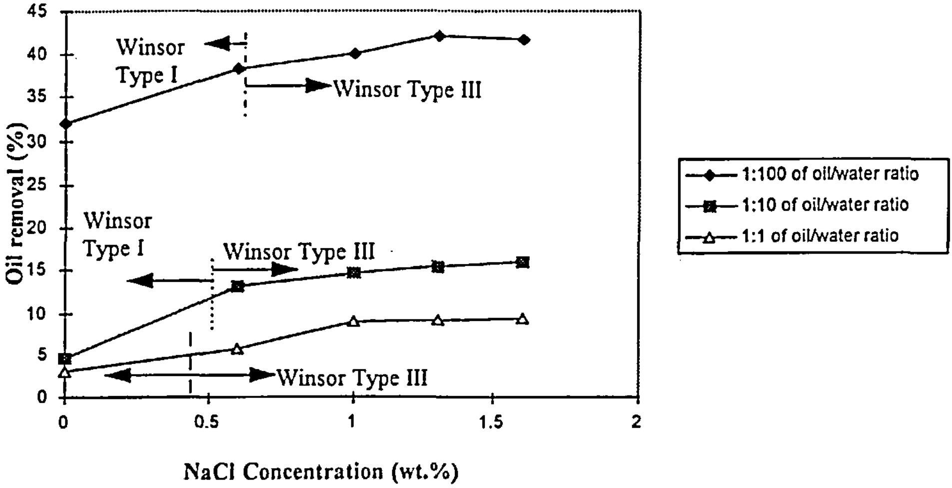


FIG. 16 Effect of NaCl concentration and oil-to-water volumetric ratio on oil removal with SDS concentration = 3.5 wt%.

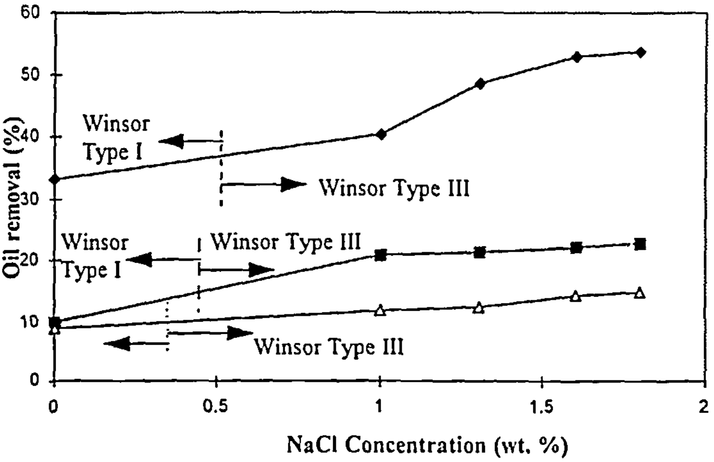


FIG. 17 Effect of NaCl concentration and oil-to-water volumetric ratio on oil removal with CPC concentration = 3.5 wt%. (◆) 1:100 of oil/water ratio, (■) 1:10 of oil/water ratio, (Δ) 1:1 of oil/water ratio.

through the column into the receiver when the salinity is above about 7.5 wt%. For all systems the oil removal increases with increasing surfactant concentration. A similar behavior has been reported for cobalt recovery (21), boron recovery (22), and oil recovery (23).

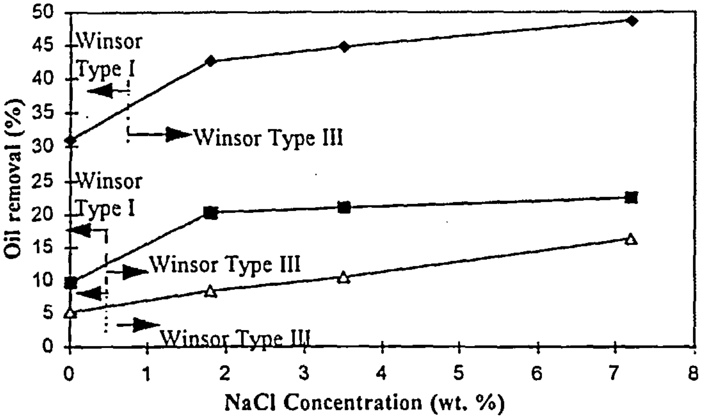


FIG. 18 Effect of NaCl concentration and oil-to-water volumetric ratio on oil removal with DADS concentration = 3.5 wt%. (◆) 1:100 of oil/water ratio, (■) 1:10 of oil/water ratio, (Δ) 1:1 of oil/water ratio.

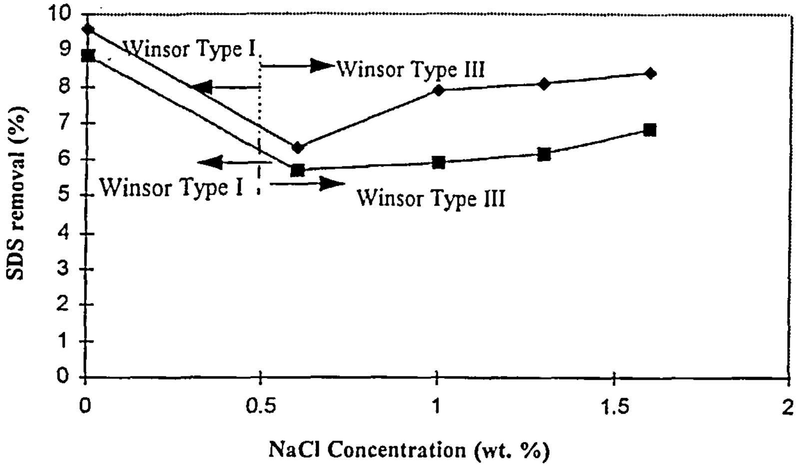


FIG. 19 Effect of SDS and NaCl concentration on SDS removal with SDS concentration = 1.0 and 3.5 wt%, initial oil/water volume ratio = 1/1. (♦) 3.5 wt% SDS, (■) 1 wt% SDS.

The effect of oil-to-water volume ratio on ODCB removal is shown in Fig. 16 through 18 and on surfactant removal in Figs. 22 to 24, respectively. The percentage of oil and surfactant removal tends to increase with decreasing oil-to-water ratio. For SDS and CPC systems with a water/oil

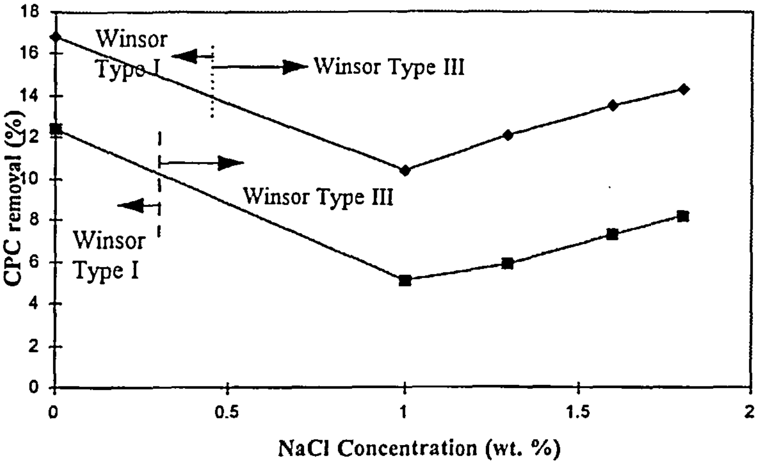


FIG. 20 Effect of CDC and NaCl concentration on CPC removal with CPC concentration = 1.0 and 3.5 wt%, initial oil/water volume ratio = 1/1. (♦) 3.5 wt% CPC, (■) 1 wt% CPC.

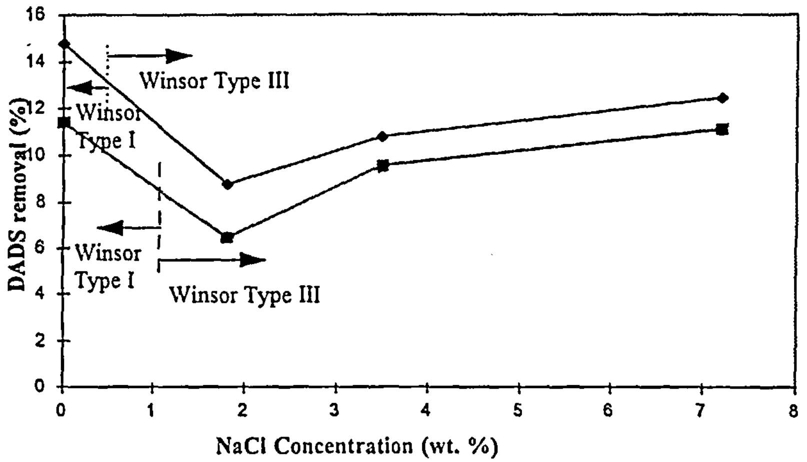


FIG. 21 Effect of DADS and NaCl concentration on DADS removal with DADS concentration = 1.0 and 3.5 wt%, initial oil/water volume ratio = 1/1. (♦) 3.5 wt% DADS, (■) 1 wt% DADS.

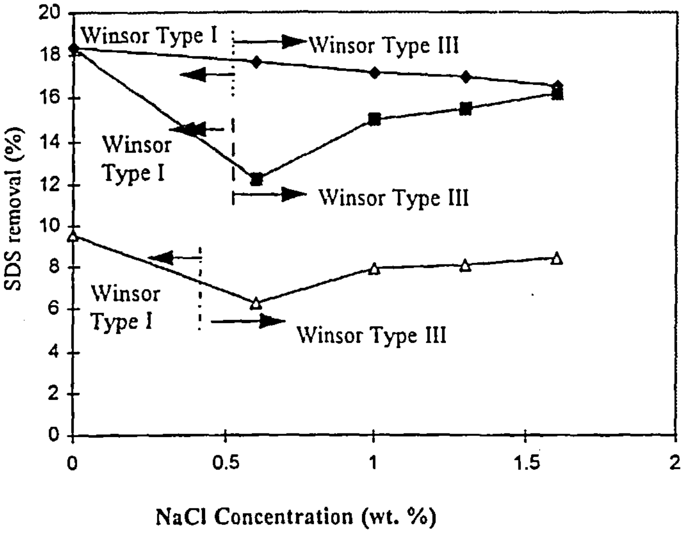


FIG. 22 Effect of NaCl concentration and oil-to-water volumetric ratio on SDS removal with SDS concentration = 3.5 wt%. (♦) 1:100 of oil/water ratio, (■) 1:10 of oil/water ratio, (△) 1:1 of oil/water ratio.

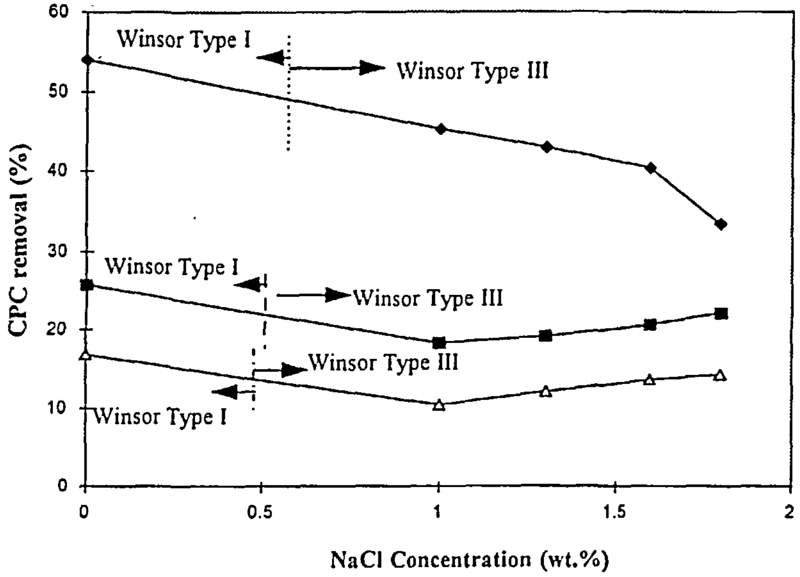


FIG. 23 Effect of NaCl concentration and oil-to-water volumetric ratio on CPC removal with CPC concentration = 3.5 wt%. (◆) 1:100 of oil/water ratio, (■) 1:10 of oil/water ratio, (△) 1:1 of oil/water ratio.

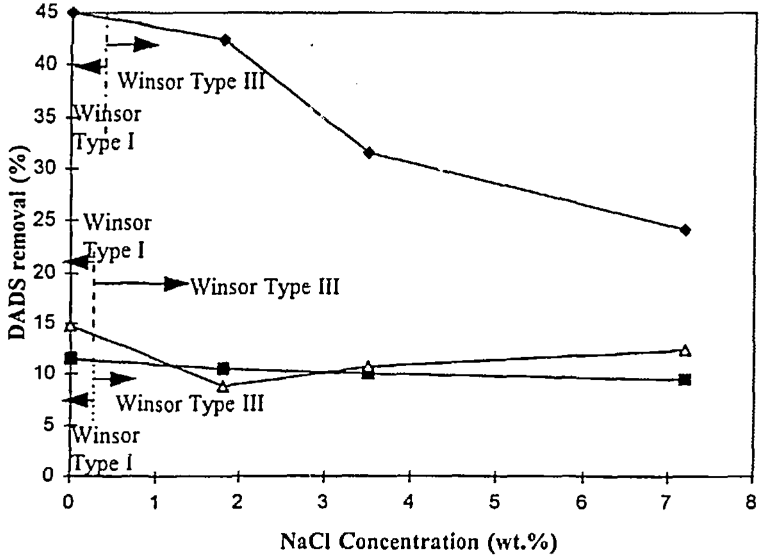


FIG. 24 Effect of NaCl concentration and oil-to-water volumetric ratio on DADS removal with DADS concentration = 3.5 wt%. (◆) 1:100 of oil/water ratio, (■) 1:10 of oil/water ratio, (△) 1:1 of oil/water ratio.

ratio of 0.01 and for the DADS system with 0.01 and 0.1 water/oil ratio, the surfactant removal decreases with increasing salinity, possibly due to liquid crystal formation. Unlike surfactant removal, the effect of salinity on removal of oil in systems with apparent liquid crystalline phases is similar to that of the systems in which the liquid crystalline phases do not appear. When the apparent liquid crystals are present, the surfactant removal decreases with increasing NaCl concentration.

The froth flotation process involves a number of physical phenomena occurring simultaneously, and numerous variables influence the process, including attachment of the oil (or microemulsion) droplet to air bubbles, the size of the oil droplets and air bubbles, oil (or microemulsion) interfacial tensions with the water phase and the air phase, froth stability, ability of the froth to suspend floated oil droplets, and nonequilibrium effects such as dynamic interfacial tensions, to mention a few effects in this complex separation process. This paper is the first investigation of which we are aware on the potential improvement in this separation process related to incorporation of the oil into a Winsor Type III microemulsion phase, with the presumed substantial decrease in oil/water interfacial tension. The improvement in oil removal observed here when a Winsor Type III microemulsion is present shows the promise of this novel approach and indicates the importance of understanding the mechanisms of synergism in more detail.

ACKNOWLEDGMENTS

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