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Formulating Microemulsion Systems for a Weathered Jet Fuel Waste Using Surfactant/Cosurfactant Mixtures

Bin Wu[a]; Bor-Jier Shiau[b]; David A. Sabatini[ac]; Jeffrey H. Harwell[d]; De Q. Vu[d]
[a] SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE, UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA, USA [b] SURBEC ENVIRONMENTAL, LLC, NORMAN, OKLAHOMA, USA [c] School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, OK, U.S.A. [d] SCHOOL OF CHEMICAL ENGINEERING AND MATERIAL SCIENCE, UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA, USA

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BIN WU
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019, USA

BOR-JIER SHIAU
SURBEC ENVIRONMENTAL, LLC
3200 MARSHALL AVENUE, SUITE 200, NORMAN, OKLAHOMA 73072, USA

DAVID A. SABATINI*
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019, USA

JEFFREY H. HARWELL and DE Q. VU
SCHOOL OF CHEMICAL ENGINEERING AND MATERIAL SCIENCE
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019, USA

ABSTRACT

This paper identifies surfactant systems capable of forming middle phase microemulsions with a weathered jet fuel at Hill AFB, Utah. A series of batch studies was conducted to characterize the hydrophobicity of this light nonaqueous phase liquid (LNAPL) and to evaluate microemulsion systems for this LNAPL. The contaminant was found to be more hydrophobic than ordinary jet fuel, thus requiring cosurfactant and electrolyte addition to formulate middle phase microemulsions. Successful salinity (NaCl) and hardness ($CaCl_2$) scans were conducted with one anionic surfactant, Aerosol OT (AOT), and three different cosurfactant systems—one alcohol (isobutanol), one hydrotrope (sodium mono- and dimethyl naphthalene sul-

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* To whom correspondence should be addressed at School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd Street, Room 334, Norman, OK 73019, USA. Telephone: (405) 325-4273. FAX: (405) 325-4217. E-mail: sabatini@ou.edu

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fonate or SMDNS), and two nonionic surfactants [POE(20) sorbitan monostearate or T-MAZ 60 and POE(20) sorbitan monooleate or T-MAZ 80]. Of the five systems which successfully microemulsified the LNAPL (versus 10 others evaluated), one was selected for implementation in a subsequent field demonstration.

INTRODUCTION

Innovative surfactant-based remediation technologies are leading candidates for expediting pump-and-treat methods (35). Surfactant-based technologies utilize two different mechanisms for enhancing remediation: surfactant-enhanced solubilization whereby hydrophobic contaminants partition into micellar cores, and surfactant-enhanced mobilization whereby contaminants and surfactant solutions form middle phase microemulsions with ultralow interfacial tensions (IFTs) causing bulk-oil displacement. Whereas surfactant-enhanced solubilization can increase remedial efficiency by one to two order(s) of magnitude, surfactant-enhanced mobilization achieves even greater efficiencies. Economic considerations obviously favor the mobilization approach; however, design and implementation of mobilization is more complicated than solubilization.

Significant progress has been made in laboratory development and field application of surfactant-enhanced mobilization (1–3, 6, 12, 13, 23–25, 31, 32, 34). However, the majority of these reports address mobilization of dense, nonaqueous phase liquids (DNAPLs,—e.g., chlorinated solvents). In contrast, only a few studies have addressed mobilization of light, nonaqueous phase liquids (LNAPLs), such as petroleum hydrocarbons (5, 8). However, LNAPLs are ubiquitous subsurface contaminants due to their widespread use (27). This paper reports on laboratory studies for designing/selecting a surfactant system for mobilizing a weathered jet fuel from Hill AFB, Utah. The selected system was utilized in a subsequent field demonstration that achieved a contaminant removal of over 90% with 6.6 pore volumes of the selected AOT/T-MAZ 80 system, as documented elsewhere (18).

BACKGROUND

Microemulsion Systems and Their Application

The term microemulsion was first used to describe transparent or translucent, thermodynamically stable systems observed when titrating an ordinary water–hydrocarbon emulsion with electrolytes (17). A microemulsion system with a density between that of water and hydrocarbons is known as a "middle phase microemulsion." The two most common electrolytes utilized in the formulation of middle phase microemulsions are NaCl (salinity scan) and $CaCl_2$ (hardness scan).

An example of the electrolyte scan is shown in Fig. 1 where the abscissa is NaCl concentration (as weight percent) and the ordinate is the relative vol-

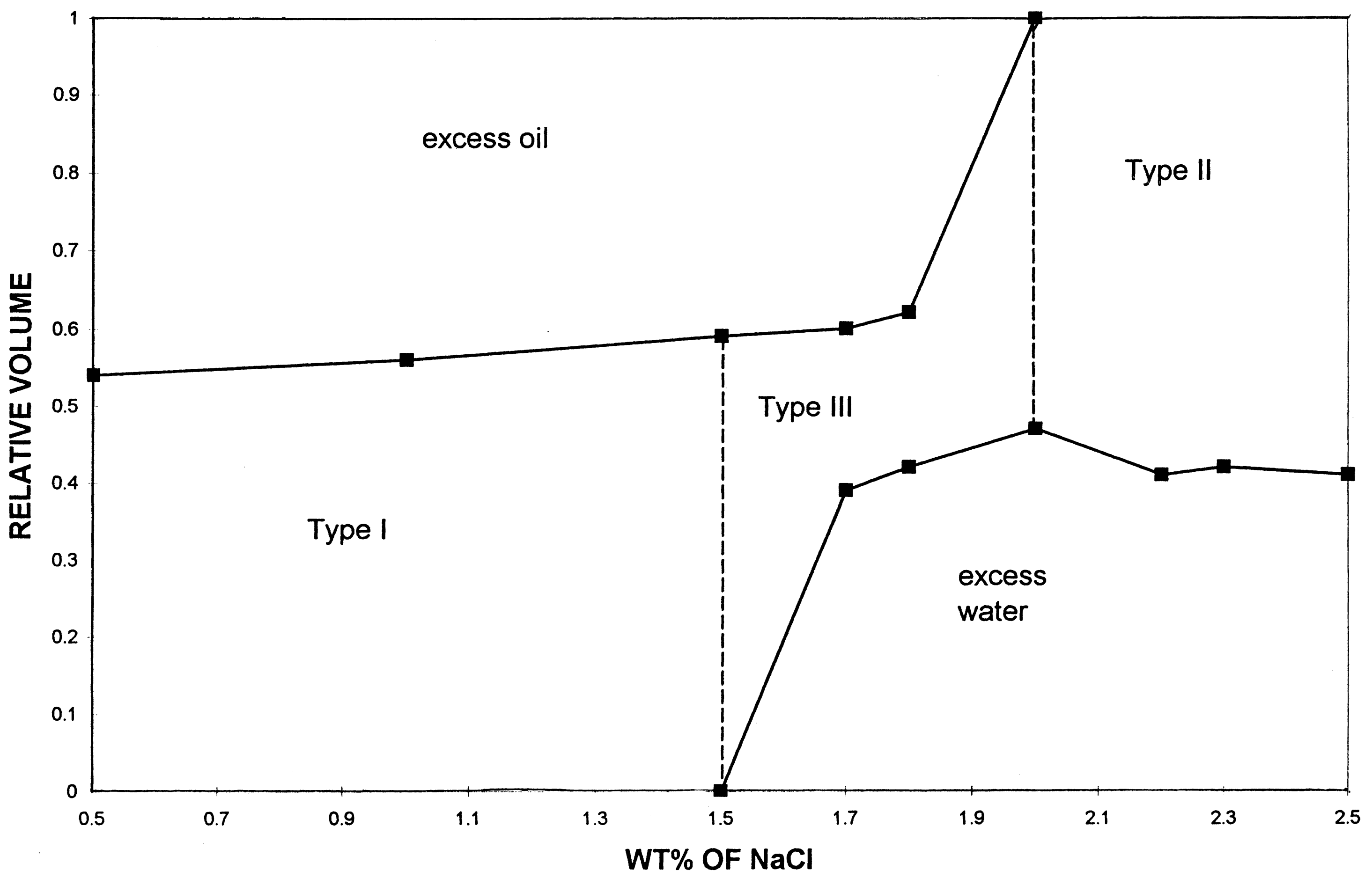

FIG. 1 Phase diagram of salinity scan on AOT/T-MAZ 60/Hill LNAPL system at 15°C. AOT concentration is 50 mM (aqueous), T-MAZ 60 concentration is 15 mM (aqueous), and volumetric ratio of oil to water is 5 mL each.

umetric fraction of the system in each phase (oil, water, or, when applicable, the middle phase). The system of sodium bis-2-ethylhexyl sulfosuccinate (Aerosol-OT, or AOT) and POE(20) sorbitan monostearate (T-MAZ 60) is used to form middle phases with the Hill LNAPL (a weathered jet fuel). The initial oil to water volumetric ratio was 1:1. At the left side of the diagram (NaCl concentration is less than 1.5 wt%) two phases exist—the water phase with micellar-solubilized oil and the excess oil phase (Winsor Type I system; 37, 38). The volumetric ratio of aqueous phase to oil phase is slightly greater than 1. This would correspond to a surfactant-enhanced solubilization system. At the right side of the diagram (NaCl concentration is greater than 2.0 wt%), the two phases are an excess water phase and an oil phase with water solubilized in reverse micelles (Winsor Type II system). In this case the volumetric ratio of water to oil is less than 1. In the middle of the diagram (NaCl concentration is in between 1.5 and 2.0 wt%), a three-phase system is observed (Winsor Type III system). Besides excess oil and water phases, a middle phase microemulsion exists containing both oil and water phases. At the middle of this three-phase system (1.7 wt% of NaCl), the middle phase contains equal volumes of oil and water. This system, known as the optimum salinity for this scan, has ultralow interfacial tension (IFT) and ultrahigh contaminant solubility (15).

The environmental application of microemulsion systems is a modification and extension of the concepts of the surfactant-based enhanced oil recovery (EOR). Select references discussing the use of microemulsions in the oil recovery include Bansal and Shah (4), Healy and Reed (14, 15), Healy et al. (16), Nelson and Pope (22), Shah (30), Nelson (21), and Schramm (29). Both processes utilize the ultralow IFTs associated with middle phase microemulsion systems to overcome the capillary forces and greatly increase the mobility of the crude oil or contaminants. However, the environmental remediation differs from EOR in several ways (25). EOR relationships need to be reevaluated before they can be directly applied to some DNAPL contaminant (34) and complex LNAPL contaminants (5). Environmental/human health considerations require low toxicity of surfactants and cosurfactants, which may restrict the direct use of EOR techniques in environmental applications.

Despite the advantages of ultralow IFTs and ultrahigh solubilities, microemulsion systems must be used with caution in subsurface formations. Middle phase microemulsions may be accompanied by high viscosities that could cause significant pressure drop and, subsequently, water table rise across a low permeable zone. Since the water–oil IFT continually decreases as a Winsor Type I system approaches the Type I–III boundary (see Fig. 1), it is not necessary to achieve a Winsor Type III middle phase microemulsion for NAPL mobilization to occur.

Factors in Microemulsion Formulation

Middle phase microemulsion formulation requires a delicate balance between surfactant type and concentration, cosurfactant, electrolyte, and oil. We will briefly discuss the impact of these variables on microemulsion formation; additional details can be found in Bourrel and Schechter (7).

Forming an optimum middle phase microemulsion requires balancing the surfactant system with the target oil. If the surfactant system is too hydrophilic a Winsor Type I system will occur, while hydrophobic surfactant systems favor formation of a Winsor Type II system. The surfactant hydrophilic–lypophilic balance (HLB) number can aid in designing surfactant systems for a given oil. Optimizing the surfactant system HLB for a target oil, which can be achieved by mixing surfactants with higher or lower HLB or by adding an electrolyte or alcohol, will produce middle phase microemulsions, unless it is precluded by mesophase formation (e.g., liquid crystal).

The solubilization capacity of a middle phase is defined by the solubilization parameters as (15):

$$SP_o = V_o/V_s \tag{1a}$$

and

$$SP_w = V_w/V_s \tag{1b}$$

where SP_o and SP_w are solubilization parameters for oil and water, respectively; V_o and V_w are volumes of oil and water solubilized in the surfactant solution, respectively; and V_s is the volume of surfactant contained in the solution, excluding the alcohol volume (if used).

A modified oil solubilization parameter was used in this study. The solubilization power is defined per surfactant unit mass rather than per unit volume, as follows:

$$SP_o = V_o/M_s \tag{2}$$

where M_s is total mass (moles) of surfactant(s) present. In this definition alcohol mass is also excluded in calculation of M_s. However, when other surfactants are used as cosurfactants, they are included in calculating the total M_s.

Three cosurfactant types were evaluated in this study: nonionic surfactants, medium-chained alcohols, and anionic hydrotropes. The degree to which cosurfactants alter system HLB depends on the type of cosurfactant used. Hydrophobic cosurfactants (e.g., medium-chained to long-chained alcohols) decrease the system HLB while hydrophilic cosurfactants (e.g., short-chained alcohols) increase the system HLB. In addition to altering the system HLB, cosurfactants (alcohols) can also prevent formation of mesophases (e.g., liquid crystals).

Hydrotropes have surfactant-like structures but do not form micelles. Recently, food-grade hydrotropes have been evaluated as environmentally acceptable alternatives to alcohols (32, 34). Designing a middle phase surfactant system requires knowledge of the contaminant HLB. The alkane carbon number (ACN, the number of carbons in an alkane chain) characterizes the hydrophobicity of alkane-type hydrocarbons, with higher ACN compounds being more hydrophobic. For a mixture of hydrocarbons or nonalkyl hydrocarbons, an equivalent alkane carbon number (EACN) is used. The EACN assigns a single "alkane analog" to represent the behavior of a mixed hydrocarbon system.

Empirical Relationship for Formulating Microemulsions

Currently, microemulsion formulation is largely a trial-and-error process. Empirical models can help to expedite this trial-and-error process. For systems containing hydrocarbon, anionic surfactant, alcohol, and salinity, the following relationship has proven valid (28):

$$\ln S^* = K{*}\text{ACN (or EACN)} + f(A) - \sigma \tag{3}$$

where S^* is optimum salinity, $f(A)$ is a value specific to the alcohol utilized, and K and σ are characteristic surfactant parameters (K equal to 0.1 for sulfated surfactants and 0.16 for sulfonated surfactants). This relationship has proven useful in formulating JP-4 microemulsions (5).

OBJECTIVES

This research focuses on formulating middle phase microemulsion systems for a weathered jet fuel from Hill AFB, Utah using environmentally friendly surfactants. Our objective was to demonstrate that we could formulate middle phase systems using a food-grade surfactant (AOT); that nonionic surfactants and hydrotropes can be used as cosurfactants to replace alcohol as an additive; that hardness can be used to replace salinity in formulating the microemulsions (as a means of reducing electrolyte addition); and that both optimum salinity and optimum hardness of petroleum hydrocarbon microemulsions can be reduced by cosurfactant type and concentration. We also expect that the existing relationships (e.g., Eq. 3) can be used as a guideline for formulating a middle phase microemulsion with the weathered jet fuel, and that formulating JP-4 microemulsions can help us understand and design microemulsion systems for weathered jet fuel contamination. Finally, this research seeks to identify one or more environmentally acceptable middle phase microemulsion system(s) for use in a subsequent field demonstration study.

MATERIALS AND METHODS

Chemicals

The hydrocarbons used in this study were commercial JP-4, which was purchased from a local airport, and the Hill LNAPL (a weathered JP-4 with other contaminants such as light lubricating oils, chlorinated VOCs, and PCBs), which was collected from a field demonstration site at Hill Air Force Base, Utah. All aqueous solutions were made with deionized water. Surfactants and the hydrotrope used in the research, along with their related properties, are listed in Table 1. Bis-2-ethylhexyl sodium sulfosuccinate (Aerosol OT or AOT, 100% solid) was purchased from Fisher Chemical, POE(20) sorbitan monostearate (T-MAZ 60) and POE(20) sorbitan monooleate (T-MAZ 80) (both 100%, liquid) were donated by PPG/Mazer Chemicals, sodium mono- and dimethyl naphthalene sulfonate (SMDNS, (100%, powder) was donated from Witco, and isobutanol (99.7%) was purchased from Fisher Chemical. All chemicals were used as received without any further purification.

Batch Studies

The visual pipette methodology, widely used in surfactant phase behavior studies (7), was utilized to evaluate microemulsion systems (31). In each pipette a 1:1 oil to water volumetric ratio was used with a total volume of oil and water equal to 10 mL. In this study, surfactant concentrations were kept at

TABLE 1
Summary of Surfactants and Hydrotrope Used in Studies: All Have Direct Food Additive Status

Chemical	Description	Molecular weight	CMC (mM)	HLB	Type
AOT	Bis-2-ethyl-hexyl sodium sulfosuccinates	445	1.1,[a] 2.5[b]	NA	Anionic surfactant
T-MAZ 60	POE(20) sorbitan monostearate	1310	0.023[a]	14.9[c]	Nonionic surfactant
T-MAZ 80	POE(20) sorbitan monooleate	1308	0.010[a]	15.0[c]	Nonionic surfactant
SMDNS	Sodium mono- and dimethyl naphthalene sulfonate	260	4.5[a]	NA[d]	Hydrotope

[a] From Shiau et al. (32).
[b] From Williams et al. (36).
[c] From McCutcheon's (19).
[d] NA, not available, but listed in order of its relative HLB as observed in this research.

50 mM (aqueous). Pipettes were flame sealed to prevent volatilization, were well shaken, and were stored in a refrigerator at 15°C (average groundwater temperature at the site). The optimum salinity was the concentration of NaCl at which equal volumes of water and oil were solubilized in the middle phase, as determined by visual observation. The visual pipette method has an accuracy of ±0.1 mL.

Determining EACNs for Unknown Oils

An unknown oil's EACN is determined by first titrating with oil and a surfactant system of known values for K, $f(A)$, and σ with NaCl, and then applying Eq. (3). However, without any prior knowledge of the EACN range for the unknown oil, a direct NaCl scan with the LNAPL is a very tedious, trial-and-error search. An alternative approach is to calculate the EACN for the unknown oil by evaluating the EACN value for a mixture of the unknown oil and a known EACN oil. Since the EACN for the mixed oil will be between that of the known EACN oil and of the unknown oil, the optimum NaCl concentration for the known EACN oil can be used as a starting salinity for the scan with the mixed oil. Based on EACN values for the known oil and the mixture, the EACN of the unknown oil can be determined using the mixing rule. Though still trial and error, this approach requires less effort than the direct scan with the unknown oil.

RESULTS AND DISCUSSION

EACN for Hill LNAPL

The method of scanning the mixed oils and inferring the EACN for the unknown oil from the EACN for the mixture, as discussed above, is used to estimate the EACN for the Hill LNAPL. JP-4 is chosen as the surrogate oil added into the Hill LNAPL based on the two considerations. We have characterized the JP-4 fuel for its EACN and molecular weight (39). In addition, JP-4 is similar to major components (i.e., aviation fuels) found in the Hill LNAPL, which makes it a logical starting point. Since the molecular weight for the Hill LNAPL is needed in order to apply the ideal mixing rules (see Eqs. 6 to 9 below), two independent salinity scans were conducted to balance the number of unknowns and the number of equations. In these two salinity scans the ratio of JP-4 to the Hill LNAPL were varied. Table 2 lists the compositions and the corresponding optimum NaCl concentrations for two JP-4/Hill LNAPL systems studied. From the salinity scans for the two systems the following six equations were constructed:

$$\ln S^*(a) = K{*}\mathrm{EACN}(\mathrm{mix.},a) + f(A) - \sigma \tag{4}$$

$$\ln S^*(b) = K{*}\mathrm{EACN}(\mathrm{mix.},b) + f(A) - \sigma \tag{5}$$

TABLE 2
Summary of Microemulsion Systems Used to Determine EACN to Hill LNAPL at 15°C

System	Surfactant	Cosurfactant	Oil	V_o:V_w	Optimum salinity[b]
a	50 mM AOT[a] (1.2 wt%[b])	0.4 g isobutanol/5 mL[a] (4.3 wt%[b])	2.18 g Hill LNAPL, 1.89 g JP-4	1:1	0.60 wt% of NaCl
b	50 mM AOT[a] (1.2 wt%[b])	0.4 g isobutanol/5 mL[a] (4.3 wt%[b])	3.16 g Hill LNAPL, 1.01 g JP-4	1:1	0.78 wt% of NaCl

[a] Based on aqueous solution.
[b] Based on total system.

$$\mathrm{EACN}(\mathrm{mix.},a) = \mathrm{EACN}(\mathrm{JP\text{-}4})*x(a) + \mathrm{EACN}(\mathrm{Hill})*[1 - x(a)] \quad (6)$$

$$\mathrm{EACN}(\mathrm{mix.},b) = \mathrm{EACN}(\mathrm{JP\text{-}4})*x(b) + \mathrm{EACN}(\mathrm{Hill})*[1 - x(b)] \quad (7)$$

$$x(a) = \mathrm{W}(\mathrm{JP\text{-}4},a)/\mathrm{mw}(\mathrm{JP\text{-}4})/[\mathrm{W}(\mathrm{JP\text{-}4},a)/\mathrm{mw}(\mathrm{JP\text{-}4}) + \mathrm{W}(\mathrm{Hill},a)/\mathrm{mw}(\mathrm{Hill})] \quad (8)$$

$$x(b) = \mathrm{W}(\mathrm{JP\text{-}4},b)/\mathrm{mw}(\mathrm{JP\text{-}4})/[\mathrm{W}(\mathrm{JP\text{-}4},b)/\mathrm{mw}(\mathrm{JP\text{-}4}) + \mathrm{W}(\mathrm{Hill},b)/\mathrm{mw}(\mathrm{Hill})] \quad (9)$$

where $S^*(a)$ and $S^*(b)$ are the experimental optimum salinities in systems *a* and *b*, respectively (where *a* and *b* refer to the two mixed NAPL systems—see Table 2). Based on previous studies (5, 39), the K value is 0.16 for AOT; EACN(mix.,*a*) and EACN(mix.,*b*) are EACNs of mixed solvents in systems *a* and *b*, respectively; the $f(A)$ value of isobutanol is −0.87; the σ value of AOT is 2.21; the EACN(JP-4) is 12.1; $x(a)$ and $x(b)$ are the mole fractions of JP-4 in the oil mixtures in systems *a* and *b*, respectively; EACN(Hill) is the EACN of Hill LNAPL; mw(JP-4) is the molecular weight of JP-4 which is 232.2 g/mol (39); mw(Hill) is the molecular weight of Hill LNAPL; W(JP-4,*a*) and W(JP-4,*b*) are masses of JP-4 in systems *a* and *b*, respectively; and W(Hill,*a*) and W(Hill,*b*) are the mass of Hill LNAPL in systems *a* and *b*, respectively.

Equations (4) and (5) are direct applications of the Salager relationship (Eq. 3) with the salinity scan results of the mixed oil systems. Equations (6) and (7) use the ideal mixing rules to estimate the EACN values of mixed oil systems. Equations (8) and (9) calculate the molar fractions of the Hill LNAPL in the mixtures.

These six equations were solved using EUREKA software. The resulting EACN of Hill LNAPL was determined to be 19.5, while the molecular weight of Hill LNAPL was determined to be 232 g/mol. It is obvious that the Hill LNAPL is more hydrophobic than JP-4 (EACN values of 19.5 and 12.1, respectively), likely the result of the weathering process (loss of low-end components) and the other contaminants present in the NAPL.

Salinity Studies with Hill LNAPL

Substituting the Hill LNAPL EACN value into Eq (3) along with other pertinent values, the optimum salinity for the 1.2 wt% AOT and 4.3 wt% isobutanol (system *e* in Table 3) is estimated to be 1.0 wt%; this compares very well with the measured optimum salinity of 0.98 wt%. The JP-4 and Hill LNAPL microemulsions obviously differ, as evidenced by the variation in their optimum salinities (0.35 and 0.98 wt% respectively—system *c* versus *e* in Table 3). The oil is the only variable between these two microemulsion systems (JP-4 versus Hill LNAPL, respectively).

Isobutanol's toxicity and flammable nature caused us to evaluate food-grade cosurfactants as alcohol substitutes. Likewise, environmental concerns of high NaCl concentrations caused us to evaluate calcium as the electrolyte. The hydrotrope SMDNS was evaluated based on its successful use in formulating chlorinated solvent microemulsions without alcohol or salinity addition (32, 34). However, forming JP-4 middle phase microemulsions with SMDNS required use of a salinity scan (see system *d* in Table 3). Scanning with SMDNS promoted the type I–III–II phase transition. If SMDNS was treated as an alcohol cosurfactant, the SMDNS $f(A)$ value was found to be -0.78 (from Eqs. 4 and 5). The negative $f(A)$ value for SMDNS confirmed our prediction that SMDNS would promote type I–III–II phase transition. Starting from the optimum microemulsion, we gradually decreased salinity while holding the concentration of AOT constant. To maintain the middle phase microemulsion, we compensated for the reduction in salinity by increasing the concentration of SMDNS. This middle phase microemulsion existed for salinity values as low as 0.1 wt%. Below this salinity, macroemulsions were encountered which took an extremely long time to equilibrate.

The optimum salinity for the AOT/SMDNS/Hill LNAPL system was predicted from Eq. (3) to be 1.0 wt% NaCl. The salinity scan showed no clear middle phase microemulsion over a wide salinity range (Fig. 2). At salinity values below 0.4 wt%, macrophases occurred which took months to equilibrate. At a salinity value of 0.8 wt%, the system was in Winsor Type I phase with about 0.1% of original Hill LNAPL solubilized in the aqueous micellar solution. At a much higher salinity (greater than 2.5 wt%) the system was in Winsor Type II phase with about 6% of the original aqueous solution solubilized in the oleic phase. Intermediate salinities (0.8 to 2.5 wt%), where a middle phase microemulsion was anticipated, did not produce a classic middle phase system. HPLC analysis showed that this intermediate phase (Phase I in Fig. 2) was much more concentrated in AOT and dilute in SMDNS than the original aqueous solution. Furthermore, GC analysis showed that the

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TABLE 3

Comparison of Different Microemulsion Systems at 15°C

System	Surfactant[x]	Cosurfactant	Oil, V_o/V_w	Optimum salinity or hardness[x]	Width of three-phase region	SP_0 at optimal state (mL/mol)
c	1.2 wt% (50 mM[w]) AOT	4.3 wt% isobutanol	JP-4, 1:1	0.35 wt% of NaCl	~0.2 wt% of NaCl	2000 ± 400
d	1.2 wt% (50 mM[w]) AOT	1.1 wt% SMDNS	JP-4, 1:1	0.35 wt% of NaCl	~0.7 wt% of NaCl	4000[y] ± 400 1600[z] ± 160
e	1.2 wt% (50 mM[w]) AOT	4.3 wt% isobutanol	Hill LNAPL, 1:1	0.98 wt% of NaCl	>1.7 wt% of NaCl	1200 ± 400
f	1.2 wt% (50 mM[w]) AOT	1.1 wt% (15 mM[w]) T-MAZ 60	Hill LNAPL, 1:1	1.7 wt% of NaCl	~0.5 wt% of NaCl	3700 ± 310
g	1.2 wt% (50 mM[w]) AOT	1.1 wt% (15 mM[w]) T-MAZ 80	Hill LNAPL, 1:1	1.8 wt% of NaCl	~0.7 wt% of NaCl	3400 ± 310
h	1.2 wt% (50 mM[w]) AOT	1.1 wt% (15 mM[w]) T-MAZ 60	Hill LNAPL, 1:1	0.30 wt% of $CaCl_2$	~0.4 wt% of $CaCl_2$	4900 ± 310
i	1.2 wt% (50 mM[w]) AOT	1.1 wt% (15 mM[w]) T-MAZ 80	Hill LNAPL, 1:1	0.23 wt% of $CaCl_2$	~0.15 wt% of $CaCl_2$	3700 ± 310

[w] Based on aqueous solution.

[x] Based on total system.

[y] Excluding SMDNS.

[z] Including SMDNS.

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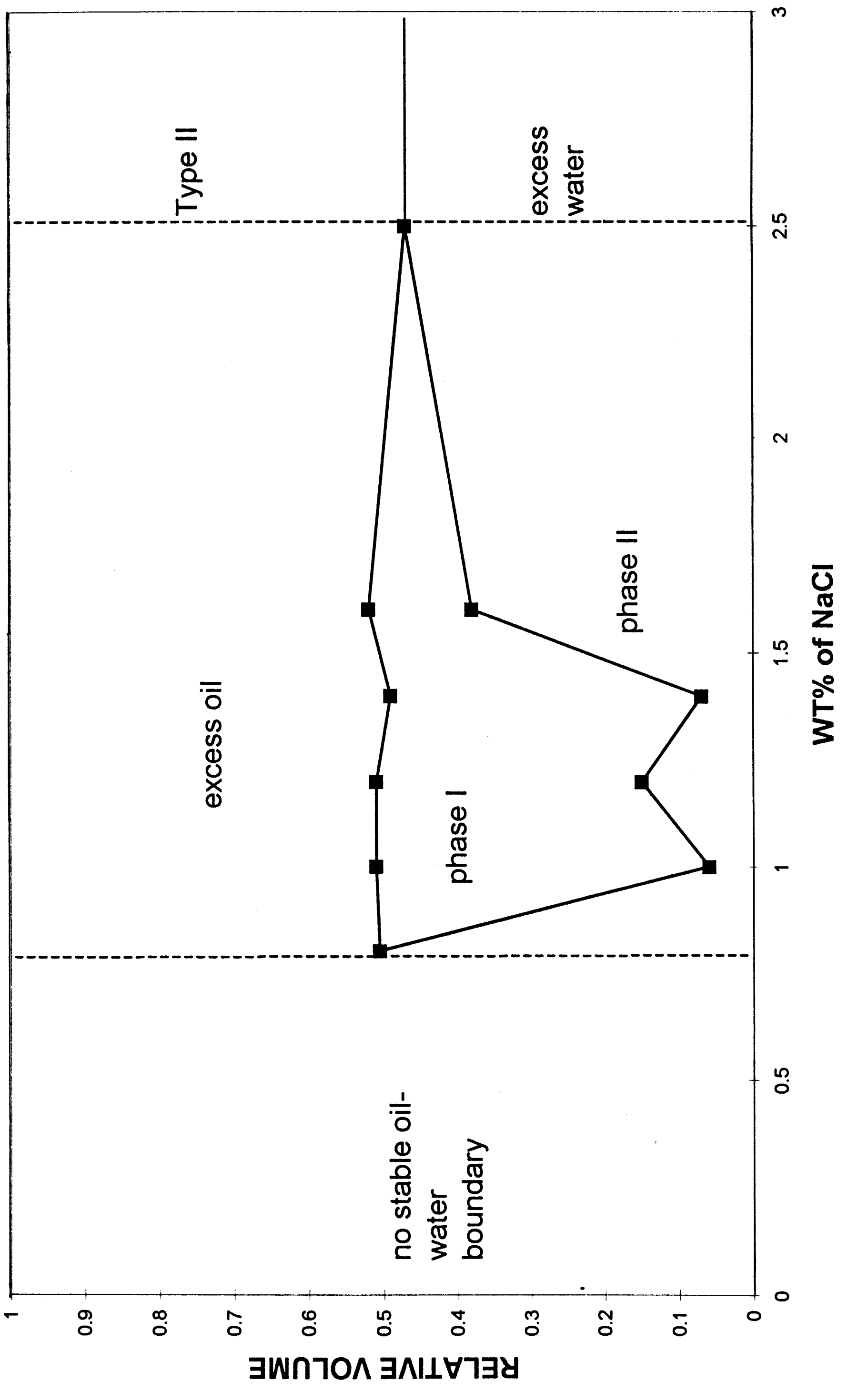

FIG. 2 Phase diagram of salinity scan on AOT/SMDNS/Hill LNAPL system at 15°C. AOT concentration is 50 mM (aqueous), SMDNS concentration is 1.1 wt% based on total system, and volumetric ratio of oil to water is 5 mL each.

level of LNAPL solubilized into this phase is comparable to that expected for the solubilization mechanism rather than the high quantity expected for the microemulsion mechanism. In contrast, the phase in the bottom of the pipette (Phase II in Fig. 2) was a brownish solution, which was concentrated in SMDNS. It is not clear what these phases were, why they occurred, or how to avoid them—answering these questions was beyond the scope of this research.

Two nonionic food-grade surfactants (T-MAZ 60 and T-MAZ 80) were further evaluated as cosurfactants in place of SMDNS. Figure 1 shows a salinity scan on AOT/T-MAZ 60/Hill LNAPL (system *f* in Table 3). The optimum salinity for this system was about 1.7 wt% (Table 3). The optimum salinity for AOT/T-MAZ 80/Hill LNAPL was about 1.8 wt% (Fig. 3 and system *g* in Table 3). Further comparison of these two systems is provided below.

Hardness Studies with Hill LNAPL

In an attempt to decrease the amount of electrolyte added, calcium (hardness) was tried in place of sodium. The hydrotrope SMDNS and the nonionic surfactants T-MAZ 60 and T-MAZ 80 were selected as cosurfactants for the hardness study. Hardness scans on AOT/SMDNS/JP-4 and AOT/SMDNS/Hill LNAPL failed to produce a middle phase microemulsion. When the $CaCl_2$ concentration was low, macroemulsions in both systems were observed. When the $CaCl_2$ concentration was increased, precipitation of SMDNS occurred. However, we did successfully formulate Hill LNAPL microemulsions using T-MAZ 60 and T-MAZ 80 as cosurfactants. Figures 4 and 5 show hardness scans analogous to salinity scans displayed in Figs. 1 and 3, respectively. Once again, similarities in the two hardness scans are observed (see system *h* and *i* in Table 3).

DISCUSSION

Based on its relatively high hydrophobicity, AOT is chosen as the surfactant to microemulsify petroleum hydrocarbons, especially for the hydrophobic Hill LNAPL. Also the branched structure of AOT can help prevent formation of liquid crystal phases (9, 11, 31). The four cosurfactants we evaluated all promoted the Winsor Type I–III–II phase transition. We estimated optimum salinities for JP-4 and Hill LNAPL with AOT alone (no cosurfactant) using Eq. (3); the resulting values are 0.76 wt% of NaCl and 2.6 wt% of NaCl, respectively. With cosurfactants, the actual optimum salinity for JP-4 and Hill LNAPL are lower (see Table 3). One advantage of cosurfactant use is that they can prevent formation of the liquid crystal phases found previously for chlorinated solvents (31).

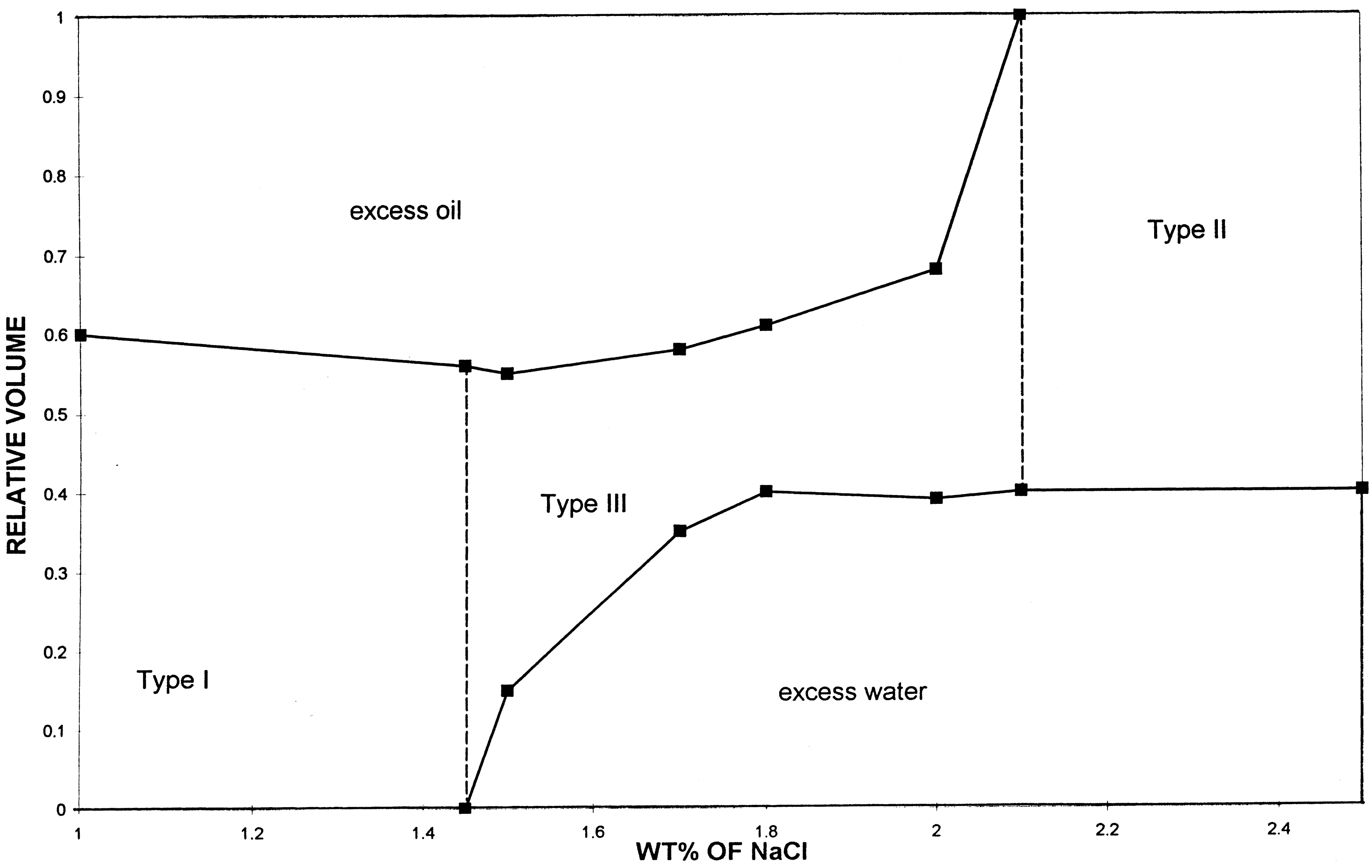

FIG. 3 Phase diagram of salinity scan on AOT/T-MAZ 80/Hill LNAPL system at 15°C. AOT concentration is 50 mM (aqueous), T-MAZ 80 concentration is 15 mM (aqueous), and volumetric ratio of oil to water is 5 mL each.

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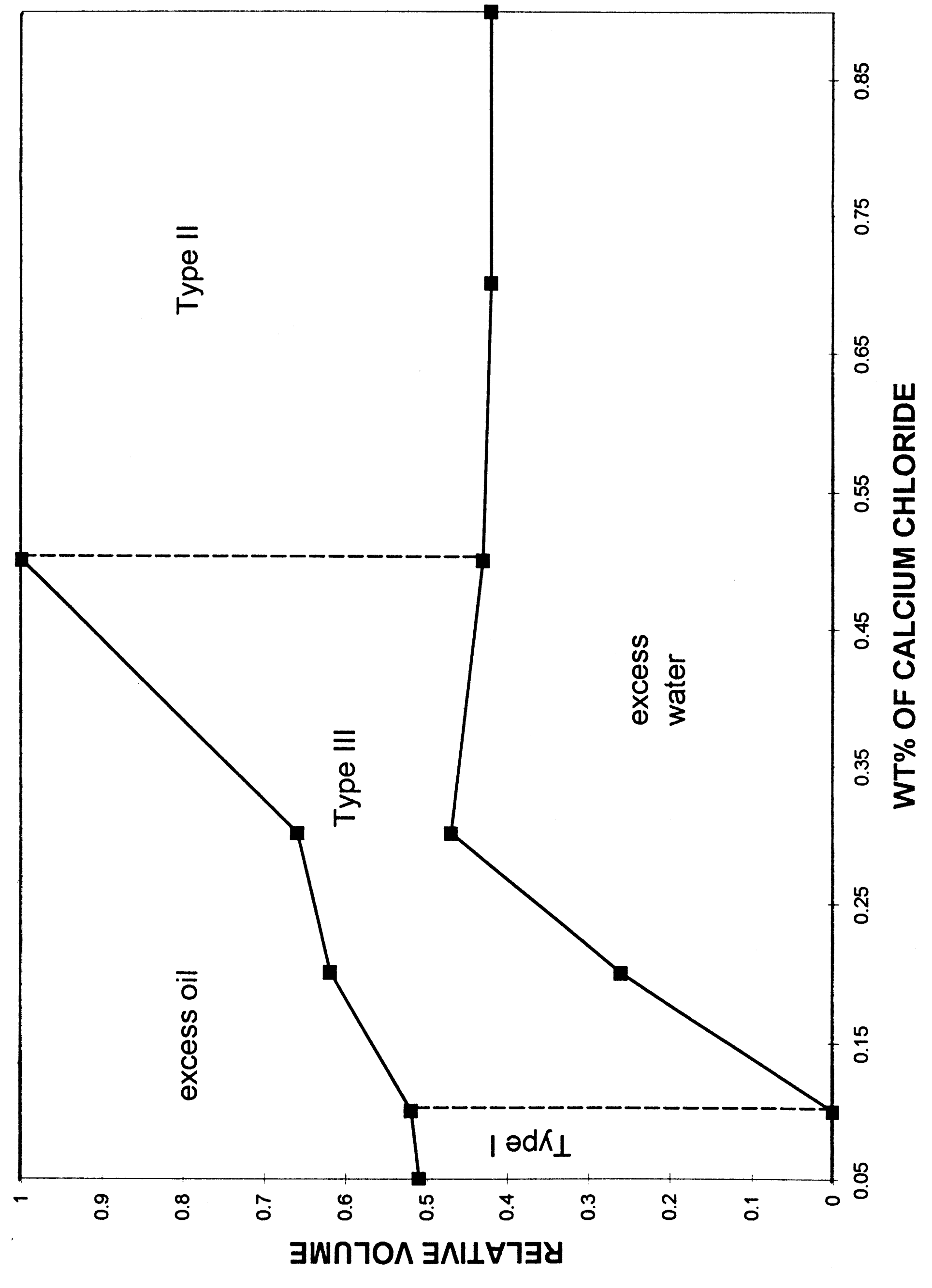

FIG. 4 Phase diagram of hardness scan on AOT/T-MAZ 60/Hill LNAPL system at 15°C. AOT concentration is 50 mM (aqueous), T-MAZ 60 concentration is 15 mM (aqueous), and volumetric ratio of oil to water is 5 mL each.

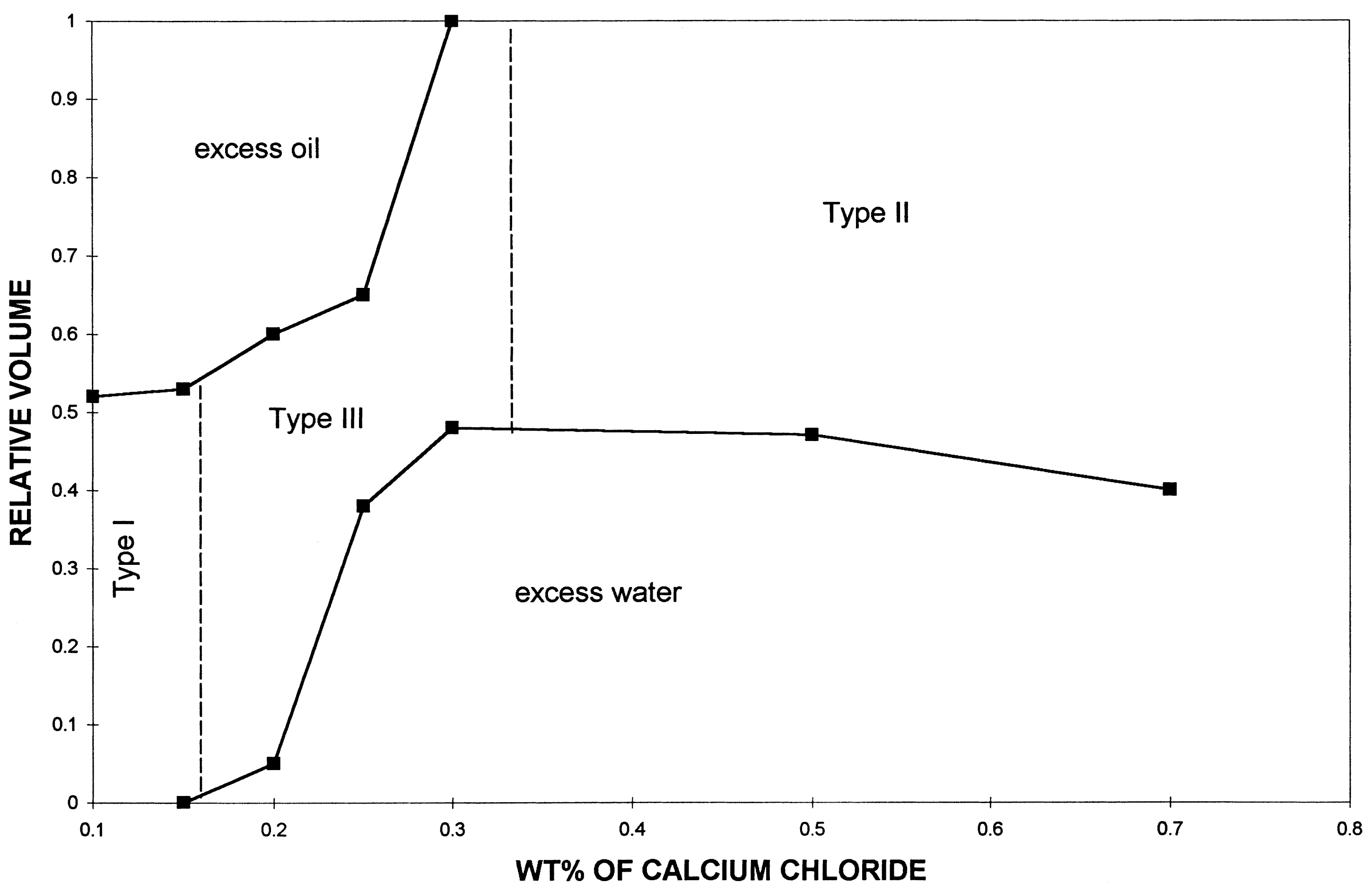

FIG. 5 Phase diagram of hardness scan on AOT/T-MAZ 80/Hill LNAPL system at 15°C. AOT concentration is 50 mM (aqueous), T-MAZ 80 concentration is 15 mM (aqueous), and volumetric ratio of oil to water is 5 mL each.

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Qualitatively, the four cosurfactants have similar effects on the phase behavior of JP-4 and Hill LNAPL microemulsions (see Table 3). Isobutanol and SMDNS both have optimum salinities of 0.35 wt% for JP-4 (systems *c* and *d*, respectively in Table 3). Thus, if we assign hydrotropes a $f(A)$ value, as with alcohols, the $f(A)$ value for 0.1 g of SMDNS would be the same as that for 0.4 g of isobutanol in the same system. However, the three phase region is wider when conducting a salinity scan with SMDNS versus isobutanol (0.7 versus 0.2 wt% NaCl, respectively—Table 3). The solubilization capacity of the two systems for JP-4 is also interesting. If SMDNS is excluded from the denominator in Eq. (2), then the SMDNS system has an SP_o value twice as large as the system using isobutanol (4000 and 2000 mL/mol, Table 3, systems *c* and *d*). However, if SMDNS is included, the SP_o of the system becomes a little smaller than the isobutanol system. The $\mathrm{SP_o}$ of the isobutanol system was probably overestimated since isobutanol could also contribute to JP-4 solubilization. Therefore, the difference between the SP_o of the isobutanol and SMDNS systems could be even closer if SMDNS is treated as a surfactant. Although SMDNS is generally regarded as a hydrotrope, it was observed to have a CMC-like break point in surface tension measurements (4.5 mM at 25°C, Ref. 34). Since its "CMC" is higher than AOT's, SMDNS is expected to have less solubilization capacity than AOT. Therefore, AOT-based microemulsion systems are expected to have a lower SP_o value when using SMDNS as the cosurfactant rather than isobutanol.

The two nonionic surfactants used have similar chain length, molecular weight, HLB and CMC; the oleate has a double bond which is absent in the stearate (see Table 1). The optimum salinity (or hardness) width of the three-phase region and SP_o are also observed to be similar (Table 3, systems *f g*, and *h* versus *i*, respectively). The isobutanol microemulsion system had a lower optimum salinity and much wider salinity window than when using nonionic surfactants as the cosurfactant (compare system *e* with systems *f* and *g* in Table 3). On the other hand, nonionic surfactant systems dissolved much more Hill LNAPL per mass of surfactant (higher $\mathrm{SP_o}$—Table 3). The enhanced solubilization power can be explained by the lower CMC of nonionic surfactants (T-MAZ 60 and T-MAZ 80).

When NaCl was replaced by $CaCl_2$, much less electrolyte was needed to achieve optimum middle phase microemulsions; at the same time, the width of three-phase region was narrowed (systems *f* versus *h* and *g* versus *i*—Table 3). The change in SP_o was less significant. The SP_os using T-MAZ 60 and T-MAZ 80 increased when salinity was replaced by hardness (25% for the system having T-MAZ 60, 20% for the system having T-MAZ 80).

The estimated EACN of Hill LNAPL (19.5) is higher than we expected relative to the EACN of JP-4 (39). One explanation for the higher EACN of Hill LNAPL is the loss of light, volatile components as a result of NAPL weathering. In addition, the presence of heavy oils (e.g., lubricants) can also raise the EACN of Hill LNAPL. Oils with higher EACN will evidence higher optimum salinity, as seen in the salinity jump from 0.35 wt% for the AOT/isobutanol/JP-4 system to 0.98 wt% for the AOT/isobutanol/Hill LNAPL system (Table 3, systems *c* and *e*, respectively). The salinity width of the three phase region increased, from 0.2 wt% for the AOT/isobutanol/JP-4 system to > 1.7 wt% for the AOT/isobutanol/Hill LNAPL system.

CONCLUSIONS

Five systems were successfully formulated for microemulsifying the Hill LNAPL and they are reported here. After evaluating these successful systems along with other failed attempts, we reached the following conclusions:

1. Starting with a NAPL having a known surfactant microemulsion system, and studying the mixed behavior of the characterized system with a new, unknown NAPL (Hill LNAPL), made it easier to design the surfactant microemulsion system for the unknown (Hill) LNAPL.
2. The empirical relationships developed from EOR were generally applicable in our JP-4 and Hill LNAPL microemulsion studies. At the same time, the reliability of the relationships depends on the specific oil, and is at best a guide for designing laboratory studies.
3. The food-grade hydrotrope SMDNS performed well as a cosurfactant in low salinity systems, but tended to separate from solutions in high salinity and hardness systems.
4. Nonionic surfactants T-MAZ 60 and T-MAZ 80 were successfully used as cosurfactants even at higher salinity and hardness. Mixed with the anionic surfactant AOT, nonionic surfactants also enhanced solubilization capacity of the middle phase microemulsions and improved electrolyte tolerance of the anionic surfactant.
5. While microemulsions resulting from hardness scans required less electrolyte addition, and achieved high solubilization potentials, the hardness window for the three-phase microemulsion was narrower than the corresponding salinity window. In addition, it should be cautioned that excess hardness and salinity can cause adverse surfactant/cosurfactant phase behaviors.

This work is mainly empirical due to the fact that the key relationship used in the study, the Salager equation, is empirical, even though the relationship has been proven valid in countless middle phase microemulsion systems (5, 7). The number of scans presented in this paper does not represent the total number of systems tested. Based on previous experience with JP-4 (39), we have evaluated about 15 systems for their ability to produce middle phase microemulsions with the Hill LNAPL. The high hydrophobicity of the Hill LNAPL and environmental considerations restrict the choice of surfactants and cosurfactants for this study.

Future research should further develop our understanding and thus improve our ability to predict formation of middle phase microemulsion systems. Important properties to know include interfacial tensions, adsorption and precipitation of surfactants and cosurfactants in porous media, the influences of temperature variation on phase behavior and system viscosity, etc. In addition, the performance of these microemulsion systems in column studies is also necessary for scale-up purposes.

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