PHYSICO-CHEMICAL PROPERTIES OF SURFACTANT-WATER-OIL 
MIXTURES: PHASE BEHAVIOR, MICROEMULSION 
FORMATION AND INTERFACIAL TENSION

by

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Chapter I

ENHANCED OIL RECOVERY

I.1. INTRODUCTION

The 1973 Arab oil embargo dramatically called the public's attention to the seriousness and urgency of the energy problem. Oil had been, for several decades, the cheapest energy source and the warnings of farsighted individuals were not sufficient to force the industrial world into considering a long lasting energy policy. The oil embargo did it.

Since then governments, industrials and consumers all around the world, particularly in developed western countries, have realized the need for an overall and long-term energy policy. However the problem is extremely complex, even when limited to those of a single nation. The long-term goal is to develop technology to economically utilize solar energy and nuclear fusion as well as some other secondary resources (Considine: 1977; Halacy: 1977). However, this seems to belong to a distant future.

Because of the decreased availability of cheap oil, other fossil fuels are becoming economically attractive again; it is probable that coal, lignite, tar sands, oil shales and the like are going to be exploited more and more during the next decades. But tapping these reserves will require the mastering of new processes such as in-situ combustion which may take quite a while.
It must also be considered that some of these processes might not be economically feasible at the current energy price. Thus it seems that the short-term alternative is still oil. Actually the known reserves of oil are quite large (Considine: 1977) but these are not economically recoverable with the current technology at the pre-crisis prices.

I.2. OIL RECOVERY TECHNIQUES

In the primary stage of recovery, oil is driven to the production well either by expanding gas, by a subjacent invading aquifer or by gravity forces. In all cases the natural forces decrease when the production proceeds and ultimately become insufficient to drive the oil to the well.

Energy must be introduced in the reservoir to allow further recovery by so-called secondary techniques; these basically consist of injecting a fluid to stimulate production. Separate wells are usually used for injection and production. The most commonly used technique, waterflooding, drags out oil mobilized by viscous forces. In certain cases where gravity drainage is effective the maintenance of the reservoir pressure by gas injection may be sufficient to in-sure additional recovery. Ultimately secondary recovery techniques reach a state where the oil production is too low to maintain profitability. At this stage the abandoned reservoir may still contain 40 to 80 percent of the oil originally in place.
The American Petroleum Institute (API: 1976) reported that the discovered crude oil in the US amounts to 420 billions barrels, of which 110 billions have been recovered. The estimated recovery by existing economical and technical conditions is about 30 billions barrels, thus leaving about 300 billions barrels in known reservoirs. The same kind of arithmetic applies to other producing countries (Considine: 1977). While a 30% recovery efficiency may appear to be very poor, its value is actually decreasing continuously (Doscher and Wise: 1976); this trend is not due to poor engineering nor mediocre management, but rather to the fact that the "easy" oil has been produced first.

This huge amount of known non-recovered oil may insure several decades of supply (Wade and Schechter: 1977; Geffen: 1973, 1975) and thus stimulate a large technological effort to develop improved oil recovery methods.

1.3. ENHANCED OIL RECOVERY

The proposed methods aimed at producing a sizeable amount of currently non-recoverable oil are grouped under the generic name of Enhanced Oil Recovery (EOR). The expression Tertiary Oil Recovery is also used, but it should strictly apply only to those cases of oil fields already treated by a secondary recovery method.

Proposed EOR techniques are numerous and depend heavily upon economical factors and reservoir characteristics (Haynes: 1976; PPC: 1976).
Three general categories of EOR methods have shown significant promise: (1) Thermal recovery, (2) chemical flooding, and (3) carbon dioxide miscible flooding.

Thermal recovery methods are the most advanced in terms of field experimentation; they basically consist of adding heat to a reservoir to reduce oil viscosity and eventually vaporize it. The various methods include stream drive, cyclic steam stimulation, in-situ combustion and different combinations of them (Weinaug et al: 1965, 1972; Haynes: 1976; PPC: 1976).

Chemical flooding methods are the most complex because of the myriad of parameters to be controlled. Some field tests have shown that they may be promising, but many failures have induced researchers to go back to their laboratories to improve their understanding of the involved phenomena and to find more flexible formulations. A review of the proposed chemical flooding methods will be considered later (see Chapter III).

Carbon dioxide miscible flooding is capable of overcoming the capillary forces which trap the oil in the porous matrix: Its miscible feature permits the recovery of most of the contacted oil which is driven to the well together with the displacing fluid. Miscibility is obtained through the formation of a CO₂ vaporized hydrocarbons mixture slug which is miscible with both oil and carbon dioxide. Field tests tend to show that the method, although technically successful in certain cases, may be limited by economical considerations.
The relative future importance of each of these EOR methods is a subject to controversy among forecasters (Geffen: 1973, 1975; Snyder: 1974; Haynes: 1976; Elkins: 1971; Arnold: 1972). However the different studies agree that an additional recovery of 60 billions barrels may be a reasonable estimate of the potential of EOR techniques, and even more if the chemical flooding technology fulfils its promises.
Chapter II
CAPILLARY AND VISCOSOUS FORCES IN POROUS MEDIA
AND PROPOSED MOBILIZATION MECHANISMS

II.1. CAPILLARY FORCES IN POROUS MEDIA

With the exception of thermal processes which are primarily designed to decrease the oil viscosity, most of the EOR methods are aimed at eliminating (miscible processes) or drastically reducing (immiscible processes) the capillary forces.

After waterflooding the residual oil, typically 30% of the void space, is trapped in the porous rock matrix as a myriad of small disconnected ganglia. The rest of the rock pores is filled with brine containing several inorganic salts in variable amounts. In some cases a third fluid is present and additional complexities may arise (Pujado and Scriven: 1972). For the sake of simplicity the basic capillary phenomena will be considered for a two-liquid system: oil-water.

The geometry of the oil-water interface is determined by the Laplace equation:

\[ \Delta P = \gamma \Gamma \]

where \( \Delta P \) is the pressure difference across the interface, \( \gamma \) the interfacial tension and \( \Gamma \) the mean curvature. Due to the irregular and complex pattern of the pore network,
the Laplace equation cannot be solved exactly in most cases. However some average behavior may be considered (Melrose and Brandner: 1974). In order to illustrate the concept of competition between capillary and viscous forces, let us consider the case of an oil ganglion trapped in one of the branches of the parallel connected pore network of Figure II.1.

The flow of water in the lower branch provides an external pressure difference $P_0 - P_1$, which corresponds to the viscous force tending to mobilize the oil globule. However the globule's two interfaces may assume shapes such that the pressure needed to mobilize the oil $\Delta P_0 - \Delta P_1$ exceeds the viscous pressure drop by several orders of magnitude. Since there is no possibility of acting on the curvature term which basically depends upon the pore size and contact angle, all emphasis has been placed on reducing the interfacial tension in order to reduce the capillary forces.

If the interface can be eliminated, the process is called miscible. However cost considerations rule out most miscible processes for field application.

It has been found that under carefully controlled conditions, dilute solutions of surface active chemical can produce extremely low interfacial tensions in the $10^{-3} - 10^{-4}$ dyne/cm range, i.e. about four orders of magnitude lower than with water (Cayias: 1975; Cash et al: 1976a).
Figure II.1. Oil ganglion trapped by capillary forces.
II.2. CAPILLARY NUMBER AND APPLICATIONS

Attempts to correlate the recovery efficiency with the interfacial tension have led to the introduction of the Capillary Number $N_{Ca}$ which represents the dimensionless ratio of the viscous forces to the capillary forces (Catchpole and Fulford: 1966). The capillary number is defined by:

$$N_{Ca} = \frac{\mu_W u_W}{\epsilon \gamma}$$

where $\mu_W$ is the viscosity of the aqueous solution, $u_W$ the superficial velocity or flow rate per cross-sectional area, $\gamma$ the interfacial tension and $\epsilon$ the porosity. This concept has been reported under several equivalent forms and its numerical value correlated with the actual recovery efficiency (Moore and Slobod: 1956; Taber: 1969; Lefebvre du Prey: 1973; Foster: 1973; Reed and Healy: 1976; Thomas, Winter and Fleming: 1977). The critical value of the capillary number at which oil recovery becomes significant has been found to be in the $10^{-5}$ - $10^{-4}$ range. However at least a tenfold increase is needed to obtain a 80% recovery in core tests; a still higher value is probably required for field tests because of accumulated practical difficulties (see Section III.3.).

Since the capillary number value is typically $10^{-6}$ for ordinary waterflooding, an increase of at least three orders of magnitude is required to obtain substantially improved oil recovery. It is not practical to significantly increase the superficial velocity because of limitations on the injection pressure.
For the same reason the viscosity of the aqueous phase cannot be increased substantially because an increase in viscosity will also produce a corresponding increase in pressure drop according to Darcy's law. Viscosity increasing additives such as polymer allow a gain about one order of magnitude in the capillary number value and also provide a good mobility control (Gogarty: 1967, 1968, 1970; Hirasaki: 1974, 1975) but cannot alone produce the required change.

Thus most of the research work has been focused on reducing the interfacial tension by several orders of magnitude. Early works (Reisberg and Doscher: 1956; Jennings: 1957) reported the occurrence of low interfacial tension between NaOH solutions and crude oil, probably due to the in-situ formation of surface active chemicals.

In the last decade several authors have reported that the occurrence of ultra low interfacial tension (below $10^{-3}$ dyne/cm) is conditioned to a very close formulation of the system. However such low tensions cannot be accurately measured by the pendant drop and related techniques, and systematic studies were only started after the development of the spinning drop tensiometer (Cayias: 1975; Cayias, Schechter and Wade: 1975; Princen, Zia and Mason: 1967).

**II.3. PROPOSED MOBILIZATION MECHANISMS**

Most of the more than 100 papers recently published reporting chemical flooding core tests (see a survey in Reed and Healy: 1976; Meister et al: 1976) agree that a low interfacial tension, typically $10^{-3}$ dyne/cm, is necessary to insure a successful displacement.
However the large scattering in the reported data dealing with the correlation NCa-Recovery suggest that an ultra low tension might not be the unique criterion. It should be also pointed out that a low tension may be transient, and that the bulk of the reported data deal only with interfacial tension between effluent fluids at equilibrium, which might be misleading with regard to the actual displacement mechanism. The actual shape of the pore and the contact angle or wettability of the rock might be quite important as shown recently by analyzing mobilization mechanism on simplified models (Oh and Slattery: 1976).

II.3.1. Low interfacial tension

The low tension mobilization mechanism rests on the concept that if the interfacial tension is sufficiently low, then the viscous forces are larger than the capillary forces and thus the oil ganglion can be dragged out (Foster: 1973; Whiteley and Ware: 1976; Widmyer et al: 1976). Conditions for mobilization are reported to be sufficient for displacement (Reed and Healy: 1976). Eventually the tension might reach a zero value i.e., the two liquids become miscible (Davis: 1968; Gogarty: 1968); however this regime cannot be maintained during the flooding because of physical degradation of the surfactant slug front by diffusion, dispersion and adsorption.

II.3.2. Spontaneous emulsification

The so-called spontaneous emulsification has been proposed as a mobilization mechanism able to displace oil from a porous rock (Jones: 1975; Cayias et al: 1975).
This phenomenon has been reported a long time ago for both low and high tension interfaces (Von Stackelberg: 1949; Bowcott: 1955, Davies: 1957; Ilkovic: 1932). Some authors have discussed the idea that interfacial tension may become negative (Schulman and Montagne: 1961; Davies and Rideal: 1963; Shah et al: 1972). However this concept seems to be an over-simplification (Miller and Scriven: 1970) in particular with systems exhibiting a large interfacial tension at equilibrium.

The currently accepted mechanism is the so-called "Diffusion and Stranding" (Ruschack and Miller: 1972) which is a non equilibrium model. When diffusion of the surfactant takes place (England and Berg: 1971), there may be some local composition corresponding to a point in the two-phase region, thus a local coacervation. The formation of a spontaneous emulsion depends upon the relative position of the diffusion path and the two-phase region. Further studies on spontaneous emulsification in systems used in chemical flooding have been reported recently (Arnold: 1977). Spontaneous emulsification may also be related to spinodal decomposition (Cahn: 1961, 1962, 1965).

**II.3.3. Phase swelling**

At high salinities surfactant and water may be transferred to the oil phase to produce a so-called swollen oil i.e., an oil phase containing a large percentage of water. Several authors Gatlin: 1960; Larson and Hirasaki: 1976; Pope and Nelson: 1977a; Nelson and Pope: 1977) have proposed a mechanism in which the swollen oil phase, which may contain more water than oil, is easily displaced because of its increased volume and properties changes. (See also Larson: 1977).
Chapter III
CHEMICAL FLOODING

III.1. DIFFERENT TYPES OF CHEMICAL FLOODING

A large number of aqueous surfactant flooding processes have been mentioned in both the technical and patent literature. Although one of the caustic processes was patented as early as 1927 (Snyder: 1974), these processes are generally recent. The current literature shows some variations as may be seen in the following list of encountered terms: Microemulsion processes (Bae et al: 1974; Cooke: 1968; Froning et al: 1973), micellar solutions (Davis and Jones: 1968), surfactant waterflood (Farmer et al: 1972), low tension waterflood (Foster: 1973), surfactant flooding (Gale and Rorie: 1972), miscible-type waterflooding with micellar solutions (Gogarty and Tosch: 1968), microemulsion flooding (Healy and Reed: 1974, 1975), emulsion modifier containing dilute aqueous system (Hill et al: 1973), immiscible microemulsion flooding (Healy and Reed: 1976), aqueous surfactant flooding (Hill, Reisberg and Stegemeier: 1973), immisible displacement (Morrow: 1970), oil-in-water emulsions (McAuliffe: 1973a, 1973b), miscible displacement (Nunge and Gill: 1969), micellar flooding (Trushenski, Dauber and Parrish: 1974). This list is not exhaustive and contains only the terms appearing in the title of some articles and patents. More labels are reported elsewhere (Reed and Healy: 1976; Meister et al: 1976).
However this large variety exists basically at a semantic level with only the following significant difference between various processes:

1. Variation of the formulation of the complex aqueous mixture containing surfactants, cosurfactants, cosolvents, viscosity-increasing polymers and other additives.

2. Formation of the surface active agents in-situ, particularly in caustic flooding (Cooke, Williams and Kolodzie: 1974; Jennings, Johnson and McAuliffe: 1974; Grave and Johnson: 1974) where the organic acids contained in crude oil react with the caustic solution to form amphipillic salts.

3. Miscible versus immiscible mechanisms; the definition of miscibility if generally related to the observation of an interface which leads to the consideration of microemulsions as a single phase. The displacement is called miscible if no interface is present between oil and injected phase. Many amphipillic compounds may be used, not only surfactants but alcohols and amines (Weinaug: 1966), to produce miscibility. Miscible displacement is particularly attractive because of the absence of capillary effects. Complete recovery of all oil is theoretically possible. However the amount of surface active agent has to be large enough to maintain miscibility during all the displacement, and thus the cost might be prohibitive.
III.2. TYPICAL CHEMICAL FLOODING PROCESSES

Independent of the variations mentioned previously, most chemical floods are designed according to a prescription which has been described extensively (Weinaug: 1966; Dreher and Sydansk: 1976; Richardson and Perkins: 1957; Davis and Jones: 1968; Wilchester et al: 1974; Childress: 1976).

Figure III.1. shows the typical sequence of injection and the oil status in all regions. From right to left are found in order of injection:

1. The waterflooded zone which contains oil at the so-called residual oil saturation, typically 30%. The oil is trapped by capillary forces in the form of disconnected ganglia.

2. The oil bank which has been formed by the accumulation of mobilized oil ahead of the surfactant slug. In this region oil is flowing in the form of threadlike streams as in a waterflood. The two-phase flow obeys to a modified Buckley-Leverett (1942) model (Larson and Hirasaki: 1976). The oil saturation in the oil bank may be typically 50%.

3. The surfactant slug front is the region where mobilization occurs; the basic mechanisms may be different but the overall result is the same for all successful displacements. At the surfactant front all disconnected oil ganglia are mobilized and coalesce to form the oil bank. Actually this front may correspond to a region rather than being a sharp discontinuity since neither the surfactant concentration nor the oil saturation vary abruptly. In this zone of mobilization-coalescence there is a high probability of forming a transient emulsion.
Figure III.1. Typical surfactant flooding.
4. The surfactant slug is in fact a reservoir for surfactant to insure that sufficient surfactant concentration levels will exist in spite of mechanisms tending to degrade the slug by dispersion or diffusion, or losses by adsorption or transfer to oil. The size of the slug, typically 5-15% of the pore volume, has been discussed by many of the authors previously cited (see also Jones: 1972). It is a particularly serious problem when scale up is based upon core experiment data (Parson and Jones: 1976).

5. Because of the problems of mobility control, which are discussed later on, the surfactant slug is followed by a "pusher" slug which is basically a high viscosity aqueous solution. The increased viscosity is generally obtained with low concentrations of high molecular weight polymers (Gogarty: 1967a, 1967b; Hill et al: 1974; Hirasaki and Pope: 1974; Klins et al: 1976). Displacement stability has been also studied by Perrine (1961a & b, 1963).

6. Ultimately the thickened water slug is pushed by the available water or brine.

Variations from this basic process consist mainly in changing the composition of the slugs. In some cases the connate water is displaced by a preflush in order to condition the reservoir. In other cases the surfactant slug will contain thickening agents.
In general the surfactant slug contains a petroleum sulfonate mixture with various additives such as low molecular weight sulfonates, disulfonates, ethoxylated phenols, sulfates, alcohols and various inorganic salts.

III.3. PRACTICAL DIFFICULTIES

The model described in the previous paragraph implies a piston-like advance of all the fluids; this behavior may be observed in core tests in which the conditions are closely controlled; however there are many effects which, in an actual displacement, may completely jeopardize the validity of the model; most of these effects are related with the degradation of the piston-like advance of the different fluid zones. For instance each front may not be moving at the same velocity. Thus the polymer may penetrate and even pass through the surfactant phase.

The general topic of flow through porous media, particularly two-phase flow, has been treated in several textbooks (Muskat: 1949; Scheidegger: 1974; Houpeurt: 1974; Collins: 1976) and survey articles (Blackwell, Rayne and Terry: 1959; Perkins and Johnston: 1963; Hirasaki: 1975; Gogarty: 1976a & b; Davis: 1977).
III.3.1. Mixing effects

Since Dankwerts (1953) introduced the Residence Time Distribution concept to treat mixing phenomena, numerous authors have used this tool to study the dispersion and diffusion effects in porous media (see references in footnotes). Various models have been proposed to take into account the departure from plug flow displacement; they include features like diffusion-type mixing, by-pass, dead volume or capacity, recycle, etc.

Most of these mixing phenomena tend to produce a diffuse front so that concentrations profiles such as step changes are transformed into a smoothed transition. The mixing may be so large that the slugs become greatly diluted and lose their effectiveness.

III.3.2. Fingering


\[1\] See the following articles:

Figure III.2. illustrates the fingering phenomenon by depicting how a small deviation from plug flow becomes unstable and grows along a preferential path. Some authors have reported photomicrographs showing dramatic arborescent fingering effects (Childress: 1975).

Fingering generally occurs when a viscous fluid is pushing a more viscous one, and can therefore be reduced or eliminated by appropriate mobility control (Gogarty: 1967a & b; Gogarty and Tosch: 1968; Gogarty et al: 1970). The parameters commanding a stable displacement have been studied extensively (Hirasaki: 1975; Hirasaki and Pope: 1974; Perrine: 1961a & b, 1963). In some cases the fingering instability can be stabilized by decreasing the permeability as for example in caustic flooding (Jennings et al: 1974). This is true since it is the mobility which is important, not the permeability or viscosity.

When polymer solutions are used to control mobility or when emulsions are formed, the behavior of the fluid departs greatly from Newtonian flow (Hirasaki and.. Pope: 1974; Metzner: 1977; Savins: 1969; Slattery: 1967); suitable rheological representations of complex fluid behavior have been studied (Bird and Carreau: 1968; Carreau, McDonald and Bird: 1968).

The principal adverse effect of fingering is to isolate some regions where the sweep efficiency is null. If the fraction of non-swept region is large, even a miscible displacement will be unsuccessful.
Figure III.2. Fingering.
III.3.3. Rock properties

The rock properties may affect the efficiency of the displacement in several ways. Large heterogeneities or stratification in layers of different permeability will produce extremely severe deviations from plug flow (Kooence and Blackwell: 1965; Kossak and Bilhártz: 1976; Talash: 1976). The wettability of the rock surface is also an extremely important factor (Ehrlich: 1974a & b; Leach et al: 1962; Lefebvre du Prey: 1973; Melrose: 1959, 1965; Mungan: 1964) which may eventually have a strong influence on the relative permeability (Johansen and Dunning: 1957) and on the very mechanism of mobilization of a ganglion (Oh and Slattery: 1976). The state of the rock surface may also influence the contact angle value and the wettability (McCaffery and Bennion: 1974; Morrow: 1974). The rock properties may also influence greatly the saturation of the trapped oil (Stegemeier: 1974).

III.3.4. Adsorption

Adsorption of surfactant on reservoir rock represents a loss of surface active products which may jeopardize the economics of the process. Many researchers have focussed on the adsorption of surfactant on various substrates (Trogus et al: 1976a & b; Hanna and Somasundaran: 1977; Malberg and Smith: 1977; Lawson and Dilgren: 1976); sacrificial agents have been evaluated (Long: 1976) as well as polymer adsorption (Whilihite and Domingez: 1977).
Several models have been proposed to interpret both static and dynamic data (Gupta: 1972; Trogus: 1977c; Satter et al: 1977).

In particular the adsorption maximum which was reported to be due to a mixed micelle phenomenon. A mixed micelle theory recently proposed has shed some light on the adsorption of binary surfactant mixtures (Trogus: 1977a, b & c).

**III.3.5. Mobilization mechanism control**

Miller and Miller's (1956) classical treatment of capillarity in unsaturated soils and related articles (Melrose: 1959, 1965, 1970) call attention to the discontinuous character of oil displacement by a wetting phase. The so-called Haines jumps (Haines: 1927, 1930) have been recorded on motion picture (Childress: 1975) and interpreted using a sinusoidally constricted model of a pore (Oh and Slattery: 1976).

These studies suggest that the actual mobilization criterion may vary from one ganglion to another, and that any criterion will only be a statistical average. Particularly important is the emulsification observed at the surfactant front and the eventual coalescence of mobilized oil droplets to form an oil bank. Several recent articles have considered these problems of emulsification and coalescence (Lissant: 1977; Jeffreys and Davis: 1971; Wasan et al: 1977). Other studies which are related to fibrous bed (Speilman and Goren: 1972a & b; Speilman and Su: 1974; Su: 1974; Chieu: 1975) design are concerned with waste deoiling but involved the same phenomenon.
Another phenomenon which may impede mobilization if the formation of viscous film at the crude oil-water interface (Kimbler, Reed and Silberberg: 1966; Bourgoyne, Caudle and Kimbler: 1972) and its consequences on the coalescence rate and oil recovery (Camacho: 1976).

It is thus extremely difficult in practice to control the mobilization mechanism even based on the dubious assumption of complete monitoring and control of the fluids involved. It seems that a successful displacement process must be flexible enough to withstand wide variations in uncontrolled parameters.

**III.3.6. Other problems**

Many other effects may be responsible for the failure of a chemical flooding project. The surfactant may be unsoluble in high salinity connate water, especially if there is a high concentration of divalent cation; even when the connate water possesses a low concentration of divalent cation, cation exchange processes may produce detrimental cation desorption (Pope, Lake and Helfferich: 1977).

The surfactant may also be incompatible with the polymer used as pusher (Noronha: 1977; Trushenski: 1977).

Furthermore, fractionation due to selective adsorption (Trogus: 1977c), as well as transfer to oil, may change drastically the properties of the surfactant.
Scaling up the core experiment results to field scale may be also hazardous because all dimensionless numbers cannot be held constant at the same time (Nielsen and Tex: 1963; Parson and Jones: 1976).

To conclude this short outline on chemical flooding, it can be said that there is still much understanding needed before a closely controlled process can be designed and implemented in full scale operations. It is hoped that a better understanding of the physico-chemical phenomena associated with the mixing of oils with aqueous solutions containing brine and surfactants will lead to the design of a process flexible enough to withstand the uncontrollable adverse effects.
Chapter IV
SURFACTANTS FOR ENHANCED OIL RECOVERY

IV.1. CRITERIA FOR SURFACTANT SELECTION

Most of the current chemical flooding processes use petroleum sulfonates or mixtures of them with property-modifying additives (Reisberg: 1967; Dunlop and Foster: 1969; Baldwin et al: 1965; Ahearn and Gale: 1967).

The choice of surfactant(s) which has been recently surveyed by various authors (Gogarty: 1967a b; Knaggs: 1976) is made based on several criteria which may be classified into two groups (Gale and Sandvik: 1973; Bae: 1974; Knaggs: 1976): performance criteria versus economic ones.

IV.1.1. Performance criteria

A chemical flooding surfactant formulation must exhibit the following properties:

1. Good displacement efficiency, i.e., it must produce a low tension against crude oil.

2. Low adsorption on reservoir rocks and clays in order to reduce the surfactant losses.

3. Good compatibility with reservoir fluids, especially tolerance to divalent cations such as Ca++ and Mg++.
Actually, as it will be seen later, the performance can be improved considerably by a proper formulation of the surfactant slug. Production of low tension may be adjusted with several parameters; however the occurrence of low tension is extremely sensitive to parameter variations and a very close control of the flood is required. Adsorption losses still appear to be a problem (Hanna and Somasundaran: 1976; Mamberg and Smith: 1976; Trogus et al: 1976a & b; some blocking agents have been found to reduce adsorption (Long: 1976) and the variations of total adsorption for mixtures have been explained recently (Trogus: 1977c); however, the current state of the art seems to indicate that adsorption cannot be avoided.

Salt tolerance may be greatly improved by special formulations including non-ionic surfactants or highly soluble compounds such as ethoxylated sulfonates or disulfonates.

**IV.1.2. Economical aspects**

The current research, effort may soon lead to formulations having excellent performances. However, economic considerations might restrict their use. Economic criteria include:

1. Availability of raw material may be a problem since enormous quantities of surfactants, polymers and additives which will be required for extensive application of chemical flooding.

2. Efficient manufacturing and low cost of production.

A recent industry survey (USITC: 1974) reports 3 billion pounds per year of anionic surfactants are produced in the US. If chemical flooding techniques are developed, production has to be increased by 50 to 100% (Sharp and Crump: 1976).
EOR demand may then unbalance the market because of a potential shortage of raw material (Houston: 1976); this demand for EOR chemical has been estimated (PPC: 1976) and will require a careful production planning. Several recent surveys deal with the economic aspects (Gogarty: 1976b), and raw material (Hinds: 1976).

IV.2. MANUFACTURING OF SULFONATES

Sulfonation processes have been described in several survey articles and books (Linfield: 1976; Edwards: 1976; Feighner: 1976; Bluestein and Bluestein: 1976; Knaggs: 1976; Gilbert: 1957; Kirk-Othmer: 1969). These processes are similar differing basically in the raw materials and the sulfonating agents used. We will classify them according to their type of manufacturing and purpose in three groups: mahogany sulfonates, petroleum sulfonates and research grade synthetic alkyl aryl sulfonates.

IV.2.1. Mahogany sulfonates

In the manufacturing of white oil for cosmetic purposes, the oleum treatment of the feedstock allows removal of all of the unsaturated aromatic and unstable hydroaromatic hydrocarbons, leaving mostly paraffinic oils. The sulfonation reaction produces an acid sludge which is neutralized to lead to the so-called mahogany sulfonates, so-called because of their color (Brown: 1955; Meyer: 1968; Sperling: 1948).
The sulfonation may also be carried out with sulfur trioxide (Gilbert and Veldhuis: 1957; Linfield: 1976).

Petroleum mahogany sulfonate production is reported to be about 300 million pounds in 1974 (Knaggs: 1976) with relatively little possibility to increase it dramatically since their output is related to white oil production. The availability of petroleum sulfonates from this source is diminishing according to some recent publications (Umland: 1974; Abosch: 1975).

**IV.2.2. Petroleum sulfonates**

Commercial petroleum sulfonates are obtained by direct sulfonation of a large variety of aromatic petroleum feedstocks (Linfield: 1976). The sulfonation may be carried out with oleum or with sulfur trioxide which tends to give a better yield (Gale and Sandvik: 1972). The obtained sulfonic acids are then neutralized with an alkali; then a purification process allows removal of some unsulfonated oil and inorganic salts (Knaggs: 1976).

The resulting commercial sulfonate contains typically 60 to 90% of active material (Mono and polysulfonates), unsulfonated oil, some polymerization and oxidation products and a variable amount of inorganic salts and moisture. The actual composition depends largely on the sulfonation feedstock and the reaction process.

Since most of the heavy fractions of crude oil refining contain aromatic hydrocarbons, the raw material availability is guaranteed unless a very specific structure is required.
IV.2.3. Research grade alkyl aryl sulfonates

Most mahogany and petroleum sulfonates contain an uncounted number of different chemicals and it is necessary for certain specific research purposes, such as studying the influence of the surfactant structure or binary mixture behavior, to use pure surfactants, even isomerically pure surfactants. Because of the non-selectivity of the sulfonation process, it is necessary to start from an aromatic hydrocarbon of the adequate purity.

Since it is not generally possible to completely separate heavy hydrocarbons by distillation, the first step is to obtain a synthetic alkyl aryl hydrocarbon by proper alkylation of an aromatic ring; the main alkyl chain possesses typically eight to sixteen paraffinic carbon atoms.

Production of isomerically pure alkyl aryl sulfonates involve complex organic chemistry syntheses and purification procedures; it has been described elsewhere (Doe, El-Emary and Wade: 1976a, 1976b). The production cost of such isomerically pure sulfonates is extremely high and of course beyond any commercial application. However they have proved to be of invaluable help in investigating the effect of the structure on surfactant properties.

All the information concerning the surfactant used in this study is gathered in appendix.
Chapter V  
CHARACTERIZATION AND ANALYSIS OF  
ALKYL ARYL SULFONATES

Isomerically pure surfactants may be properly characterized by their chemical structure; however this is not possible for commercial petroleum sulfonates which may contain a myriad of different chemicals. A recent paper (Sandvik et al: 1976) reports several techniques to characterize commercial petroleum sulfonates; most of these techniques are derived from analytical methods described elsewhere (Longman: 1975; Cross: 1977).

V.I. EQUIVALENT MOLECULAR WEIGHT

The equivalent molecular weight is obtained by dividing the weight of a surfactant sample by the number of moles of sulfonate groups.

This concept may be extremely misleading as far as the structure is concerned (see Figure V.1.); it is also useless to describe very pure surfactants since their properties depend on their isomerization state (Doe, El Emary and Wade: 1976a & b).

However the equivalent molecular weight has been found to correlate roughly with the properties of commercial petroleum sulfonates; the correlation may be extremely good when properties of mixtures such as interfacial tension minimum (Wade et al: 1976) or
**Figure V.I.** Various alkyl aryl sulfonates with their Equivalent Molecular Weights.
phase behavior (see Chapter IX) are considered.

Even more descriptive of the surfactant is its equivalent molecular weight distribution which gives an approximate idea of the spectrum of structures present in the commercial petroleum sulfonates. Equivalent molecular weight distributions may be obtained by successive solvent extractions as described by Sandvik and Gale (1976). If the proportion of polysulfonates is negligible and if the aromatic feedstock is a narrow cut (i.e., there is a single species of aromatic ring with differences only in alkyl chains), then the equivalent weight distribution provides excellent information on the lipophillic chain length distribution.

High Performance Liquid Chromatography (HPLC) on reversed phase column may allow separation of surfactants according to their lipophillic chain lengths; this method is extremely useful for mixtures of relatively pure surfactants (see Figure V.2.), but fails in general for commercial petroleum sulfonates because of the continuous spectrum of molecular weight of these products. Other liquid chromatographic techniques are discussed elsewhere (Gabriel and Mulley: 1977).

Another method is to desulfonate the surfactant and study the produced hydrocarbons by gas chromatography (Uno and Nakagawa: 1977).
Figure V.2. HPLC Chromatogram of a mixture of C12 and C14 alkyl benzene sulfonates (Courtesy Ch. Koukounis).
V.2. ULTRAVIOLET SPECTROSCOPY

UV absorbance spectroscopy provides a simple and quick technique to measure or estimate the concentration of alkyl aryl sulfonates. All aromatic compounds exhibit a strong absorbance peak near 220 nm and secondary peaks in the 260-280 nm range (Weber: 1962). The UV spectrum may ultimately provide some information on the surfactant alkyl structure. Figure V.3. shows that linear alkyl benzene sulfonates exhibit secondary peaks at 262-270 nm, while alkyl orthoxylene sulfonates (as well as alkyl ethyl-benzene sulfonates) have their secondary peaks at 270-280; compared with them, the UV spectrum of Witco TRS 10-80 seems to indicate the presence of different structures.

UV spectroscopy is a very accurate technique for determining the concentration of pure surfactants; however it only yields estimates for mixtures because the UV spectrum may be affected by fractionation, i.e. by the fact that the mixture does not behave as a single component. Since the adsorptivity (on a mole basis) of the different components of a mixture varies from one structure to another, even a mixture of two compounds having the same UV spectrum cannot be analyzed accurately if some fractionation has occurred.

However in systems where fractionation cannot occur, such as between two or more phases, the UV absorbance at a properly selected wavelength provides an excellent measurement of the concentration.
Figure V. 3. UV Spectrum of several alkyl aryl sulfonates
In HPLC separation techniques, UV detection can successfully measure the concentration of separated surfactants. UV spectroscopy techniques applied to anionic surfactant analysis are surveyed in two recent publications (Longman: 1975; Gabriel and Mulley: 1977).

V.3. VOLUMETRIC TITRATIONS

All volumetric titration methods involve the formation of a colored complex between the anionic surfactant and a cationic dye such as methylene blue. The titrant is also a cationic surfactant, such as hyaminel, which is able to compete with the indicator to form a complex with the anionic surfactant. Since these complexes are very insoluble in water, they are extracted in an oily layer, generally chloroform, and are thus given the name "two-phase titrations".

Initially the anionic surfactant (A-) is dissolved in water with a small amount of the indicator (In+) and a chloroform layer is added; all the indicator is complexed to form a salt AIn which is insoluble in water and thus is extracted in the chloroform phase which becomes colored. The titrant (T+) is then added and complexes the anionic surfactant to give a water insoluble compound (color-less AT, which is also extracted in the organic phase. At the end point, the free A- ions being exhausted, T+ replaces the indicator.

\[1\] Hyamine 1622 (Rohm and Hass) is a p-ter-octyl (phenoxyethoxyethyl) dimethyl benzyl ammonium chloride.
In+ cations in the complex, thus liberating In+ cations which return to the water layer. The organic phase decolorizes as the In+ indicator returns to the water layer. The end point is generally obtained when the two phases have the same color, since complete transfer of In+ ions to water phase is not possible because of the equilibria.

\[
\text{In}^+ + \text{A}^- \not \rightarrow \text{InA} \\
\text{Ta}^+ + \text{A}^- \not \rightarrow \text{TA}
\]


V.4. MISCELLANEOUS METHODS

Many other methods of characterization and analysis are available, but in general they are accurate only for relatively pure surfactants or simple mixtures. Longman (1975) discusses extensively the use of other instrumental methods such as IR spectroscopy (see also Gabriel and Mulley: 1977), Raman Spectroscopy, polarography, electrophoresis and nuclear magnetic resonance (see also Konig: 1977; Shah et al: 1976).

The degree of sulfonation may be estimated by HPLC techniques on ion exchange columns (Zornes, Willhite and Michmick: 1977; Suffridge and Taggart: 1977).

Purification of the surfactant is also an important step to insure a well defined product free of oil and inorganic salts.
Desalting is easily done by dissolution in hot ethanol or organic solvents.

The deoiling procedure used in this work consists in a selective adsorption of the surfactant on a silica gel column; the column is filled with a silica gel-chloroform sludge which is then packed by flooding with chloroform under gravity. Packing with a vibrator was found to yield a non-homogeneous porous bed in large diameter (3") columns with resulting fingering. Hence this packing technique was used only for small diameter columns. The surfactant dissolved in a minimum amount of chloroform is then introduced in the column and elution with chloroform is carried out until no trace of oil is detected (UV) in the effluent. The surfactant remains adsorbed on the silica gel. Then elution with methanol is carried out; because of the favorable partition coefficient the surfactant migrates with the methanol front. The surfactant is then recovered from the methanol solution by evaporating to dryness under vacuum.
Chapter VI

PROPERTIES OF THE SOLUTIONS OF A TYPICAL
PETROLEUM SULFONATE: TRS 10-80

VI.I. SOLUBILITY OF TRS 10-80 IN BRINE

TRS 10-80 is a petroleum sulfonate manufactured by Witco Chemical Corporation, Sonneborn Division. It is a brown extremely viscous liquid containing approximately 80% of active material, 10% of unsulfonated oil and 10% moisture (see Appendix A). This surfactant has been used as a reference in numerous studies and was thus selected in this work as a typical example of commercial petroleum sulfonate.

Its equivalent molecular weight ranges from 415 to 425 depending on the batch and it has been found to contain a small percentage of disulfonates (Zornes, Willhite and Michnick: 1977). Like most commercial petroleum sulfonates, TRS 10-80 exhibits a relatively broad equivalent molecular weight distribution. Unless otherwise mentioned, TRS 10-80 was used as supplied. When purified to 100% active material, the term deoiled is employed.

The solubility of TRS 10-80 in brine is the concentration of surfactant remaining in solution in equilibrium with excess solid.

The procedure to measure the solubility consists of filling a test tube with a known brine solution, then adding enough surfactant to exceed the saturation level; the system is then shaken several times for three days, and then centrifuged for one hour (at 25°C).
The supernatant solution is then analyzed for surfactant by UV absorbance at 262 nm.

As shown in Figure VI.1., two different regimes are found; from 0 to 2 gpdl (grams per deciliter) NaCl the supernatant solution is turbid and the excess solid has a gel-like appearance. Several experiments have shown that the turbidity is very stable; no significant concentration change is found if the samples are centrifuged for six hours instead of one; filtration through a 5 micron Millipore filter does not separate any solid phase.

The second regime starts at 3 gpdl NaCl; the supernatant solution is clear and the excess solid surfactant is precipitated as an amorphous apparently non-birefringent solid; however it was not examined under a polarizing microscope as reported elsewhere (Hwan et al: 1976).

As mentioned previously, the UV absorbance technique allows measurement of the concentration of aromatic rings but presents some difficulties if fractionation occurs. Actually the UV spectra of the supernatant solutions corresponding to regime (1) and regime (2) are quite different in the 270-280 nm region (see Figure VI.2.).

The turbid supernatant solution found in regime (1) is diluted to approximately 100 ppm and a UV spectrum is recorded in the 250-300 nm range; the resulting UV spectrum (regime 1) exhibits a strong absorbance from 260 to 280 nm, with the presence of "peaks" at 262, 272 and 280 nm.
Figure VI.1. Solubility of TRS 10-80 in Brine ($10^4$ ug/ml 1% wt).
Figure VI. 2. UV Spectra of Regime (1) and Regime (2) supernatant solutions.
On the other hand, the clear supernatant solution found in regime (2) has a different UV spectrum; the 262 nm peak is still present but the 272 and 280 peaks have disappeared. The product responsible for these peaks is thus probably separated in the precipitate (see regime 2 on Figure VI.2.).

Figure VI.2. shows also the difference between the two spectra (1-2); this difference is presumed to represent the UV spectrum of a product, so-called 280 nm product, which is present in solution in regime 1 (low salinity) but absent in regime 2 (high salinity); it should be noted however that the shape and intensity of the (1-2) curve depends on the relative intensity of spectra 1 and 2; it is thus indicative of a qualitative difference, but is not susceptible to quantitative interpretation.

In the aging study (Section VI.6.) it will be shown that a TRS 10-80 fresh solution (in low salinity brine) possesses a UV spectrum identical to regime 1 while the same solution aged, i.e., left to settle in a bottle a few months has a UV spectrum similar to regime 2; furthermore both fresh and aged solutions spectra exhibit the same absorbance value at 262 nm. For lacking of a better reference it is thus assumed here, by analogy, that regime 1 and regime 2 spectra coincide at 262 nm for equal concentration of surfactant.

\[\text{\underline{1}}\text{Actually the UV spectrum shows a composite peak in the 260-280 region; however discontinuities are found at the indicated wavelengths.}\]
In order to quantify the change in UV spectrum, let us define the absorbance parameter AR as:

\[
AR = \frac{\text{Absorbance at 280 nm}}{\text{Absorbance at 262 nm}}
\]

This definition allows the characterization of the shape of the spectrum independent of the total surfactant concentration. If regime 1 and regime 2 spectra are assumed to coincide at 262 nm, that is (1-2) spectrum exhibits a zero absorbance at 262 nm, then AR can be shown to vary linearly with the proportion of 280 nm product.

\(AR\) is measured for all supernatant solutions of the solubility experiment and then plotted versus salinity; the obtained curve (Figure VI.3.) is similar to the solubility plot; the similarity is even more evident on Figure VI.4 which shows \(AR\) versus solubility. This may be interpreted as the presence of two different products in solutions of regime 1 and regime 2.

A recent article (Gaboriaud et al: 1977) shows that the saturation concentration of a solute in an electrolyte mixed solvent may be expressed as:

\[
\log \frac{C_{\text{sat}}^{\text{Electrolyte solution}}}{C_{\text{sat}}^{\text{pure solution}}} = \log C_{\text{sat}}^{\text{pure solution}} - f_{\text{solute}} g_{\text{electrolyte solvent}}
\]
Figure VI.3. Absorbance Ratio of (TRS 10-80) saturated solutions versus salinity.
Figure VI.4. Absorbance ratio of (TRS 10-80) saturated solutions versus solubility level of the surfactant in these solutions (from right to left experimental points corresponds to 0, 1, 2, 3, 4, 6, 8, 10% wt NaCl).
Where \( c_{\text{sat}} \) stands for solubility, \( f \) is a constant characteristic of the solute and \( g \) is called the solvent variable and depends on the mixed solvent composition. The generality of this relation-ship has been reported for many systems (Letellier et al: 1972, 1973a & b, 1976; Gaboriaud et al: 1976). For sodium chloride aqueous solution the solvent variable \( g \) is proportional to the concentration of NaCl up to 20 gpol. Hence:

\[
\log c_{\text{sat}}^{\text{Brine S}} = \log c_{\text{sat}}^{\text{water}} - K_{\text{solute NaCl}}
\]

The slopes of the two regimes solubility curves in FigureVI.1. lead to two different values of the solute constant \( K_S \):

Regime 1: \( K_S = 0.23 \) deciliter/gram NaCl
Regime 2: \( K_S = 0.03 \) deciliter/gram NaCl

Let us define \( \alpha_t \) as the transfer activity coefficient (Gaboriaud et al: 1977) to pass from a solute-saturated water solution to a solute-saturated S gpdl NaCl aqueous solution:

\[
\alpha_t = \frac{c_{\text{sat}}^{\text{Brine S}}}{c_{\text{sat}}^{\text{water}}}
\]

Then the constant \( K_S \) is defined by partial differentiation with respect to salinity:

\[
K_S = - \frac{\partial \log \alpha_t}{\partial S_{\text{NaCl}}}
\]
VI.2. SURFACE TENSION AND CRITICAL MICELLE CONCENTRATION

The surface tension of the surfactant solution is measured at room temperature (25°C) in the spinning drop tensiometer; it is the tension between the solution and a bubble of air. The tension is measured until a stable value is obtained for one hour; this equilibrium is generally reached after two to three hours.

Figure VI.5. shows the variation of the surface tension versus TRS 10-80 concentration at different salinities. The "ppm" concentration scale correspond to microgram of surfactant per milliliter of solution; 1 ppm is equivalent to 1.9 micromol of active material per liter of solution.

Figure VI.6. shows the variation of the surface tension versus TRS 10-80 concentration at 1 gpdL NaCl and different concentrations of sec-butanol.

The critical micelle concentration (CMC) is taken as the point where the variation of the surface tension with concentration exhibits an abrupt change (see Adamson: 1967).

The previous data allows plotting the variation of CMC versus salinity (Figure VI.7.) and concentration of sec-butanol (Figure VI.8). As expected, increasing salinity and alcohol concentration tend to depress the CMC (Shinoda: 1954). It is interesting to note that Figure VI.7 plot becomes linear if a logarithmic scale is used for salinity; the zero salinity point actually corresponds to a non-zero concentration if counterions brought by the surfactant and
Figure VI.5. Surface tension versus concentration of TRS 10-80 at different salinities.
Figure VI.6. Surface tension versus concentration of TRS 10-80 at 1 gpd/l NaCl and various concentrations of sec-butanol.
Figure VI.7. Variation of Critical Micelle Concentration (CMC) of TRS 10-80 solutions versus salinity.
Figure VI.8. Variation of Critical Micelle Concentration (CMC) of TRS 10-80 solutions (with 1 gpdl NaCl) versus sec-butanol concentration.
inorganic impurities are taken into account; however it is not possible to calculate this accurately.

VI.3. CLEAR POINT OF SOLUTIONS

When a petroelum sulfonate, as well as many other surfactants, is dissolved in brine (and sometimes water) the resulting solution appears cloudy or turbid. Some authors have reported quantitative measurements of this turbidity (Shah et al: 1976).

With TRS 10-80 the turbidity appears to be most pronounced for brine concentrations just below the solubility transition point, i.e. for 1 to 2 gpdl NaCl. Several experiments were carried out to determine whether these turbid solutions were actually solutions or suspensions of solids; a test solution containing 1 gpdl TRS 10-80 and 1 gpdl NaCl was left in a bottle for several months. There was no gravity separation, i.e. no apparent sedimentation except a slight brown residue which was analyzed as an iron compound (see Appendix); it must be stressed that the composition of this solution is below the solubility curve. The same result was obtained after 70 hours of centrifugation at 5000 RPM. In another experiment the solution was filtrated on a 5 µ Millipore filter with no solid separated.

Hence it may be concluded that the size of the light scattering particles is in the 0.2-4 µ range.

It was found that these solutions could be made clear by adding a proper amount of alcohol.
VI.3.1. Experimental procedure

The determination of the concentration of alcohol required to obtain a clear solution (clear point at 25°C) is carried out by the following procedure:

1. a sample of a TRS 10-80 solution in water (1 to 4 ml) is introduced in a small Erlenmeyer flask;

2. a known amount of NaCl solution (of concentration ranging from 1 to 15 gpdl) is then added and agitated; the solution appears cloudy with eventually formation of a precipitate;

3. then the tested alcohol is added drop by drop from a buret, like in a titration, until the solution changes from turbid to clear. This change is very sharp and can be detected very accurately if the original solution is cloudy enough;

4. finally all concentrations are calculated on the basis of the final volume.

The transition turbid → clear is reversible and another method consists in adding successive aliquots of brine and corresponding necessary amounts of alcohol; after the first clear point is obtained a known small amount of brine is added to make the solution cloudy again; then more alcohol is added until the solution clears again, and so on.

VI.3.2. Accuracy and range of the data

The transition turbid → clear is extremely rapid; most of the time only 0.05 ml of alcohol is required to produce it.
However the main problem is to deal with a cloudy solution which is turbid enough to be recognized to be so with the naked eye. This requirement sets the lower limit of surfactant concentration to approximately 0.25 gpd/l and the lower limit on salinity to 0.3 gpd/l NaCl.

The upper limit on brine concentration is set by the solubility level of the alcohol; when the solubility level of the surfactant is reached, the surfactant precipitates but can be dissolved back by addition of the alcohol. However the upper limit on surfactant concentration is chosen at 2.5 gpd/l, which is just below the solubility level at 2 gpd/l NaCl.

**VI.3.3. Clear point results**

Figures VI.9 to VI.17 show the minimum concentration of alcohol needed to obtain a clear solution at room temperature (25°C) versus the actual salinity and for several concentrations of TRS 10-80.

Studied alcohols are: methanol, ethanol, n-propanol, isopropanol, n-butanol, iso-butanol, sec-butanol, ter-butanol and ter-amyl alcohol. The results show that:

A change of surfactant concentration from 0.25 to 2.5 gpd/l does not change significantly the minimum concentration of alcohol needed to produce a clear solution.

The concentration of alcohol at clear point correlates strongly with salinity, i.e., it depends only on the salinity.
Figure VI.9. Clear point with methanol.
Figure VI.10. Clear point with ethanol.
Figure VI.11. Clear point with N-propanol (1-propanol).
Figure VI.12. Clear point with Iso-propanol (2-propanol).
Figure VI.13. Clear point with N-butanol (1-butanol).
Figure VI.14. Clear point with Iso-butanol.
Figure VI.15. Clear point with Sec-butanol.
Figure VI.16. Clear point with Ter-butanol.
Figure VI.17. Clear point with Ter-amyl-alcohol.
molecular weight, i.e. the heavier the alcohol the less alcohol needed to produce a clear point at a given salinity.

(4) The effectiveness of the alcohol decreases with its branching, i.e. with its solubility in water.

Figure VI.18 compares the behavior of studied alcohols; n-butanol and iso-butanol are not included because the data are too scattered (very low salinity) and hence no average curve can be accurately drawn.

The transition from turbid to clear solution may be associated with the formation of a microemulsion in which the micellar aggregates (which may be swollen by the unsulfonated oil) become small enough not to scatter light. Because of the extremely sharp transition this interpretation would imply that the swollen micelle size distribution is very narrow and rigidly controlled by the alcohol type and concentration, and environment composition. Another observation tends to favor this scheme. It was found that a deoiled solution of pentadecyl-orthoxylene sulfonate in water was extremely turbid, while the non-deoiled solution (at the same concentration) was limpid; however this difference may be due not only to the absence of oil but also of heavy molecular weight fractions which may have been discarded as a result of the deoiling procedure and thus cannot nucleate a microemulsion.

Whatever the aggregates or particles which cause the turbidity, their size or structure seems to be extremely sensible to the chemical environment: salinity, alcohol and oil.
Figure VI. 18. Clear point curves for various alcohols
Temperature was also found to be an important variable in determining the clear point. Figure VI.19 shows that salinity tends to increase the clear point temperature while alcohol tends to decrease it. Such observations have been reported recently also for isomerically pure surfactants (Fernandez: 1977).

In order to check for a structure change in the solution, several dynamic adsorption runs were carried out with solutions below and above the clear point; Figure VI.20. shows a net decrease of the adsorption above the clear point; it is worth mentioning also that in the case of the clear solution (6 gpdl sec-butanol) the chromatographic effect discussed in the next section is practically nonexistant.

VI.4. CHROMATOGRAPHIC EFFECT DURING ADSORPTION

Dynamic adsorption experiments were carried out in a 1 foot Berea sandstone core. The core is initially filled with 1 gpdl NaCl brine, then a surfactant solution of the same salinity is injected at a frontal velocity of 4 ft/day, thus producing a step change in concentration.

The effluent is collected in fractions equivalent to 1/20th of the pore volume, and analyzed by UV spectrometry.

Figure VI.21 shows the dimensionless concentration response versus dimensionless time (number of pore volumes) for three different surfactant concentrations; concentration is measured by UV absorbance at 262 nm and in spite of some change in the UV spectrum
Figure VI.19. Clear point temperature at two different salinities versus concentration of sec-butanol.
Figure VI.20. Adsorption of TRS 10-80 on Berea sandstone (dynamic experiments) versus sec-butanol concentration. (Frontal velocity is 4 ft/day).
Figure VI. 21. Surfactant breakthrough curves in a dynamic adsorption experiment. (Concentrations are estimated by UV spectroscopy at 262 nm)
shape, the values obtained are consistent: adsorption amounts to $1.1 \pm 0.1$ umol of TRS 10-80 per gram of Berea sandstone, as calculated from the area between the step response (tracer) curve and the surfactant breakthrough curve.

However the UV spectra changes with dimensionless time, indicating that fractionation occurs. Figure VI.22 shows the change of the UV spectrum of the effluent versus dimensionless time (pore volume) for an injected concentration of 0.5 gpd/l TRS 10-80/1 gpd/l NaCl. All the curves are referred to a 200 ppm concentration and shifted vertically to better exhibit the change.

The black arrow indicates the point where the 280 nm peak starts appearing, i.e. the arrival of the wave corresponding to regime (1) seen previously (refer to Figure VI.1.).

An even better illustration of this chromatographic effect is shown in Figure VI.23 where the absorbance ratio AR is plotted versus pore volume. It may be thus concluded that regime (2) product is very little adsorbed while the remaining (1-2) product is absorbed considerably.

**VI.5. SURFACTANT AGING**

The fact that surfactant solution properties change with time has been known for some time (Lawrence: 1935) but has not received much attention until recently when the aging of a petroleum sulfonate was found to affect its properties during the time span of a chemical flood (Cash et al: 1975).
Figure VI. 22. Chromatographic effect during a dynamic adsorption experiment: UV spectrum of effluent versus pore volume.
Figure VI.23. Surfactant breakthrough curve (analyzed by UV spectroscopy at 262 nm) and absorbance ratio $A_R$ versus pore volume.
These authors reported several results concerning the aging of TRS 10-80 solutions; they found that the interfacial tension against various hydrocarbons tends to change in time, particularly that the preferred alkane carbon number (see EPACNUS concept in Chapter IX) tends to decrease with aging; they also found that temperature and alcohols influence the aging process. Finally they reported that aging depends on the surfactant concentration and seems to be physical in character, i.e. not to involve a chemical reaction.

The present study was started by noting that the UV spectrum of aged TRS 10-80 solutions was similar to the one of the supernatant solutions at high salinity (regime 2 - see Section VI.1.) in the solubility study.

Figure VI.24 shows the UV spectra of freshly prepared (less than three days) TRS 10 - 80 solutions in different solvents. The spectra are slightly different and the absorbance at 262 nm is the same ± 5% for the same concentration of surfactant; curves on Figure VI.24 are shifted to provide a clear graph but actually they practically coincide at 262 nm. Figure VI.25 shows the UV spectra of an aged solution (1 gpdl TRS 10-80 and 1 gpdl NaCl) which was left at room temperature in a closed container for 6 months. Small samples of the solution (1 ml, i.e. $10^{-2} \text{ g}$ of surfactant) were dried under vacuum and redissolved in different solvents\textsuperscript{2} to obtain a 100 ppm solution.

\textsuperscript{2}Actually methanol and water solutions contain 0.01 gpdl NaCl.
Figure VI.24. UV spectra of fresh TRS 10-80 solutions in different solvents (curves are shifted).
Figure VI.25. UV spectra of aged TRS 10-80 (6 months in 1 gpdl NaCl) in different solvents (curves are shifted).
Figure VI.25 shows that the UV spectrum of that solution is about the same whatever the solvent, but is drastically different from the fresh solution one. A striking fact is the similarity with regime 2 spectrum in Figure VI.2 and initial effluent spectrum in Figure VI.22.

A two-dimensional series of solutions was put to age with surfactant concentrations 0.05, 0.1, 0.5, 1.0, 1.5 and 2.5 gpdl and salinities 0.0, 1.0 and 2.0 gpdl. Higher salinities were not used since they lead to "instant" aging as seen in Section VI.1.

Each solution was stored in a closed bottle and a UV spectrum scan was taken each week for the first three weeks, then every other week up to 11 weeks. A new measurement was made after 20 and 30 weeks. In each case the solution was vigorously stirred then a 1 ml sample was drawn and diluted in reagent grade methanol to produce a 50 or 100 ppm solution.

The ratio of UV absorbance at 280 nm to UV absorbance at 262 nm ($A_R$) was taken as the yardstick to measure the aging. $A_R$ varies from 0.93 for a fresh solution down to a low 0.60 for a very aged solution (50 weeks); the longer the aging the lower $A_R$.

Figures VI.26 to VI.34 show the variations of $A_R$ versus time for different conditions of surfactant concentration and salinity. The general conclusion is that aging depends on both salinity and surfactant concentration. At high concentration of surfactant (Figure VI.26.) the aging rate is about the same at all salinities.
Figure VI.26. Absorbance ratio versus aging time Surfactant concentration 2.5 gpdL, various salinities.
This aging rate is maintained at moderate concentrations of surfactant in absence of salt (Figures VI.27 to 29.); however the aging rate is increased in presence of salt. Finally at low surfactant concentration (Figures VI.30 and 31.) the effect of salinity becomes extremely clear: the higher the salinity, the faster the aging.

Figures VI.30 and 31 show that at very low surfactant concentrations $A_R$ exhibits a sharp change at 1 and 2 gpdl NaCl, in-stead of the smooth and continuous change found in other cases; this sharp decrease may be related to the disappearance of one product.

The total surfactant concentration does not greatly influence the rate of aging in pure water (Figure VI.32.) but produces a sizeable change when salinity increases (Figures VI.33. and VI.34.).

It is not known whether the aging is due to a reversible physical process or a chemical reaction. It was reported (Cayias: 1975) that the interfacial tension properties of the solution could be restored by evaporating the solution and drying the surfactant or extracting it with a solvent; these procedures were aimed at breaking the micellar or any other structure existing in the solution because of aging. However, the UV spectrum could not be restored by drying or extracting the surfactant. After these micelle-breaking operations were performed, the UV spectrum of the surfactant had the same "old solution" aspect. Chemical reaction cannot be ruled out, particularly since aging seems to be affected by light (Baviere: 1977).
Figure VI.27. Absorbance ratio versus aging time. Surfactant concentration 1.5 gpdL, various salinities.
Figure VI.28. Absorbance ratio versus aging time. Surfactant concentration 1 gpd/l, various salinities.
Figure VI.29: Absorbance ratio versus aging time. Surfactant concentration 0.5 gpol, various salinities.
Figure VI.30. Absorbance ratio versus aging time. Surfactant concentration 0.1 gpdl, various salinities.
Figure VI.31. Absorbance ratio versus aging time. Surfactant concentration 0.05 gpd/l, various salinities.
Figure VI.32. Absorbance ratio versus aging time. Various surfactant concentrations in water.
Figure VI.33. Absorbance ratio versus aging time. Various surfactant concentrations in 1 % NaCl solutions.
Figure VI.34. Absorbance ratio versus aging time. Various surfactant concentrations in 2 % NaCl solutions.
Property changes with time have been found with several surfactants, not only petroleum solfonates, but also sulfates. A study on isomerically pure surfactants would allow a determination of whether it is of chemical nature or a mixed micelle physical phenomenon.
Chapter VII
TERNARY DIAGRAM

VII.I. PHASE BEHAVIOR OF AMPHIPHILIC COMPOUNDS

It has long been known that ternary systems consisting of an amphiphilic compound, water and oil can form a microemulsion (Schulman and coworkers: 1946, 1948, 1949, 1951, 1959, 1960; Bowcott and Schulman: 1955; Stoeckenius et al: 1960; Cooke and Schulman: 1965), or a micellar solution (McBain: 1942, 1946) in equilibrium with excess oil, excess water or both.

Some authors have discussed the differences between the two terms (Shah: 1972, 1974, 1976; Prince: 1975); however there is no complete characterization of the molecular aggregation of such systems; micellar solutions tend to be defined as the ones containing aggregates in the 10-100 Å range, i.e., basically micelles, while microemulsion would describe a solution containing large aggregates in the 100-1000 Å range, i.e., swollen micelles or microdroplets. Several survey papers (Shinoda and Friberg: 1975; Reed and Healy: 1976; Robbins: 1976) use only the term "microemulsion" to describe such isotropic surfactant-oil-water systems.

The phase behavior of this kind of ternary systems was characterized by Winsor (1948, 1954) who defined three types of ternary diagrams as shown in Figure VII.1.
Figure VII.1. Winsor ternary diagram types for amphiphilic compound/water/oil systems (tie lines are figured in two-phase regions).

VII.1.1. Type I diagram
This diagram has a two-phase region with tie line slopes such that any system, the composition of which lays in the two-phase region, will separate into an aqueous phase rich in amphiphilic compound and containing some solubilized oil, and an hydrocarbon phase consisting of almost pure oil.

In this case almost the surface-active chemical partitions into the aqueous phase microemulsion, i.e., the hydrophilic properties of the amphiphilic compound prevail; we will denote it by stating that the surfactant has an hydrophilic (I-H) status.

**VII.1.2. Type II diagram**

The bottom diagram of Figure VII.1 shows a type II diagram. It has a two-phase region like type I, but this time the slope of the tie lines is such that any system, the composition of which lays in the two-phase region, will separate into an oil phase rich in amphiphilic compound and containing some solubilized water, and an aqueous phase consisting of almost pure water.

In this case the surface-active chemical partitions preferentially into the oil phase microemulsion, i.e., the lipophilic properties of the amphiphilic compound prevail; the surfactant will be said to have a lipophilic (II-L) status.

**VII.1.3. Type III diagram**

As seen in Figure VII.1, type III diagram is more complex and contains below the single phase region (1$\phi$) two two-phase regions (2 $\phi$) and a three-phase region (3 $\phi$).
Figure VII.2 (top diagram) shows that a system, the composition of which (square dot) lays in the three-phase region, will separate into three phases in equilibrium:

- A microemulsion middle phase (M dot) which contains almost all the surfactant and approximately equal amounts of oil and water.

- An aqueous phase (aq. dot) consisting of almost pure water.

- An hydrocarbon phase (hc. dot) consisting of almost pure oil. In this first case of type III diagram the surfactant status is denoted III-M.

Figure VII.2 center diagram shows that a system, the composition of which (square dot) lays in the left lobe of the two-phase region, will separate into two phases in equilibrium:

- A surfactant-rich hydrocarbon phase (hc) which contains a large amount of solubilized water and thus is called a "swollen" oil phase.

- An aqueous phase (aq) consisting of almost pure water.

In this second case of type III diagram the surfactant partitions in the oil phase and thus its lipophilic properties prevail like in type II diagram; the surfactant status will be de-noted III-L by analogy.

\[^1\text{The term "middle phase" is generally used because the inter-mediate density of this phase makes it separate between the oil phase (upper phase) and the aqueous phase (lower phase); however in some cases it might not be the actual middle phase.}\]
Figure VII.2. Type III ternary diagrams showing phase separation.
Figure VII.2 bottom diagram shows a system, the composition of which lays in the right lobe of the two-phase region. Such a system will separate into two phases in equilibrium:

- A surfactant-rich aqueous phase (aq) which contains a large amount of solubilized oil, and thus is called a "swollen" aqueous phase.
- An hydrocarbon phase (hc) consisting of almost pure oil.

This case is similar to type I diagram, in which the surfactant hydrophilic properties prevail; by analogy the surfactant status will be denoted III-H.

**VII.1.4. "Bottom tie line" in type III diagram**

It was seen in Figure VII.2 top diagram that three phases (M, aq and hc) were in equilibrium. The excess water (aq) and excess oil (hc) contain almost pure water and pure oil respectively; however they do contain a small concentration of surfactant; there must be thus a tie line between the point "aq" and "hc". This line is called the "bottom tie line" (Anderson et al: 1976) and its position is shown on Figure VII.3 which possesses an exaggerated surfactant scale.

On the other hand, since water and oil are virtually immiscible in absence of surfactant, the bottom side of the triangle (WO) consists of a two-phase region. Figure VII.3 shows the "bottom two-phase region" which lays between the bottom tie line and the zero-surfactant side of the diagram.)
Figure VII.3. Bottom tie line and bottom two-phase region in type III diagram.
Measurements at very low surfactant concentration seem to confirm the existence of this bottom two-phase region (Cash et al: 1976; Cayias et al: 1975).

As far as the following discussion is concerned, the bottom two-phase region will be referred to in cases of extremely low surfactant concentrations. In all other situations this region can be neglected.

VII.2. PSEUDO TERNARY DIAGRAM

Most of the micellar systems involved in chemical flooding are composed of three principal components: water, oil and an amphiphilic substance generally called surfactant. These three compounds correspond to the three vertices of Winsor diagrams. However in all practical cases the actual number of involved chemicals is much larger; in order to use the concept of Winsor ternary diagram it is necessary to group several components at the same vertex and to assume that each of the three groups behaves as a single pure component.

This approximation leads to the construction of a so-called pseudo-ternary diagram which simplifies the study of the phase behavior of mixtures of three pseudo-components. Each of the three pseudo-components corresponds to some extent to the actual mixture of compounds found in a field displacement.

The aqueous phase in this study is generally a sodium chloride solution which simulates reservoir connate water.
In this study the salinity is expressed in gram of sodium chloride per deciliter of aqueous phase (gpdl); this unit is often improperly called % weight in the literature, although the difference is not very significant.

The oil phase can range from a pure hydrocarbon to an extremely complex mixture such as a crude oil. With the help of the concept of Equivalent Alkane Carbon Number (EACN) introduced recently (Cayias, Schechter and Wade: 1976), it may be possible to use a single numerical scale to characterize any oil or oil mixture. The EACN concept correlates the low tension behavior of an oil with the low tension behavior of an equivalent alkane which may be found by a simple averaging procedure. As mentioned in a recent article (Wade, Morgan, Jacobson, Salager and Schechter: 1977), it will be shown later that the low tension state and the occurrence of type III ternary diagram are two manifestations of the same phenomenon. Assuming that the EACN scale will apply for phase behavior studies, the whole liquid alkane series is used in this work. The utilization of pure alkanes simplifies considerably the analysis, particularly concentration measurements by ultraviolet spectroscopy.

As far as the amphiphilic compound is concerned, many different formulations have been proposed (see a recent survey by Reed and Healy: 1976); most of them contain petroleum sulfonates, i.e., complex mixtures of alkyl-aryl-sulfonates mixed with ethoxylated compounds and other additives such as alcohols or ethers. Some mixing rules have been reported for the obtaining of the minimum interfacial tension with a mixture of surfactants (Wade, Schechter, Morgan and Jacobson: 1976); they suggest that a mixture of surfactants behaves as an equivalent pure surfactant.
One of the main problems in providing an acceptable ternary representation is to decide where to place the alcohols; some authors (Healy and Reed: 1973; Hsieh and Shah: 1977) use a fixed surfactant/alcohol ratio as amphiphilic compound, i.e., they assume that surfactant and alcohol always partition in the same ratio. A large number of experimental data reported later in this work shows that this assumption would in many cases negate the use of ternary diagrams. Alcohols which are not completely soluble in water are able to drastically modify phase behavior. If a constant surfactant/alcohol ratio is selected in such a case, the observed phase behavior would markedly depend upon the concentration of the amphiphilic mixture, which contradicts with Winsor type III diagram concept. Alcohol concentration is thus considered as an independent parameter in this study.

Another source of difficulty is the fact that the interfacial tension and phase behavior of certain surfactants vary with the surfactant concentration (Doe, El-Emary, Morgan, Schechter and Wade: 1976; Wade et al: 1977). For such surfactants it will be necessary to specify the concentration.

The previous discussion seems to indicate that a reasonable approximation of a ternary diagram cannot be obtained for such multicomponent systems. While it may not be possible to, accurately construct the phase boundary lines, it is perfectly possible to define the type of diagram and to estimate most of its characteristics provided that:

1) the water vertex represents a sodium chloride aqueous solution,
2) the oil vertex represents an alkane or an hydrocarbon phase in general,

3) the surfactant vertex will include a surfactant or surfactant mixture, but excludes any alcohol. If the surfactant behavior is concentration dependent, the overall concentration of surfactant will be kept constant.

The main purpose of the pseudo-ternary diagram is to provide a convenient way of interpreting the transitions $I \rightarrow III \rightarrow II$ or inverse as a function of the change of formulation variables.

**VII.3. EFFECT OF THE FORMULATION VARIABLES ON THE OBSERVED PHASE BEHAVIOR**

**VII.3.1. System variables**

The behavior of a given system depends upon the values of the independent variables which define the state of the system. These variables can be classified into three groups: formulation variable, external variables and position variables.

The formulation variables are those which define the type of compound represented at each vertex of the ternary diagram; alcohol type and concentration are also included as formulation variables, keeping in mind that a quaternary diagram could be needed to take it fully into account.
The formulation variables are:

1) Surfactant structure and composition if it is a mixture and its concentration if its properties are concentration dependent.

2) Salinity of the aqueous phase.

3) Oil structure, i.e., alkane carbon number (ACN) for the alkane series of the EACN value for other hydrocarbon or for mixtures.

4) Alcohol type and concentration.

The only external variable to be considered here will be the temperature. Pressure effects have not been measured and are probably small since chemical potentials are not very sensitive to pressure.

Finally the position variables refer to the position on the ternary diagram of the point representing the overall composition of the system; there are two independent variables which may be chosen as (6) the water/oil ratio (WOR), i.e., the relative amount of water and oil, and (7) the surfactant concentration.

The experimentally observed behavior depends on the type of ternary diagram (controlled by formulation and external variables) and on the position of the point representing the composition of the system on the ternary diagram (position variables). The effect of the position variables will be analyzed later on; it is generally small compared with the effects of the other variables, provided that the selected representative point lies in the multiphase region. Typically used values were WOR = 4 and surfactant concentration about 1% weight.
The following paragraph describes the observed qualitative variation of the phase behavior upon changing one of the formulation variables and holding all the other variables constant. Some of the following trends have been reported in recent articles (Baviere: 1976; Hsieh and Shah: 1976; Reed and Healy: 1976; Puerto and Gale: 1976; Wade et al: 1977; Salter: 1977; Jones and Dreher: 1976).

VII.3.2. Salinity scan

A salinity scan is obtained by preparing a series of test tubes having an identical composition except the concentration of sodium chloride in the aqueous phase. Table VII.1. shows a typical experimental procedure; in the illustrated example "x" ml of 8 gpdl brine determines the final salinity of the aqueous phase before contacting with oil; by changing "x" step by step, a complete salinity scan can be obtained.

Observation of the test tube series will allow classification of the phase behavior as pertaining to one of the three types of diagram: I-H, II-L or III-M; the occurrence of type III-H and III-L (see Figure VII.2.) will be detected by observing a large phase swelling but will qualitatively be associated with types I-H and II-L respectively.

---

2By definition salinity, surfactant concentration and alcohol concentration as indicated on the graphs refer to gram of NaCl, surfactant and alcohol per deciliter of aqueous phase, which is taken as total volume minus oil volume, and in most cases represents 80% volume of the total unless otherwise stated.
Table VII.1

Typical experimental procedure

1) Pour 4 ml of an aqueous solution containing 2 gpdl surfactant and 6 gpdl alcohol in a test tube.

2) Add X ml of a brine containing 8 gpdl NaCl.

3) Add 4 - X ml of distilled water and shake slightly the 8 ml of resulting aqueous phase, the composition of which is:
   1 gpdl surfactant + 3 gpdl alcohol + X gpdl NaCl.

4) Add 2 ml of a given alkane (WOR = 4).

5) Close the test tube and equilibrate it at constant temperature: kick it upside down twice every 2 hours for 6 hours, then repeat the next day and leave it to settle at least 24 hours before reading.
When salinity of the aqueous phase is increased, a transition \( I \rightarrow III \rightarrow II \) is observed (see Table VII.2.) if the proper range is studied. In some cases a direct \( I \rightarrow II \) transition is observed with no apparent intermediate middle phase formation, i.e., type III-M behavior; this is either because the salinity increments from one test tube to the next are too large, or because no three-phase region exists for this set of position variables. There is thus a critical region (or value) of the salinity for which either type III-M behavior or direct \( I \rightarrow II \) transition occurs. However it should be noted that the transition may be out of the feasible salinity region for certain extreme cases, especially with no alcohol present. The surfactant may precipitate at a salinity which is not high enough to produce the transition. This may be corrected by using a proper alcohol. On the other hand the surfactant may be so insoluble in brine that the salinity due to its counterions is sufficient to produce type II behavior even with no added sodium chloride.

Referring to the status of the surfactant, an increase in salinity of the aqueous phase produces a \( H \rightarrow (M) \rightarrow L \) transition.

**VII.3.3. Alkane scan**

The procedure is the same as the one mentioned in Table VII.1., but this time the oil is changed from tube to tube at step 4. Integer ACN values are obtained by using the liquid alkanes and intermediate values are provided by linear mixing of the nearest alkanes according to the EACN concept (Cash et al: 1977).
Table VII.2. Transition due to increasing salinity

<table>
<thead>
<tr>
<th>Surfactant (gpd/l)</th>
<th>Alcohol (gpd/l)</th>
<th>Oil</th>
<th>ACN</th>
<th>Salinity gpd/l in aqueous phase for:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Type I-H</td>
</tr>
<tr>
<td>TRS 10-80 (1)</td>
<td>Sec-C4 (3)</td>
<td>7</td>
<td></td>
<td>+ 0.85</td>
</tr>
<tr>
<td>TRS 10-80 (1)</td>
<td>N-C4 (1)</td>
<td>12</td>
<td></td>
<td>+ 1.2</td>
</tr>
<tr>
<td>C₉ABS (0.5)</td>
<td>Iso-C5 (3)</td>
<td>6</td>
<td></td>
<td>+ 1.3</td>
</tr>
<tr>
<td>C₉ABS (0.5)</td>
<td>Iso-C5 (3)</td>
<td>11</td>
<td></td>
<td>+ 1.8</td>
</tr>
<tr>
<td>C₁₅ABS (0.5)</td>
<td>Sec-C4 (3)</td>
<td>11</td>
<td></td>
<td>+ 2.4</td>
</tr>
<tr>
<td>C₁₂OXS (1)</td>
<td>Sec-C4 (3)</td>
<td>14</td>
<td></td>
<td>+ 2.8</td>
</tr>
<tr>
<td>C₁₂OXS (1)</td>
<td>Iso-C5 (2)</td>
<td>11</td>
<td></td>
<td>+ 0.35</td>
</tr>
<tr>
<td>C₁₂OSO₃ (1)</td>
<td>Iso-C5 (5)</td>
<td>10</td>
<td></td>
<td>+ 2.2</td>
</tr>
<tr>
<td>Amoco 151 (1)</td>
<td>Sec-C4 (3)</td>
<td>13</td>
<td></td>
<td>+ 1.0</td>
</tr>
</tbody>
</table>

Notes: WOR = 4; ABS: alkyl benzene sulfonate;
OXS: alkyl ortho-xyléne sulfonate;
C₁₂OSO₃: dodecyl sulfate;
Alcohols: C4 = butanol, C5 = pentanol.
Table VII.3 shows that increasing ACN usually produces a II → III → I transition. A direct II → I transition may in some cases be observed for the same reasons pointed out in the previous paragraph.

Referring to the surfactant status, an ACN increase would produce a L - (M) ~ H transition, if any.

VII.3.4. Alcohol scan

All tested alcohols do not produce the same transition. Lower molecular weight alcohols (methanol, ethanol and propanols) tend to produce a II → III → I transition as their concentration is increased. However the effect is not very pronounced.

On the other hand, N-butanol and higher molecular weight alcohols produce a I → III → II transition with increasing concentration (see Table VII.4.). As a general rule the higher the molecular weight of the alcohol and the lesser its branching, the more rapid the transition with increase of alcohol concentration.

VII.3.5. Surfactant structure

Table VII.5 shows the transition observed for the alkyl orthoxylene sulfonate series. When the lipophilic chain length increases, the observed transition is I → III → II, which is equivalent to a change H → M → L in surfactant status.
### Table VII.3. Transition due to increasing oil ACN

<table>
<thead>
<tr>
<th>Surfactant (gpd1)</th>
<th>Alcohol (gpd1)</th>
<th>Aq. Phase salinity (gpd1)</th>
<th>Oil (E)ACN for:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Type II-L</td>
</tr>
<tr>
<td>TRS 10-80 (1)</td>
<td>Sec-C4 (3)</td>
<td>1</td>
<td>+ 6</td>
</tr>
<tr>
<td>TRS 10-80 (1)</td>
<td>Sec-C4 (3)</td>
<td>2</td>
<td>+ 9</td>
</tr>
<tr>
<td>TRS 10-80 (1)</td>
<td>N-C3 (7)</td>
<td>1</td>
<td>+ 6</td>
</tr>
<tr>
<td>Siponate (1)</td>
<td>Mixture*</td>
<td>3</td>
<td>+ 7</td>
</tr>
<tr>
<td>C9OXS Na (1)</td>
<td>Sec-C4 (3)</td>
<td>4</td>
<td>+ 5</td>
</tr>
<tr>
<td>C12OXS MEA (1)</td>
<td>Sec-C4 (3)</td>
<td>3</td>
<td>+ 9</td>
</tr>
</tbody>
</table>

*Mixture (3) Sec-C4 + (1) Iso-05

**Notes:**
- OXS = alkyl orthoxylene sulfonate;
- MEA = monoethanol amine salt;
- Alcohols: C3 = propanol, C4 = butanol.
Table VII.4. Example of transition due to "heavy" alcohol

- surfactant = 1 gpd/l C_{12}OXS MEA
- salinity of aqueous phase: 1 gpd/l
- oil ACN = 10
- WOR = 4
- Alcohol = Isopentanol

<table>
<thead>
<tr>
<th>Alcohol concentration (gpd/l) for:</th>
<th>Type I-H</th>
<th>Type III-M</th>
<th>Type II-L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~0.75</td>
<td>0.85 - 1.00</td>
<td>~1.15</td>
</tr>
</tbody>
</table>
Table VII.5. Example of transition due to surfactant structure

- **surfactants:** Alkyl orthoxylene sulfonates
- **concentration:** $4 \times 10^{-2} \text{ M}$
- **salinity:** 2 gpd/l NaCl
- **alcohol:** 3 gpd/l sec-butanol
- **WOR** = 4

<table>
<thead>
<tr>
<th>Lipophilic chain length for:</th>
<th>Type I-H</th>
<th>Type III-M</th>
<th>Type II-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_9$OXS-Na</td>
<td>C$_{12}$OXS-Na</td>
<td>C$_{15}$OXS-Na</td>
<td></td>
</tr>
</tbody>
</table>
VII.4. EFFECT OF TEMPERATURE

When the temperature is increased, the critical salinity at which three phases are observed tends to increase for anionic surfactants. An increase in temperature thus produces a transition $\text{II} \rightarrow \text{III} \rightarrow \text{I}$, and a $\text{L} \rightarrow \text{M} \rightarrow \text{H}$ change in the status of anionic surfactants.

It should be pointed out that this transition for anionic surfactants is just the opposite of the one reported for non-ionic surfactants (Saito and Shinoda: 1970; Shinoda and Kumieda: 1973; Robbins: 1976). This behavior is consistent with the variations of the solubility in water versus temperature (Anderson et al: 1976).

VII.5. EFFECT OF POSITION VARIABLES

The values of the position variables may affect the observed behavior as can be seen on Figure VII.2. However a change in formulation which produces a $\text{I} \rightarrow \text{II}$ transition is observed in the same way independent of the position variables, provided the composition of the system falls within the two-phase region.

The influence of the water/oil ratio is most important in the interpretation of type III diagrams. Different values of water/oil ratio lead to a shift in the observed transition position; however this is a small change when compared with the effect of formulation variables (see Section IX.3.5.). On the other hand the surfactant concentration must be kept low enough to insure multiphase behavior.
In this study the surfactant concentration is generally selected in the 0.2-1 gpd/l range, i.e., lower than the observed height of the multiphase region; the oil volume is taken to be 20%, which leads to a WOR in the vicinity of 4.

Table VII.6 recapitulates the qualitative changes in phase behavior of anionic surfactants when formulation, external and position variables are modified.
<table>
<thead>
<tr>
<th>Scanned variable (INCREASE)</th>
<th>Ternary diagram transition</th>
<th>Surfactant status change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>I → III → II</td>
<td>H → M → L</td>
</tr>
<tr>
<td>ACN</td>
<td>II → III → I</td>
<td>L → M → H</td>
</tr>
<tr>
<td>Temperature</td>
<td>II → III → I</td>
<td>L → M → H</td>
</tr>
<tr>
<td>High MW Alcohol</td>
<td>I → III → II</td>
<td>H → M → L</td>
</tr>
<tr>
<td>Surfactant HC chain length</td>
<td>I → III → II</td>
<td>H → M → L</td>
</tr>
<tr>
<td>WOR</td>
<td>NA</td>
<td>H → M → L</td>
</tr>
<tr>
<td>Surfactant concentration</td>
<td>NA</td>
<td>Complex</td>
</tr>
</tbody>
</table>
Chapter VIII
OPTIMUM FORMULATION FOR PHASE BEHAVIOR

VIII.1. CONCEPT OF OPTIMUM VALUE

When $n - 1$ of the previously mentioned variables (see Table VII.6.) are held constant, and when the $n^{th}$ variable is scanned, there may be a critical value (or range) of the scanned variable for which the system exhibits three phases. Of course, in the general case where the $n - 1$ variables which are held constant have arbitrary values, the critical value of the scanned variable may lay out of scale, i.e. out of the accessible range of variation of this scanned variable.

In some cases, particularly at low surfactant concentration or in absence of alcohol, a transition $I \rightarrow H \rightarrow II \rightarrow L$ or inverse is observed with no apparent intermediate type $III \rightarrow M$ behavior; in this case the transition is characterized only by the surfactant status change $H \rightarrow L$ (or inverse) which corresponds to the minimum tension. The equivalence of these two cases will be discussed later on; see also a recent article (Wade et al: 1977).

This transition corresponds certainly to a structural change in the microemulsion; however little is known on microemulsion structure (Robbins: 1974a & b, 1976; Shinoda and Kunieda: 1973).
VIII.2. PROPERTY CHANGES DURING A TRANSITION II → III → I

(L → M → H)

The independent variables which can produce a II → I or a I → II transition are listed in Table VII.6. To fix the ideas, suppose property changes are going to be studied using an ACN scan, i.e., increasing the oil ACN with all other variables constant. However the whole discussion would be unchanged if increasing the ACN is replaced by:

- Increasing temperature, increasing concentration of low molecular weight alcohols.

- Decreasing salinity\(^1\), decreasing concentration of high molecular weight alcohols, decreasing surfactant lipophilic chain length.

Figure VIII.1 shows a series of ternary diagrams at increasing ACN. The ACN increments between the diagram do not correspond to a specific value, but are only arbitrarily selected to show all the steps of the transition II → III → I. As before, the diagrams are labeled according to their Winsor type (I, II or III) and the surfactant status (H, M, L). The square dot represents the composition of the tested system and the circle dots the composition of the phases in equilibrium when separation occurs into two or three phases, whichever applies.

\(^{1}\)A ternary diagram transition vs. salinity has been reported recently (Anderson et al: 1976; Nelson and Pope: 1977; Reed and Healy: 1976).
Figure VIII.1. Ternary diagram changes with increasing oil alkane carbon number (ACN).
Figure VIII.1. (Continued)
This sequence of diagrams allows the collection of a large amount of information about the change of the partition coefficient and the solubilization parameters.

The partition coefficient of the surfactant is defined as the ratio of its concentration in oil phase to its concentration in aqueous phase, whether a middle phase is present or not.

\[ p = \frac{C_s^O}{C_s^W} \]

The solubilization parameters have been defined by Reed and Healy (1976); the oil solubilization parameter \( V_O/M_S \) is the volume of oil \( V_O \) solubilized in the microemulsion phase (surfactant rich phase) per unit mass of surfactant in that phase. The water solubilization parameter \( V_W/M_S \) is the volume of water \( V_W \) solubilized in the microemulsion phase per unit mass of surfactant in that phase.

Let's follow the sequence of diagrams when oil ACN increases with all other variables held constant, and determine the available information which can be obtained from the phase diagram.

Diagram II-L represents a state in which an almost pure water phase is in equilibrium with an oil phase which contains most of the surfactant and a small amount of solubilized water. The microemulsion phase is the oil phase, the partition coefficient has a high value and \( V_W/M_S \) a rather low value (if the plait point is near the w vertex, as in the illustrated case).
For a slightly higher ACN, diagram III-L is a type III diagram; however the point representing the composition of the system is still in a two-phase region. The aspect of the system is similar to the previous case with the difference that now the micro-emulsion oil phase contains a sizeable amount of solubilized water. The partition coefficient is still high, and the solubilization parameter $V_w/M_s$ is larger than the previous case. This increase of water solubilization in the oil phase microemulsion is referred to as swelling.

In the next diagram, labeled III-M(a), the point representing the composition of the system is now in the three-phase region. The system separates into three phases: an almost pure water aqueous phase, an almost pure oil hydrocarbon phase and a middle phase microemulsion. No information can be obtained on the partition coefficient value in three-phase systems unless the bottom tie line slope is known. From the position of the point representing the microemulsion middle phase it can be said that $V_w/M_s$ has still increased but that the middle phase contains more oil than water; thus $V_o/M_s$ has a large value, greater than $V_w/M_s$.

With increasing ACN, diagram III-M(b) is obtained. The system separates also into three phases, but in this case the middle phase microemulsion contains roughly the same amount of oil and water. Thus the two solubilization parameters are approximately equal, $V_w/M_s$ having increased and $V_o/M_s$ having decreased.

The next diagram, III-M(c) is the mirror image of III-M(a); the system separates into three phases, but now the middle phase contains more water than oil. $V_w/M_s$ has still increased, while $V_o/M_s$ has decreased.
With increasing ACN, diagram III-H is obtained; this is a type III diagram but the point representing the composition of the system lays in a two-phase region. The system separates into two phases: an almost pure oil hydrocarbon phase and an aqueous phase which contains most of the surfactant and still some solubilized oil. Thus the partition coefficient is very small and the oil solubilization $V_o/M_s$ has still decreased.

The last diagram I-H is the mirror image of the first one. It is a type I diagram with the system separating into a surfactant rich aqueous phase containing a very small amount of solubilized oil, and an almost pure oil hydrocarbon phase. The partition coefficient is still low and the oil solubilization has decreased to an almost zero value.

The observation of this sequence of diagrams through a II-L $\rightarrow$ I-H transition has shown that qualitatively the partition coefficient is expected to change from a high value (II-L) down to a low value (I-H), and that the solubilization parameters have a similar value in the intermediate type III diagram.

Experimental measurements are required to know the quantitative changes as well as other properties of interest like the interfacial tension.
VIII.3. ACN SCAN - TYPICAL EXPERIMENTAL RESULTS

The following results reported for TRS 10-80 petroleum sulfonate are typical of the behavior of all tested sulfonates.

Figure VIII.2 shows the effect of increasing the ACN in a series of test tubes, together with the value of the solubilization parameters. Non integer values of ACN are obtained by linear mixing of the nearest alkanes according to the EACN concept.

As expected from the previous discussion, the solubilization parameters curves show the swelling effect on both sides of the three-phase region and their crossing point, which corresponds to an equal volume of water and oil in the middle phase, occurs near the center of the middle phase range.

Figure VIII.3 shows the value of the interfacial tension and the partition coefficient for the same system and ACN scan. The interfacial tension curve is composed of two branches. The left branch, labeled $\gamma_{mw}$, corresponds to the tension between the microemulsion and the excess water phase; when three phases are present it is the tension between the middle phase and the lower (aqueous) phase. The right branch, labeled $\gamma_{mo}$, corresponds to the tension between the microemulsion and the excess oil phase; when three phases are present it is the tension between the middle phase and the upper (hydrocarbon) phase.

$^2$See Reed and Healy (1976).
Figure VIII.2. Phase behavior and Solubilization parameters for an ACN scan.
Figure VIII.3 Partition coefficient (oil/water) and interfacial tension versus alkane carbon number.
Figure VIII.3 shows that the two interfacial tension curves cross near the center of the three-phase region; this low tension state is thus also a characteristic of the three-phase region (Reed and Healy: 1976; Wade et al: 1977).

Figure VIII.3 shows also that, as expected from the previous discussion (Section VIII.2.), the partition coefficient changes from a very high value (at low ACN for cases II-L or III-L) down to a very low value (at high ACN for cases III-H or I-H).

However the most interesting fact is that the partition coefficient is near unity in the entire three-phase region; in other words, when there is a surfactant rich middle phase, the concentration of surfactant in the excess water and excess oil phases are roughly equal.

TRS 10-80 is a commercial petroleum sulfonate which is a mixture of several components; thus the UV absorbance technique used to estimate the concentration may lead to inaccuracies if fractionation occurs. i.e., if different fractions of the mixture partition preferentially in different phases; for example the high molecular weight fraction may partition into oil while the low molecular weight fraction remains in the aqueous phase. Figures VIII.4 and VIII.5 show the partition coefficient vs. ACN for the same surfactant but for different salinities and alcohol concentrations. The partition coefficient is also found to be near unity when three phases are present. Table VIII.1 shows that this result is also valid for a variety of alkyl aryl sulfonates, from isomerically pure compounds to commercial products with a largely spread molecular weight distribution.
Figure VIII.4. Partition coefficient (oil/water) versus alkane carbon number at varying salinity.
Figure VIII.5. Partition coefficient (oil/water) versus alkane carbon number at various concentrations of isopentanol.
Table VIII.1. Partition coefficient values for 3-phase systems

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Salinity</th>
<th>Alcohol</th>
<th>Oil ACN</th>
<th>Scanned variable</th>
<th>Partition coefficient ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRS 10-80 (1)</td>
<td>1.0</td>
<td>Sec-C4 (3)</td>
<td>6.5-7.5</td>
<td>oil ACN</td>
<td>0.2, 1-2, 20</td>
</tr>
<tr>
<td>TRS 10-80 (5)</td>
<td>1.5</td>
<td>Sec-C4 (3)</td>
<td>9-10.5</td>
<td>oil ACN</td>
<td>0.2-0.4, 1.1-1.8, 25-40</td>
</tr>
<tr>
<td>TRS 10-80 (1)</td>
<td>1.0</td>
<td>Sec-C4 (3)+Iso-C5 (0.6)</td>
<td>10-12</td>
<td>oil ACN</td>
<td>0.2, 1.1-2, 20-30</td>
</tr>
<tr>
<td>TRS 10-80 (2)</td>
<td>1.0</td>
<td>Sec-C4 (3)</td>
<td>8-9</td>
<td>oil ACN</td>
<td>0.2-0.3, 0.9-1.1, 15-20</td>
</tr>
<tr>
<td>Siponate (1)</td>
<td>3.0</td>
<td>Sec-C4 (3)+Iso-C5 (1)</td>
<td>9-12</td>
<td>oil ACN</td>
<td>0.01, 0.8-1.0, 120-150</td>
</tr>
<tr>
<td>C12ABS-Na (1)</td>
<td>1.9-2.4</td>
<td>Sec-C4 (3)+Iso-C5 (1)</td>
<td>9</td>
<td>salinity</td>
<td>0.01, 0.6-1.0, 140-160</td>
</tr>
<tr>
<td>S(pEt)C10S* (1)</td>
<td>1.1-1.2</td>
<td>Sec-C4 (3)</td>
<td>8</td>
<td>salinity</td>
<td>0.04-0.05, 0.8-1.0, 60-70</td>
</tr>
</tbody>
</table>
The partition coefficient change (from II-L to I-H) varies between two and four orders of magnitude, with the largest variation corresponds to the purest surfactant (Vasquez: 1977). Then a near unity partition coefficient may be taken as a characteristic property at transition point just as equal solubilization parameters or low interfacial tension. One of the consequences of the near unit value of the partition coefficient between excess oil and excess water phase is that the bottom tie line is nearly horizontal. This allows a further comparison between the two cases: (1) at high surfactant concentration and with alcohol present the transition II-L → III-M → I-H occurs, while (2) at low surfactant concentration the transition II-L → I-H occurs without apparent intermediate type III-M behavior. Since type I and type II diagrams have tie lines exhibiting opposite slope, there must be some point during a direct II → I transition where the slope of the tie lines changes sign, because of continuity in the variation. This point would correspond to a reversal of the status of the surfactant, i.e. a large change of the partition coefficient value. This transition has been found to occur in an extremely narrow range of the scanned variable as shown by the sharpness of the interfacial tension minimum.

A direct II-L → I-H transition for low surfactant concentration may be explained considering that the point representing the composition of the system lays in the bottom two-phase region located below the bottom tie line.
However this explanation is not satisfactory for systems containing 1 or 2 gpdl of surfactant. For such cases the three-phase step may be overlooked because it occurs over an extremely small range of variation of the scanned variable (see Tables VII.2. and VII.3.); however in the absence of alcohols most of the systems exhibit some kind of three-phase behavior where the transition II-L → I-H occurs, but the "third phase" often appears as a precipitate or a gel rather than a microemulsion. If in such a case the test tubes are shaken, an extremely viscous macroemulsion is produced and does not coalesce under normal gravity for months; centrifugation produces the coalescence of the emulsion but also precipitates the surfactant near the oil-water interface. In the absence of alcohol the intermediate stage of a L - H transition cannot be studied accurately because of the formation of a solid precipitate and thus brings into question the validity of the equilibration procedure. There is thus no evidence that a two-phase region with horizontal tie lines might exist as an intermediate during a direct II → I transition.

VIII.4. SALINITY SCAN - TYPICAL EXPERIMENTAL RESULTS

It has already been seen in Section VII.3 that an increasing salinity of the aqueous phase produces a transition I-H → III-M → II-L i.e., opposite to the transition due to an increase in ACN.

Figure VIII.6 shows the observed typical phase behavior and solubilization parameters variation when salinity of the aqueous phase is scanned.
Figure VIII.6. Phase behavior and Solubilization parameters for a salinity scan.
This behavior is similar to the one obtained from Figure VIII.2 if ACN is decreased (from right to left).

Figure VIII.7 shows the interfacial tension and the partition coefficient variations versus salinity, for the same system. Again the observed variation is similar to the one shown in Figure VIII.3 if ACN is decreased.

Figure VIII.4 showed the partition coefficient variations versus ACN for different salinities. Figure VIII.8 shows the partition coefficient variations versus salinity for a similar system, for different hydrocarbons.

These data demonstrate that there is an equivalence between the two kinds of unidimensional scans; then the three-phase region may be found either by an ACN scan at constant salinity or by a salinity scan at constant ACN. Scanning both variables (all others held constant) allows the definition of a bidimensional optimal region in the ACN-salinity subspace for each set of values of the remaining variables. Figure VIII.9 shows these bidimensional optimal regions for two different surfactants.

In principle, bidimensional subspaces could be determined for any pair of formulation and external variables mentioned in Table VII.6. However for practical purposes (see experimental procedure in Table VII.1.) salinity scans and ACN scans are preferred. Furthermore, since the salinity scan allows a continuous variation of the scanned variable, there is then a strong incentive to explore the salinity-ACN subspace by varying the salinity for different hydrocarbons.
Figure VIII.7. Interfacial tension and Partition coefficient versus salinity.
Figure VIII.8. Partition coefficient versus salinity for various oils in contact with the same surfactant/alcohol system.
Figure VIII.9. Three-phase region in the Salinity-ACN subspace for two different systems.
There is also another reason to select the salinity-ACN subspace as a way to record the data. In practical field cases the crude oil EACN will be fixed as well as the salinity of the reservoir connate water (although it could be eventually altered by a preflush). Hence the problem will be to bring the three-phase region to scale by acting on the remaining controllable formulation variables e.g., surfactant structure and alcohol type and concentration.

VIII.5. PROPERTIES OF THE THREE-PHASE REGION

Before pursuing the three-phase region in higher dimensional subspaces, it is convenient to analyze the properties of the three-phase region, especially those of the middle phase microemulsion.

VIII.5.1. Middle phase composition versus position variables

As discussed previously, the idealized pseudo-ternary diagram qualitatively represents all of the observed transitions. However, the question is to know how quantitative it is. We know that the phase boundaries cannot be defined accurately. Nevertheless for our purpose the most important thing to know is whether the middle phase representative point is actually invariant when the position variables are changed to sweep the whole three-phase region.

Figure VIII.10 shows the volume of obtained middle phase
Figure VIII.10 Volume of middle phase versus weight of surfactant in test tube (9 ml of aqueous phase + 2 ml of oil).
versus the amount of surfactant in the test tube; since the excess water and excess oil contain only negligible quantities of surfactant, the amount of surfactant in the middle phase is practically equal to the amount in the tube. The formulation of this system corresponds to the center of a middle phase region previously mentioned; the actual surfactant concentration in the system is changed from 0.2 to 3.5 gpd/l. In this case the middle phase volume is found to be proportional to the amount of surfactant, i.e., the concentration of the surfactant in the middle phase is constant. Such a behavior is found for most systems in a certain range of concentration; however at low concentration deviation may occur because of the so-called "concentration shift" to be considered later on.

The other parameter to be checked to secure the invariance of the middle phase composition is its water-oil content. Figure VIII.11 shows the percentage of oil and water for the series discussed previously; the composition of the middle phase hence seems reasonably invariant when the surfactant concentration is changed in the considered range. When the water/oil ratio is changed, the middle phase composition is found to remain relatively constant for the range of composition 10%-50% oil (WOR = 9 - 1); however it may change more than 20% if lower values of WOR are considered (see Section IX.3.5).

The middle phase representative point has thus a reasonably constant composition when obtained from different position variables values.
Figure VIII.11. Volumetric composition of middle phase versus weight of surfactant in test tube (9 ml of aqueous phase + 2 ml of oil).
It is thus possible to determine with accuracy the type of diagram; however, the inaccuracy (10-20%) is large enough to make a precise definition of the boundaries of the multiphase region difficult, if not impossible.

**VIII.5.2. Middle phase composition versus formulation variables**

As may be seen from Figure VIII.9., it is possible, by changing both ACN and salinity according to an adequate rule, to move inside the three-phase region. It is also possible to do so by changing any two of the formulation variables.

Figure VIII.12 shows the volume of middle phase per gram of surfactant versus the ACN of the oil for the same surfactant but at different alcohol and salinity. Each point represents a value obtained in the middle of a scan. There is some scatter, but there is an evident downward trend with increasing ACN. In other words, the concentration of the surfactant in the middle phase tends to increase with ACN (see Figure, VIII.13.). It may then be said as a general rule for the numerous systems we have checked that:

1) At constant alcohol concentration, when both ACN and salinity are increased to maintain three-phase behavior, the concentration of the surfactant increases in the middle phase.

2) At constant salinity, when both ACN and high molecular weight alcohol concentration are increased to maintain three-phase behavior, the concentration of the surfactant increases in the middle phase.

3) At constant ACN, when high molecular weight alcohol
Figure VIII.12. Middle phase volume per gram of surfactant for various systems.
Figure VIII.13. Surfactant concentration in middle phase for various systems.
concentration is increased and salinity decreased accordingly to maintain three-phase behavior, the concentration of the surfactant in the middle phase increases as Figure VIII.14 shows. The concentration of the surfactant in the middle phase has a practical importance as a measurement of the multiphase region height (Reed and Healy: 1976; Salter: 1977; Baviere: 1976).

The other characteristic of the middle phase is its oil and water composition. When the ACN is increased to produce a II → I transition (see Figure VIII.1.), the middle phase representative point moves from left to right, i.e. from a high concentration in oil to a high concentration of water. The critical value of the scanned parameter may be defined by:

- The center of the ACN range for which three phases are observed.
- The center of the salinity range (if a salinity scan is carried out).
- The crossing point of the solubilization parameter curves, i.e. equal amounts of oil and water in the middle phase.
- The crossing point of the two tension curves or the minimum tension.

When the middle phase range is small, all these points practically coincide. However they are different when the middle phase range is relatively wide. Figure VIII.15 shows that the center of the ACN range does not correspond always to an equal solubilization of oil and water in the middle phase.
Figure VIII.14. Middle phase volume per gram of surfactant versus concentration of alcohol.
Figure VIII.15. Volume fraction of oil in middle phase for various systems versus ACN at center of middle phase ACN range.
VIII.5.3. Concentration shift

It has been found that when the interfacial tension is plotted versus ACN, the alkane giving minimum tension ($n_{\text{min}}$) may tend to change with the concentration of surfactant (Wade et al: 1977). The so-called concentration shift seems to be related to the purity of the surfactant; isomerically pure surfactants do not produce a concentration shift, while petroleum sulfonates do (Vasquez: 1977). As a general rule, the preferred ACN tends to decrease when the concentration of surfactant increases.

The equivalent experiments for three-phase behavior were carried out for a surfactant, TRS 10-80, which is known to exhibit a large concentration shift (Wade et al: 1977).

Figure VIII.16 shows the partition coefficient curves versus oil ACN for several concentration of TRS 10-80. The concentration shift is illustrated on Figure VIII.17 where the ACN range for three-phase behavior is plotted versus the concentration of surfactant. Figure VIII.18 shows the salinity range for three-phase behavior versus the concentration of surfactant. These three figures show that the concentration shift observed for three-phase occurrence is identical to the one found for low tension; this is a further corroboration of the equivalence of the two phenomena.

The change of surfactant properties with concentration may be explained by a mixed micelle phenomenon. For the sake of simplicity let us consider a binary mixture of two surfactants; surfactant (1) is the more water soluble, and will be called the lighter; surfactant (2) is the less water soluble and will be called the heavier.
Figure VIII.15. Partition coefficient at different surfactant concentrations, showing preferred ACN shift.
Figure VIII.17. Change of preferred ACN (for 3-phase formation) versus surfactant concentration in aqueous phase (9/11).
Figure VIII.18 Change of salinity for 3-phase formation versus surfactant concentration in aqueous phase.
Trogus (1977c) has recently shown that micelle and monomer concentration and composition depend on the total concentration. Figure VIII.19 shows the critical micelle concentration of a mixture and the composition of the micellar phase (Y<sub>1</sub>) versus component 1 mole fraction (X<sub>1</sub>). Let us assume that the surfactant mixture contains 50% (molar) of each component.

At very low total concentration (L), say at CMC, the surfactant is in the monomer form, thus X<sub>1</sub> = 0.5 and Y<sub>1</sub> is very close to zero, i.e., the first micelles to be formed contain mostly component 2.

On the other hand, at high total concentration (H) most of the surfactant is present in the micelles and thus Y<sub>1</sub> = 0.5. In this case X<sub>1</sub> is close to unity, i.e., the monomer contains mostly, component 1.

An increase in surfactant mixture total concentration hence produces an increase in both X<sub>1</sub> and Y<sub>1</sub> that is both micelles and monomer get richer in the lighter component. As a consequence the surfactant mixture behaves as a lighter surfactant when the total concentration increases; its n<sub>min</sub> and preferred ACN for three-phase behavior decrease, while its optimal salinity for three-phase behavior increases.

The critical parameter, the change of which produces the shift is likely to be the micelle composition since no middle phase nor low tension is observed below CMC.
Figure VIII.19 Mixture CMC and mole fraction of lighter component in micelles \((Y_1)\) versus mole fraction of lighter component in monomer \((X_1)\) for a binary mixture of surfactants. (After Trogus: 1977c).
Figure VIII.20 shows the concentration shift of optimum salinity for various mixtures of nonyl and pendadecyl-orthoxyTene sulfonates; the maximum shift seems to happen with an equimolar mixture.

VIII.6. DEFINITION OF AN OPTIMUM PHASE BEHAVIOR CRITERION

In practice it is difficult to handle calculations and to attempt to find a numerical correlation for a variable which exhibits a range of values instead of a single one. Hence it is advantageous to define one single value (among the range of values of the scanned variable which gives three-phase behavior) as the optimum value.

Different criteria are available, depending upon the scanned variable and property or transition considered important. The following discussion shows the advantages and disadvantages of the different available criteria.

VIII.8.1. Solubilization parameters

It has been seen that the solubilization parameter curves cross within the three-phase region. At this point the middle phase contains exactly the same proportion of oil and water, i.e., is represented by a point exactly on the vertical axis of symmetry of the ternary diagram. This criterion is attractive because it represents exactly the intermediate state between type I and type II diagrams. However it can be used only if the solubilization parameters can be measured accurately.
Figure VIII.20. Concentration-shift of salinity for three-phase behavior (bars) for several surfactant mixtures.
If the volume of the obtained middle phase is small, it is not possible to measure with precision the amount of solubilized water or solubilized oil since these are obtained as a small difference between two large volume readings. The method would thus apply only at relatively high concentration of surfactant, say in the 1% wt range and above.

This is a very serious limitation which cannot be ameliorated unless large volume test tubes, say 100 ml and up, are used; if so the amount of chemical spent might reach prohibitive levels.

However this criterion can be used as a secondary standard. Several authors have referred to an optimum salinity or a preferred ACN on this basis (Reed and Healy: 1976; Shah et al: 1977; Puerto and Gale: 1976; Thurston, Salager and Schechter: 1977).

**VIII.6.2. Interfacial tension(s)**

Another criterion is the interfacial tension minimum (apparently direct transition I ↔ II) or the crossing point of the $\gamma_{mw}$ and $\gamma_{mo}$ curves.

It is relatively easy to measure the interfacial tension between two fluids having a relative difference of density of 10% or more. As mentioned elsewhere (Thurston, Salager and Schechter: 1977) the density of the middle phase microemulsion in general varies linearly with its oil/water composition. In some cases the density difference is so small that no accurate measurement of the interfacial tension can be obtained even with a spinning drop tensiometer.
As a general rule, it is extremely difficult to obtain accurate values of the interfacial tension between the microemulsion middle phase and the excess oil phase (Ymo) near the minimum. Hence the crossing of the interfacial tensions curves is not a very good criterion for three-phase systems.

For two-phase systems, it is relatively easy to obtain accurate measurements of the interfacial tension. At very low surfactant concentration the tension minimum turns out to be the uniquely available criterion. At high surfactant concentration and direct I → II transition (such as with no alcohol), the equilibration of a microemulsion oil phase and an excess water may become difficult if solid surfactant precipitates at the interface.

VIII.6.3. Center of ACN region for three-phase behavior

When an ACN scan is performed, a certain range of value leads to the formation of three phases. The center of the ACN range can be taken as the optimum criterion. However there are three objections to that choice. First, the ACN scale is not continuous, and obtaining intermediate non-integer values by the mixing of hydrocarbons may lead to error if fractionation occurs.

The second objection is that the alkane scale is limited to those that are liquid at the temperature of interest, i.e. ACN from 5 to 16 at room temperature. Using the EACN concept may allow EACN values ranging down 0 with alkyl benzenes, but at the expense of some inaccuracies (Cayias, Schechter and Wade: 1976; Vasquez: 1977).
The third reason was discussed earlier (Section VIII.5.2.). The center of the ACN range does not correspond exactly to the equal oil-water solubilization point or to the minimum tension point; actually the arithmetic ACN average seems to be higher than the value obtained from the other criteria. This is consistent with the intuitive feeling that the ACN scale is not linear, i.e., that whatever the hydrocarbon property responsible for phase behavior, it is likely to change more between pentane and hexane than between pentadecane and hexadecane.

VIII.6.4. Unit partition coefficient

Interpolation between the nearest type II-L or III-L value and the nearest type I-H or III-H value will allow the location of the scanned variable value at which the interpolation cord crosses the unit value. However this method is not accurate for wide three-phase regions because it is not known whether the partition coefficient scale should be arithmetic or logarithmic, and also because the actual value of the partition coefficient may not be exactly unity (particularly for mixtures).

VIII.6.5. Center of salinity scan

As for the ACN scan, the center of the range of salinity for which the system exhibits three phases can be taken as the optimal salinity. There is some evidence that the average salinity\(^1\)

\[^1\]The geometric average seems to be more logical from the results discussed later on. However in most practical cases there is no significant difference from the arithmetic average.
gives a better agreement with the solubilization parameters and interfacial tensions criteria than the average ACN. Furthermore, the salinity can be scanned continuously over a very large range of values.

VIII.6.6. Generalized optimum salinity

Other properties such as electrophoretic mobility (Shah et al: 1976), streaming birefringence frequency response or density (Thurston, Salager and Schechter: 1977) can be theoretically used to define an optimum value too; however these methods involve complex experiments.

According to the previous discussion the salinity is taken as the unidimensional scan variable and the optimum salinity $S^*$ is defined as (whichever applies):

- The geometric average of the range of salinity for which the system exhibits three phases.

- The salinity at which the interfacial tension is minimum for systems which do not exhibit an apparent three-phase behavior during an I ↔ II transition.

The optimal salinity $S^*$ will be expressed in gram of NaCl per 100 milliliters of aqueous phase (gpdl), an unit almost equal to % weight.
IX.1. BIDIMENSIONAL CORRELATION: $S^\ast$-ACN

By performing a series of salinity scans for different alkanes (at all other variables held constant), a bidimensional cut of the three-phase region is obtained. Figure IX.1 shows a typical three-phase region in a Salinity-ACN subspace. As defined in the previous chapter, the optimum salinity $S^\ast$ is taken as the average salinity for three-phase behavior at constant ACN.

By changing one or more of the parameters the shape of the region remains approximately the same with an apparent shift. The $S^\ast$ curve is found to vary exponentially versus ACN and the salinity scale is taken as natural logarithm of the salinity expressed in gpol$^1$.

Figures IX.2 and IX.3 show the optimal salinity versus ACN for TRS 10-80 with different alcohol concentrations. The curve labeled 3 SecC4 on Figure IX.2 corresponds to the data reported in Figure IX.1 but plotted using a logarithmic salinity scale.

$^1$Of course any other logarithmic scale can be taken in base of any concentration unit.
Figure IX.1. Phase diagram Salinity-ACN, showing the optimum salinity curve $S^*$. 
Figure IX.2. Correlation ln $S^*$ vs. ACN for TRS 10-80 at different alcohol concentrations (Sec C4: sec-butanol, IC5: isopentanol).
Figure IX.3. Correlation $\ln S^*$ vs. ACN for TRS 10-80 at different alcohol concentrations (NC5: n-pentanol).
Two important facts are readily deduced from the observation of these figures:

1) The in S*-ACN correlations for three-phase behavior are straight lines.

2) These straight lines have the same slope, whatever the alcohol type and concentration\(^2\); this is a first clue that there is a chance to separate the effect of the variables.

Hence it can be said that for TRS 10-80 the correlation between S* and ACN for optimum three-phase behavior is:

\[
\ln S^* = K (ACN) + ... \\
\]

where K is the slope and the dots represent terms which depend upon all other variables, particularly alcohol type and concentration.

If this relationship holds for TRS 10-80, it is of interest to determine if it holds for other alkyl aryl sulfonates.

Figure IX.4 shows the correlation for Siponate DS-10, a commercial product (ALCOLAC) mostly composed of dodecyl benzene sulfonates.

Figure IX.5 deals with the monoethanol-amine salt of the dodecyl orthoxylene sulfonate, also a commercial product manufactured by EXXON.

Figure IX.6 shows the correlation for another commercial petroleum sulfonate, AMOCO 151, which has a high equivalent molecular weight.

\(^2\)Actually some light molecular weight alcohol produce a slight deviation as will be discussed later on.
Figure IX.4. Correlation ln $S^*$ vs. ACN for SIPONATE DS-10 (dodecylbenzene sulfonate, ALCOLAC) at different alcohol concentrations.
Figure IX.5. Correlation ln S* vs. ACN for the monoethanolamine salt of C12 orthoxylene sulfonate (Exxon) at different alcohol concentrations.
Figure IX.6. Correlation \( \ln S^* \) vs. ACN for AMOCO 151 alkylbenzene sulfonate.

\[
\ln S^* \quad (S^* \text{ in g NaCl / 100 ml aqueous phase})
\]

**AQUEOUS PHASE**
- 1 gpd/1 Amoco 151 ABS
- WOR = 4
- Alcohol and NaCl as indicated
The slight deviation at ACN = 7 can be corrected if the amount of sodium ions brought in by the surfactant is taken into account.

Figures IX.7, IX.8 and IX.9 concern "research grade" alkyl benzene sulfonates supplied by MONSANTO and CONOCO; from other studies these MONSANTO products have been found very pure and may be assumed to be an isomeric mixture of the indicated linear alkyl benzene sulfonate.

Figure IX.10 gathers the data for three "research grade" synthetic alkyl orthoxylene sulfonates supplied by EXXON; the corresponding alkyl chain corresponds to a propylene polymer, and there is then a methyl group lateral branching every other carbon.

These large amount of data allow us to assert that the relationship:

\[ \ln S^* = K (\text{ACN}) + \ldots \]

applies for petroleum sulfonates and alkyl aryl sulfonates and that the value of the slope K is the same for all of them; the average value being:

\[ K = 0.16 \pm 0.01 \text{ \frac{\ln (S \text{ gpd/l NaCl}) \text{ unit}}{ACN \text{ unit}}} \]

As far as the experimental method is concerned, it is necessary to remark that because of the logarithmic salinity scale the range below 1 gpd/l NaCl is very extended. However it is necessary to take several precautions when interpreting the data at low
Figure IX.7. Correlation $\ln S^*$ vs. ACN for Cg alkylbenzene sulfonate (Monsanto).
Figure IX.8. Correlation $\ln S^*$ vs. ACN for C14 alkylbenzene sulfonates (Monsanto and Conoco products).
Figure IX.9. Correlation $\ln S^*$ vs. ACN for C15 alkylbenzene sulfonate (Monsanto).
Figure IX.10. Correlation ln S* vs. ACN for three alkyl ortho-xylene sulfonates (Exxon products).
salinities; first of all it may be necessary below, say 0.5 gpdl, to take into account the
cations brought in by the surfactant itself. Furthermore, there is still a risk of error due to
residual inorganic salt such as sulfates which are often present in commercial surfactants.
It should be also noted that because of the logarithmic scale, the increment in salinity from
a test tube to the next should be taken on a relative variation basis, not an absolute one. This
study used increments comprised between 5% and 10%, i.e. a factor 1.05 to 1.10 from one
tube to the next.

IX.2. EFFECT OF ALCOHOLS

The previous figures have shown that for a given surfactant the position of the
straight line $\ln S^* = K(ACN) + \ldots$ varies with the alcohol type and concentration for a
given surfactant. The trend has been reported qualitatively by several authors (Reed and
been published.

The problem we face now is to isolate an alcohol term from the other remaining
variables. To be independent from other variables, the alcohol term should be the same for
several surfactants, different ACN and salinities.

The goal of the next step is to find an expression of the form:

$$\ln S^* = K(ACN) + f(A) + \ldots$$
where \( f(A) \) is a certain function of the alcohol type and concentration only, with the data indicating the contributions of the surfactant structure, temperature and position variables. This relationship thus implies the separation of all variables, i.e. the absence of cross terms; a large amount of data on the effect of alcohol on phase behavior show that:

1) The relationship \( \ln S^* = K(ACN) + \ldots \) holds accurately for most of the studied systems, thus corroborating the independence of \( S^* \) and ACN from other variables.

2) \( f(A) \) is independent of the surfactant system for some alcohols (pentanols and higher molecular weight alcohols), but is not for some others such as N-butanol.

The following alcohol study is based on the hypothesis that \( f(A) \) depends only upon the alcohol type and concentration. Deviation from this behavior will be apparent in the data and taken into account later on, when alcohol partitioning will be discussed.

In order to separate the alcohol effect from the surfactant structure, it is necessary to choose an origin for \( f(A) \). By definition \( f(A) \) is taken arbitrarily equal to zero when no alcohol is present. However it is not possible, in general, to observe well defined three-phase behavior in the absence of alcohol because the actual "middle phase" may range from a gel to a precipitate especially at high concentrations of surfactant and high salinity. Also the macroemulsions tend to be very persistent and equilibration is difficult to achieve.
The measurement of the minimum tension versus ACN or salinity scan might be useful in some cases; however preequilibration may be difficult to achieve with certainty and the surfactant may precipitate at high salinities. It is thus necessary to select an auxiliary standard reference which can be experimentally attained in most cases.

Figure IX.11 shows the optimal salinity at constant ACN and optimal ACN at constant salinity versus concentration of Sec-Butanol for the system 1 gpdl TRS 10-80. The deviation from zero-alcohol is very constant over a very large range of alcohol concentration. The zero alcohol value was found by interfacial tension measurement.

The deviation obtained at 3 gpdl Sec-Butanol (relative to no alcohol) is approximately the same within the accuracy of the experiments for several surfactants. Out of scale values have to be extrapolated from mixture behavior and are thus uncertain.

The average value below will be hence taken to calculate the standard zero-alcohol state whenever a direct measurement cannot be made.

\[
f (3 \text{ gpdl Sec-Butanol}) = -0.16 \pm 0.1
\]

Hence the relationship: \( \ln S^* = K (\text{ACN}) + f(A) + \ldots \) is tested by assuming that in the same conditions, but 3 gpdl Sec-Butanol:

\[
\ln S^* = K (\text{ACN}) - 0.16 +
\]

the data obtained from this reference will be labeled Ref. 3SB (for reference at 3 gpdl Sec-Butanol).

Two systems for which \( f(A) \) remains approximately independent of the surfactant structure were investigated extensively.
Figure IX.11 Variation of optimal salinity and preferred ACN for three-phase behavior versus sec-butanol concentration. (Zero alcohol data corresponds to minimum tension measurement).
Figure IX.12 shows the values of f(A) for aqueous phases containing 3 gpdl Sec-Butanol plus variable amounts of isopentanol. f(A) measures the downward shift (from its zero alcohol position) of the straight line correlation on the ln S*-ACN plot, when alcohol concentration is changed.

Figure IX.13 shows the same kind of data for isopentanol only. The correlation is also rather good. The slight scattering which is observed may be due to the fact that some values are obtained by reference to Figure IX.12 data, thus cumulating eventually two errors.

Figure IX.14 shows the values of f(A) for two mixtures of alcohols: 3 gpdl Sec-Butanol plus N-Pentanol and 3 gpdl Sec-Butanol plus N-Hexanol. The agreement is also rather good. However Figure IX.15 shows that for low molecular weight alcohol there is a large scattering; this is an indication that at least one of the hypotheses is incorrect, either f(A) depends on the surfactant or the reference at 3 gpdl Sec-Butanol is incorrect. A recent paper (Wade et al: 1977) shows that the n_min shift due to low molecular weight alcohols depends strongly on the surfactant; although the reported data use some extrapolated values (from presumed linear behavior in mixtures), the discrepancies are so large that they must be due to a new phenomenon, probably differences in alcohol partitioning.

It is here worthwhile to mention that the general effect of the alcohols versus alcohol molecular weight (at constant concentration) is ranked in the same way that the clear point efficiency (see Section VI.3.) and CMC depression (Shinoda: 1954).
Figure IX.12. $f(A)$ for 3 gpdl sec-butanol plus various concentrations of isopentanol.
Figure IX.13. $f(A)$ versus isopentanol concentration.
Figure IX.14. $f(A)$ for 3 gpdl sec-butanol plus various concentrations of n-pentanol and n-hexanol for several surfactants.
Figure IX.15. $f(A)$ versus N-butanol concentration for various systems.
IX.3. MULTIDIMENSIONAL CORRELATION FOR ALKYL ARYL SULFONATES

IX.3.1. Characterization of a surfactant: EPACNUS

After considering the first three formulation variables (S, ACN, f(A)) and assuming in first approximation that f(A) depends only on the alcohol type and concentration, it is necessary to consider the effect of the surfactant structure. Let us define the surfactant by a characteristic parameter $\sigma$ such that:

$$\ln S^* = \kappa (\text{ACN}) + f(A) - \sigma + \ldots$$

where the dots represent terms which depend only upon the temperature and WOR and are arbitrarily taken to be zero at $25^\circ C$ and WOR = 4. In these conditions the correlation for optimal phase behavior is at $25^\circ C$, WOR = 4:

$$\ln S^* = \kappa (\text{ACN}) + f(A) - \sigma$$

The parameter $\sigma$ depends only on the surfactant and its concentration (if it exhibits a concentration shift). This parameter may be easily related to a familiar concept of preferred ACN by the definition of EPACNUS (for Extrapolated Preferred ACN at Unit Salinity and no alcohol):
Figure IX.16 shows how to obtain graphically the value of EPACNUS when one experimental data for three-phase behavior is known. The different steps correspond to the calculation:

\[
\text{at unit salinity } \ln S^* = 0 \\
\text{at no alcohol } f(a) = 0 \\
\text{thus the ACN is: } EPACNUS = \frac{\sigma}{K} 
\]

where \(S^*, ACN\) are replaced by their experimental values, \(f(A)\) by the value corresponding to the alcohol type and concentration used and \(K\) by its numerical value 0.16.

Figure IX.17 shows the variation of EPACNUS versus molecular weight for the linear alkyl benzene sulfonates series (MONSANTO products); Figure IX.18 shows the same data for the alkyl orthoxylene series (EXXON products). This data shows that the EPACNUS correlates linearly with the lipophille chain length in the considered range.

Table IX.1 indicates the values of EPACNUS for all studied sulfonates; the surfactant concentration is included since for some of them the EPACNUS depends on the concentration.

Some of these data are plotted in Figure IX.19 versus presumed molecular weight of the surfactant. They show a fairly good correlation of EPACNUS versus equivalent molecular weight for the whole category of alkyl aryl sulfonates.
Figure IX.16. Graphical obtention of EPACNUS
Figure IX.17. EPACNUS versus molecular weight for alkyl benzene sulfonates (Monsanto products at 0.5 gpdI).
Figure IX.18. EPACNUS versus molecular weight for alkyl orthoxylene sulfonates (Exxon products at 1 gpdl)
Table IX.1.
EPACNUS for various petroleum sulfonates and alkyl aryl sulfonates

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant concentration in aqueous phase (WOR = 4)</th>
<th>EPACNUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRS 10-80</td>
<td>1.0 gpd/l</td>
<td>6</td>
</tr>
<tr>
<td>TRS 10-80</td>
<td>0.2 gpd/l</td>
<td>7</td>
</tr>
<tr>
<td>TRS 10-80</td>
<td>0.1 gpd/l</td>
<td>8</td>
</tr>
<tr>
<td>Siponate DS-10</td>
<td>1.0 gpd/l</td>
<td>-5.5</td>
</tr>
<tr>
<td>Amoco 151</td>
<td>1.0 gpd/l</td>
<td>10</td>
</tr>
<tr>
<td>Monsanto ABS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₉ABS</td>
<td>0.5 gpd/l</td>
<td>-9.5</td>
</tr>
<tr>
<td>C₁₁ABS</td>
<td>&quot;</td>
<td>-5.2</td>
</tr>
<tr>
<td>C₁₂ABS</td>
<td>&quot;</td>
<td>-3.2</td>
</tr>
<tr>
<td>C₁₄ABS</td>
<td>&quot;</td>
<td>1.5</td>
</tr>
<tr>
<td>C₁₅ABS</td>
<td>&quot;</td>
<td>4</td>
</tr>
<tr>
<td>Conoco C₁₄ABS</td>
<td>0.5 gpd/l</td>
<td>2.8</td>
</tr>
<tr>
<td>Exxon OXS</td>
<td>2.10⁻² Mol/lt</td>
<td></td>
</tr>
<tr>
<td>C₉OXS-Na</td>
<td>&quot;</td>
<td>-4.2</td>
</tr>
<tr>
<td>C₁₂OXS-Na</td>
<td>&quot;</td>
<td>3.5</td>
</tr>
<tr>
<td>C₁₅OXS-Na</td>
<td>&quot;</td>
<td>9.5</td>
</tr>
<tr>
<td>C₁₂OXS MEA</td>
<td>1 gpd/l</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Figure IX.19. General correlation EPACNUS versus equivalent molecular weight of studied alkyl aryl sulfonates
IX.3.2. Tridimensional correlation $S^*\text{-ACN-f(A)}$

As the bidimensional correlation $S^*\text{-ACN}$ for optimum phase behavior was represented by a line in a $\ln S^*$-$\text{ACN}$ plane, similarly the $S^*\text{-ACN-Alcohol}$ correlation can be represented by a surface in a three-dimensional space.

Let us take three axis where $\ln S^*$, ACN and f(A) are plotted respectively. The advantage of using f(A) instead of the actual concentration of alcohol is that the diagram will be then valid for any alcohol; the relationship between f(A) and the alcohol concentration can be taken into account under the form of a table or by graduating the f(A) axis with an appropriate (non linear) scale.

From the expression of the correlation:

$$\ln S^* - K(\text{ACN}) - f(A) + a = 0$$

this is the equation of a plane in $\ln S^*$, ACN and f(A) axis; this plane is shown in Figure IX.20 with the origin or coordinates at:

$$\ln S^* = 0, \text{ACN} = 0, f(A) = 0$$

the f(A) negative axis is figured to give more reality to the diagram since f(A) is negative for most alcohols of interest.

A cut by a vertical plane at constant f(A) gives an isoalcohol line which corresponds to the $\ln S^* = K(\text{ACN}) + ...$ found for the bidimensional correlation $S^*\text{-ACN}$. Some isoalcohol lines are traced on the optimum formulation plane at regular intervals. A cut at constant ACN gives an iso-ACN line which shows the bidimensional correlation $S^*\text{-f(A)}$ to be also a straight line:

$$\ln S^* = f(A) + ,,$$
Figure IX.20. Tridimensional correlation for optimum phase behavior.
Finally a cut at constant salinity gives an iso-S* line of equation:

\[ f(A) = K (\text{ACN}) + ... \]

One of the interesting features of this representation is that the optimum phase behavior plane cuts the three axis at some points related to the surfactant characteristic parameter:

- the \( \ln S^* \) axis is cut at \( \ln S^* = -\sigma \)
- the \( f(A) \) axis is cut at \( f(A) = \sigma \)
- the \( \text{ACN} \) axis is cut at \( \text{ACN} = \sigma/K = \text{EPACNUS} \)

The vector normal to the optimal formulation plane has the following components:

\[
\begin{align*}
1 & \text{ along } \ln S^* \text{ axis} \\
- K & \text{ along } \text{ACN} \text{ axis} \\
- 1 & \text{ along } f(A) \text{ axis}
\end{align*}
\]

Hence it does depend only on \( K \) which has been found to be the same for all sulfonates.

Hence different sulfonates, having different EPACNUS will have parallel optimum formulation planes such that each plane will cut the ACN axis at the corresponding EPACNUS value. This observation allows us to consider a further reduction of the dimension of the correlation.

**IX.3.3. Reduced correlation S*-RACN-f(A)**

Let us define the Reduced ACN (RACN), the difference between actual oil ACN and surfactant Extrapolated Preferred ACN at unit salinity and no alcohol.
\[ \text{RACN} = K (\text{ACN} - \text{EPACNUS}) \]

With this new variable which includes the effects of oil and surfactant structure, the correlation becomes:

\[ \ln S^* = \text{RACN} + f(A) \]

which is the equation of a plane of normal vector:

\[
\begin{cases}
1 & \ln S^* \text{ axis} \\
-1 & \text{RACN} \text{ axis} \\
-1 & f(A) \text{ axis}
\end{cases}
\]

passing through the origin of coordinates:

\[
\begin{align*}
\ln S^* &= 0 \text{ at } S^* = 1 \text{ gpd l NaCl} \\
\text{RACN} &= 0 \text{ at } \text{ACN} = \text{EPACNUS} \\
f(A) &= 0 \text{ at no alcohol}
\end{align*}
\]

which is shown in Figure IX.21. This plane represents the optimum phase behavior formulation for all sulfonates. An advantage of this representation is that it can be used directly on a two-dimension graph by drawing some kind of ternary diagram containing iso-\(S^*\), iso-RACN and iso-\(f(A)\) curves as shown in Figure IX.22 which is a plane representation of the space triangle 0AB which can be shown to be equilateral by elementary analytical geometry. Figure IX.22 diagram can be also deduced directly from the expression:

\[ \ln S^* = \text{RACN} + f(A) \]

Provided three of the four following variables: salinity, oil EACN, alcohol type and concentration, surfactant type and concentration, are fixed, the value of the fourth variable which will give an optimal phase behavior is readily determined from the reduced correlation on diagram IX.22.
Figure IX.21. Reduced correlation S-RACN-f(A).
Figure IX.22. Plane representation of reduced correlation.
IX.3.4. Temperature effects

The temperature effect is studied by equilibrating several series of salinity scans in a thermostated air bath maintained at temperatures ranging from 4°C up to 50°C. Figure IX.23 shows the variation of the optimum salinity ($\ln S^*$) versus temperature for several systems selected for covering a large range of ACN and salinity. The data show that $\ln S^*$ varies approximately linearly with the temperature. Some scattering at low temperature corresponds to systems exhibiting extremely viscous middle phase for which equilibration may not be reached in a short time.

The slope is approximately $10^{-2} \pm 2 \times 10^{-3}$ $\ln S^*$ units per °C as shown on Figure IX.24. This average value of $\frac{\ln S^*}{dT}$ is consistent with the few data (4 data points) reported elsewhere (Reed and Healy: 1976; Shah et al: 1976) and corroborate them. Let us define the temperature coefficient by:

$$a_T = \frac{d \ln S^*}{dT}\bigg|_{\text{other variables constant}} = 10^{-2} \frac{\ln S \text{ units}}{°C}$$

thus at all other variables held constant

$$\ln S^* (T_1) = \ln S^*(T_0) + a_T (T-T_0)$$

With the reference at $T_0 = 25°C$ the correlation becomes:

$$\ln S^* = K (ACN) + f(A) - \sigma + a_T (T-25)$$
Figure IX.23 Variations of $\ln S^*$ versus temperature (at all other variables constant) for various systems (alkyl aryl sulfonates/ oil/alcohol).
Figure IX.24. Local slope $d \ln S^*/dT$ at all other variables constant, versus $S^*$ for alkyl aryl sulfonates.
IX.3.5. Water-oil ratio effect

Provided that the WOR influences the position of the experimental point (representing the overall composition) on the ternary diagram, it would produce a change on optimal formulation.

The extent of that change depends on the rate of variation of the ternary diagram (I → III → II or inverse) with the scanned variable. Several systems were tested and showed that the preferred ACN changes from one to two units when the water-oil ratio passes from (90/10) to (20/80). Figure IX.25 shows a typical preferred ACN change (iPACN) with water-oil overall composition of the system, the zero value corresponding to the optimum ACN at WOR = 1.

One of the main problems in changing the WOR is to maintain all other variables constant. For extremes values the concentration in one of the phases may become very large and complications such as gel formation or severe fractionation may occur. On the other hand, the alcohol concentration may be held constant with respect to the aqueous phase volume, oil phase volume or total volume. Slightly different results are obtained according to what is selected and depending on the alcohol. High molecular weight alcohol may have an extremely strong effect. The problem is that a pseudo-ternary diagram is not well defined at extreme WOR values because the approximations which lead to it do not hold anymore.

By studying the WOR influence with an alcohol such as Secbutanol (a weak shifter) there is thus less risk to have the WOR effect masked by an alcohol concentration effect.
Figure IX.25. Optimum formulation shift versus oil percent volume or water/oil ratio.
The complete knowledge of the effect for strong shifter alcohol would require an extensive study on the alcohol partitioning.

The value WOR = 4 was taken as reference because, as shown in Figure IX.25., there is practically no effect in the range WOR = 9 - 2 (water/oil = 90/10 - 70/30) and also because it corresponds to an intermediate between a likely value for residual oil saturation and the high WOR values used in the spinning drop tensiometer measurements.

Figure IX.26 shows that a WOR change does not alterate the S*-ACN correlation and thus can be included as a correction term, like the temperature term on the surfactant concentration term which is also shown in the figure but was included in EPACNUS. An appropriate correction term may be chosen in this case as:

\[ \ln S^*(WOR) = \ln S^*(WOR = 4) + \frac{0.05}{WOR} - \frac{0.05}{4} \]

IX.3.6. Analytical expression of the multidimensional correlation for optimum phase behavior for sulfonates

All the previously studied effects can be gathered in a single relationship, as a condition for optimal phase behavior:

\[ \ln S^* = K(ACN) + f(A) - \sigma + a_T(T - 25) + \frac{0.05}{WOR} - \frac{0.05}{4} \]

where:

\[ S^* = \text{salinity in g NaCl per deciliter aqueous phase} \]
Figure IX.26. Influence of WOR and surfactant concentration on ln $S^*$ vs. ACN correlation.
K = 0.16 for alkyl aryl sulfonates/alkanes/NaCl
ACN = oil alkane carbon number
f(A) = alcohol effect (see Section IX.2.)
a = surfactant characteristic parameter
(\sigma/K = EPACNUS see Table IX.1. and Figures IX.17. to 19.)
\(a_T\) = temperature coefficient = 10-2
T = temperature °C (5-50°C)
WOR = water-oil ratio (9 > WOR > 0.5)
Chapter X
OPTIMUM FORMULATION FOR OTHER ANIONIC SURFACTANTS AND FOR MIXTURES

X.1. CORRELATION FOR ANIONIC SURFACTANTS OTHER THAN SULFONATES

X.1.1. Alkanoates

The sodium salt of myristic acid (tetradecanoic acid) was obtained by neutralizing the acid by a hot aqueous solution of sodium hydroxide. The soap was then dried, dissolved in hot methanol and precipitated as a curd in cold methanol; the washed precipitate was then dried under vacuum for several hours. Two different starting products yielded soaps having slightly different properties; the resulting sodium tetradecanoates are labeled "pure" and "technical" respectively, after the starting myristic acid grade.

Figure X.1 shows a In s*-ACN plot which indicates that the slope K has approximately the same value as in the case of alkyl aryl sulfonates. It is not known whether this is true for all alkanoates. Attempts to use sodium docosanoate failed to provide a range of data wide enough to estimate the value of K. The main experimental problem encountered when working with alkanoates solutions is that they form gels even at extremely low concentrations; high salinity and high oil ACN tend to favor the formation of gels in both phases, while increasing temperature and alcohol concentration tend to reduce it; the attainable experimental region is thus limited to rather low molecular weight soaps, high alcohol concentrations and light alkanes.
Figure X.1. In S* plot for sodium tetradecanoate (purified) at various alcohol concentrations.
The effect of alcohols on tetradecanoate could not be studied starting with the standard 3 gpd/l sec-butanol because of the excessive salinity required to obtain three phases. However, the data shown on Figure X.2 are consistent with results shown in Figure IX.2., which refer to f(A) for the same alcohol, if the optimum salinity at no alcohol is taken as 16.4 gpd/l NaCl (ln S* = 2.8). With a K value equal to 0.16, the EPACNUS of sodium tetradecanoate is readily estimated at -10.5 ± 1. The same calculation, assuming the correlation is strictly obeyed, leads to an EPACNUS of +3 (±2) for sodium docosanoate.

X.1.2. Alkyl sulfates

Alkyl sulfates are obtained by sulfation of an alcohol; the sulfation involves the replacement of the 0-H bond with a 0-S bond. The alkyl sulfates used in this study were sodium salts of alkyl sulfuric acids deriving from long chain primary alcohols; their general formula is:

\[ \text{CH}_3 - (\text{CH}_2)_n - 0 - \text{SO}_3^- \text{Na}^+ \]

Figure X.3 shows the ln S*-ACN plot for decyl, dodecyl and tetradecyl sodium sulfates (Eastman chemicals). A large concentration of isopentanol was required because these surfactants are extremely hydrophilic. The data show that there is still a linear relationship between ln S* and ACN; however, the slope differs from
Figure X.2. Effect of iso-pentanol on ln S* for sodium tetradecanoate (purified).
Figure X.3. In $S^*$-ACN plot for alkyl sulfates (Eastman) at various alcohol concentrations.
the previously found value; it is found to be:

\[ K = 0.10 \pm 0.01 \]

Eastman chemicals were taken as a reference because the C8-C14 series was available; they have a crystalline appearance and are presumed to contain less impurities than other commercial products. Some experiments with Richonol A (Richardson trade name for lauryl sulfate) have yielded slightly different results, perhaps due to the presence of residual alcohol or inorganic salts; furthermore Richonol A solutions were found to age quickly, e.g. after 48 hours the optimal salinity was found 10-15% higher than with a fresh solution.

The effect of alcohol was tested on Eastman dodecyl sodium sulfate. Figure X.4 shows \( \ln S^* \) versus concentration of isopentanol and is equivalent to Figures IX.12 and IX.13 with a shifted ordinate scale; the data are scattered, but roughly correspond (±0.2 units on \( \ln S^* \) scale) with Figures IX.12 and IX.13 if the zero alcohol optimal salinity is taken in these conditions to be 30 gpdl NaCl (\( \ln S^* = 3.4 \)).

Because of the extremely high salinity involved, a complete alcohol study cannot be carried out, even with tetradecyl sodium sulfate. Such an investigation would have to be realized in the octadecyl or docosyl range.

Assuming that the correlation holds (with \( K = 0.10 \)), it is possible to estimate the EPACNUS as follows:
Figure X.4. Effect of Isopentanol on ln S* for sodium dodecyl sulfate (Eastman).
Decyl sodium sulfate  EPACNUS = -32  
Dodecyl sodkum sulfate  EPACNUS = -27  
Tetradecyl sodium sulfate  EPACNUS = -22  

It should be stressed here that if the alcohol effect is not the same as for sulfonates, these values can be grossly in error; however the 2.5 unit increase of EPACNUS per added methylene group to the alkyl chain is well established.

X.2. MIXTURES OF ALKYL ARYL SULFONATES

All commercial petroleum sulfonates are known to be mixtures of a large number of compounds; however they are found to behave like a pure component except for the concentration shift. A recent paper (Wade, Schechter, Morgan and Jacobson: 1976) has shown that the scaling rule for obtaining minimum tension for mixtures is quite simple; the preferred ACN (N min) at 1% wt. NaCl and 0.2% wt. total surfactant concentration (of the mixture) is the weighted sum of the preferred ACN of the components of the mixture; the weighting factors are the molar fractions of the different species, based on the equivalent molecular weights. However the definition of N min involves a 0.2% wt. surfactant concentration, and thus a different total concentration on a molar basis when surfactants of different molecular weight are mixed although these differences are generally small. The data reported in this section are for a constant total molar concentration. Since the minimum tension and three-phase behavior are different manifestations of the same optimal formulation, it is expected to find similar mixing rules.
We have shown previously that any sulfonate optimal formulation is represented by a plane in the three-dimensional space ln S-ACN-f(A). Two different sulfonates would have two different parallel planes, each of them crossing the ACN axis at an abcissa equal to its respective EPACNUS. Since surfactants like TRS 10-80 and Siponate DS-10, which are mixtures, have an optimal formulation plane parallel to all others, it is expected that any sulfonate mixture will give such a plane.

Figure X.5 shows that the correlation valid for two sulfonates is also valid for their mixtures. Because of the parallelism of the mixture planes with the base planes any cut along a straight line axis in ln S-ACN-f(A) space would be sufficient to determine the position of the mixture plane.

Figure X.6 shows such a cut along the vertical axis (ln S direction) at constant ACN (3 values) and f(A); the experimental data correspond to 0, 25, 50, 75 and 100% mol of the lighter component of the mixture; this plot shows two things: (1) the logarithm of the optimal salinity varies linearly with the composition, and (2) the variation is identical for different alkanes, thus corroborating the fact that the mixture optimal surface is a plane. Figure X.7. shows another cut, this time parallel to the ACN axis (at 1 gpdl NaCl and 3 gpdl sec-butanol); the extrapolated preferred ACN (EPACN) at 3 gpdl sec-butanol is equal to EPACNUS + 1.
Figure X.5 in $S^*$-ACN plot for mixtures of TRS 10-80 and Siponate DS-10.
Figure X.6 Optimum salinity versus composition of mixtures of TRS 10-80 and Siponate DS-10.
Figure X.7. Extrapolated preferred alkane carbon number in a given environment versus composition of mixtures of TRS 10-80 and Siponate DS-10.
Figure X.8. Optimum salinity versus composition for mixtures of dodecyl benzene sulfonate (Monsanto) and pentadecyl-orthoxylene sulfonate (Exxon).
Other data on sulfonates mixtures (see Figure X.B.) as well as Wade et al (1976) data show that:

1) the correlation applies for mixtures

2) the EPACNUS of a mixture can be calculated by a linear mixing rule involving the mole fraction weighting factors (Xi):

\[ \text{EPACNUS}_{\text{mixture}} = \sum x_i \text{EPACNUS}_i \]

However it has been noted by some authors (Doe et al: 1978) that binary mixtures of isomerically pure sulfonates do not mix according to this rule.

Using two of the purest surfactants available in sufficient amounts (C₉ and C₁₅ ortho-xylene sulfonate sodium salts), it was found that a slight deviation from linear mixing rule exists (see Figure X.9.); these two surfactants are not isomerically pure as can be shown on Figure X.10 since they exhibit a slight concentration shift; however they are so different that the molecular weight distribution of any mixture of them is certainly very strongly bimodal. An interesting fact found in Figure X.9 and X.10 is that the deviation from linear rule is positive towards the lighter surfactant molecular weight; however it should be noted that negative deviations have been also found (Doe et al: 1978).

The conclusion of this section on mixtures of alkyl aryl sulfonates is that commercial products mix according to a linear rule, while isomerically pure surfactant binaries may exhibit deviations from this rule.
Figure X.9. Optimum salinity versus composition of mixtures of nonyl- and pentadecyl-orthoxylene sulfonates (Exxon).
Figure X.10. Optimum salinity versus total concentration for various mixtures of nonyl- and pentadecylorthoxylene sulfonates.
X.3. MIXTURES OF DIFFERENT ANIONIC TYPES

Mixtures of surfactants bearing different hydrophiles have been studied and found to exhibit a variety of behaviors.

Figure X.11 shows the behavior of a mixture of a sulfonate (TRS 10-80) and an alkanoate (technical tetradecanoate). The correlation is quite linear with respect to composition and hence the EPACNUS of the mixture will be too; it should be noted that the two curves which correspond to different f(A) values are not exactly parallel; this may be an indication that the K value for alkanoates is not exactly the same than for sulfonates, although it can be just experimental error.

Figure X.12 shows the optimal salinity of a mixture containing a sulfonate (Siponate DS-10, an Alcolac trademark for dodecyl benzene sulfonate) and a sulfate (Richonol A, a Richardson trademark for dodecyl sulfate), at constant ACN and f(A), versus composition. The correlation approaches linearity and the observed deviations are believed to be due to experimental error, which is about ±0.1 In S unit at these high salinities; the three lines are not parallel, due to different values of K for sulfonates and sulfates.

It is interesting to consider the different cases that may eventually occur when two surfactants with different K are mixed. Figure X.13 shows some of the expected properties on an iso-f(A) plane, i.e., in S-ACN coordinates. Provided the correlation is obeyed, the two iso-f(A) lines would cross at some point, so-called
Figure X.11. Optimum salinity versus composition of mixtures of TRS 10-80 and sodium tetradecanoate (technical).
Figure X.12. Optimum salinity versus composition of mixtures of dodecyl sulfate (Richonol A) and dodecyl benzene sulfonate (Siponate DS-10).
Figure X.13. Expected behavior of mixtures of surfactants possessing different K values.
equivalent point because at this salinity, ACN and f(A), the two surfactants have the same phase behavior. The iso-composition lines (dashed) form a beam converging at the equivalent point. In three dimension we would have an equivalent line which would be the intersection of the two optimal formulation planes.

More interesting is the feature illustrated in the bottom graph of Figure X.13.; it shows clearly that above the equivalent point an increasing amount of surfactant (2) will increase the preferred ACN of the mixture, while the reverse is true below the equivalent point.

**X.4. MIXTURES OF ANIONICS AND NONIONICS**

Studies of anionic and nonionic mixtures were undertaken using the system TRS 10-80 and Igepal-CO series (GAF trade name for polyethyleneoxy nonyl phenols).

Figure X.14 shows the mixing rules for Igepal CO 710, 630 and 610 which contain respectively an average of 10.5, 9 and 8.5 ethylene oxyde groups. It is interesting to note that the mixtures behave like a single surfactant; however extrapolation may lead to erroneous conclusions because the linear rule may not in fact hold for all compositions. Figure X.15 shows the phase behavior of a mixture of TRS 10-80 and Igepal CO-530 (6 ethylene oxyde groups), the latter being almost insoluble in water. In this case the non linearity of the mixing rule is pronounced. On the right part of the diagram,
Figure X.14. Optimum salinity versus composition for mixtures of TRS 10-80 and various Igepal CO series nonionics.
Figure X.15. Salinity range for three-phase behavior versus composition of mixtures of TRS 10-80 and Igepal CO 530.
at 50% mol. Igepal C0-530 or more, the two kinds of bars refer to different observations; the solid bars indicate the range of salinity in which a middle phase is observed with clear excess phases, while the wavy bars indicate the range of salinity in which a middle phase is observed but with a cloudy lower phase. Eventually the two regions seem to separate, leaving an intermediate salinity region where only two phases are present. It is not known whether this region is thermodynamically stable. Its existence was found to be very sensitive to the variation of temperature; it actually tends to disappear in tubes left to settle at room temperature for several weeks. An explanation of this double middle phase region, if real, would involve measuring the concentrations of the two surfactants.

To conclude this section it may be said that highly ethoxylated, nonionic surfactants tend to substantially increase the salt tolerance of the mixture and that the mixing rules are in general not linear, which may be due to some kind of interaction or simply because nonionics alone do not obey the same correlation.
CONCLUSION

Some colligative properties of a commercial petroleum sulfonate have been studied, in particular aging and clear point. Solution aging may be an important factor in practice since it changes the effective behavior of the surfactant; aging rate was found to be accelerated by increased salinity and retarded by increased surfactant concentration. Aged solutions exhibit a different UV spectrum than fresh ones. However the cause of aging was not determined.

Most sulfonate solutions in brine are turbid but may be made clear by addition of an alcohol in proper concentration. A systematic study with various alcohols showed that the alcohol concentration required to obtain a clear solution (clear point at constant temperature) increases with salinity but is independent of the surfactant concentration. The clear point temperature for a given formulation was found to be extremely sensible to the chemical environment.

A systematic study of the phase behavior of surfactant/ alcohol/sodium chloride brine/alkane systems showed that the occurrence of three phases is related with minimum interfacial tension, equal solubilization parameters and near unity partition coefficient. The effects of salinity, alkane carbon number, alcohol type and concentration and surfactant structure were determined.
For a given surfactant and at constant alcohol concentration, constant temperature and constant water/oil ratio a linear relationship was found between salinity and oil ACN for the system to exhibit three phases:

\[ \ln S^* = K (\text{ACN}) + \ldots \]

where \( S^* \) is the optimum salinity (in g NaCl/100 ml of aqueous phase) defined as the center of the salinity range for which the system exhibits three phases, ACN is the alkane carbon number and \( K \) a constant (0.16 for NaCl/alkanes/sulfonates); the stand for terms depending on other variables.

A systematic study of alcohol, surfactant and temperature effects allowed one to obtain a more general correlation for optimum phase behavior (at WOR = 4):

\[ \ln S^* = K (\text{ACN}) + f(A) - \sigma + a_T (T - 25) \]

where \( S^* \), ACN and \( K \) are the same as previously, \( f(A) \) is a functional depending only on alcohol type and concentration, with an exception for butanol and lower molecular weight alcohols for which \( f(A) \) may also depend on other factors, \( \sigma \) is a characteristic parameter of the surfactant, \( a_T \) is a temperature correction term and \( T \) is the temperature in °C.

The value \( \sigma/K \) which is the Extrapolated Preferred Alkane Carbon Number at Unit Salinity and no alcohol (EPACNUS) was correlated with the molecular weight of the surfactant.
The correlation allows one to predict the phase behavior of a surfactant/alcohol/alkane/brine system and to find compensatory actions when some variables such as salinity and ACN are imposed.

Exploratory work on other anionic surfactants tends to show a similar correlation with simple linear mixing rules, as well as surfactant mixtures.
APPENDIX A

DATA ON USED PETROLEUM SULFONATES AND

ALKYL ARYL SULFONATES

A. 1. PETRONATE TRS 10-80

Manufacturer: Witco Chemicals Sonneborn Division Type: Petroleum sulfonate sodium salt

Appearance: Brown viscous liquid

Structure: Unknown, presumed to contain naphtalene and phenanthrene aryl groups, and more than one alkyl chain.

Equivalent Molecular Weight: 425 Active material: 80 % wt.

Moisture: 9 % wt.

Unsulfonated oil: 10 % wt.

Inorganic salts: 1 % wt.

Other: When a solution is left to settle several days, or in partitioning experiments with oil/water systems, a brown solid residue separates from the solution; it was identified as an iron compound by the characteristic reaction with KSCN.
A. 2. SIPONATE DS-10

Manufacturer: Alcolac Inc.

Type: Synthetic alkyl benzene sulfonate sodium salt Appearance: Light beige flakes

Structure: Mainly dodecyl benzene sulfonate Active material: 98 % wt.

Unsulfonated oil: 0.5 % wt.

Inorganic salts: 1 % wt.

Other: Contains probably a high percentage of dodecyl benzene sulfonate, with some higher molecular weight impurities; it exhibits a concentration shift (Vasquez: 1977)

A.3 DODECYL ORTHOXYLENE SULFONATE MONOETHANOLAMINE SALT

Trade name: PDM-337/FA-400 Used symbol: C12 OXS-MEA Manufacturer: Exxon

Type: Synthetic alkyl aryl sulfonate

Structure: Lipophilic chain is a propylene polymer Appearance: Brown viscous liquid

Active material: 84 % wt. (C120XS: 62 % wt. of active) Unsulfonated oil: 13 % wt.

Amine sulfate: 2 % wt

Moisture: 1 % wt
A. 4. ALKYL ORTHOXYLENE SULFONATE SODIUM SALT (CₓOXS-Na) Supplied by: Exxon

Type: Synthetic alkyl aryl sulfonate sodium salt Structure: Lipophilic chain is a propylene polymer

Appearance: Brown viscous liquid (Deoiled products are light beige crystals)

Isomeric purity: unknown, but presumed to by high (almost no concentration shift)

A. 5. TETRADECYL BENZENE SULFONATE SODIUM SALT Supplied by: Conoco

Type: Synthetic alkyl benzene sulfonate

Deoiled and desalted product is near 100 % active Structure and branching: unknown

A. 6. ALKYL BENZENE SULFONATE SODIUM SALT (CₓABS) Supplied by: Monsanto

Type: Research grade

Appearance: White crystals

Structure: Linear alkyl benzene sulfonate

Active material: near 100 % wt (See Trogus: 1977c) Other: Presumed to contain a high percentage of maximum branched isomers, e.g. for C₁₂ABS: 5φ₁₂ABS and 6φ₁₂ABS
BIBLIOGRAPHY


31. Carreau, P. J., I. F. McDonald and R. B. Bird "A nonlinear viscoelastic model for


36. Cayias, J. L., R. S. Schechter and W. H. Wade 1975 "The measurement of low interfacial tension via the spinning drop technique". ACS Symposium series, No. 8: Adsorption at interfaces, paper No. 17, 234.


42. Coats, K. H. and B. D. Smith 1964 "Dead end pore volume and dispersion in porous media". SPE J., March, 73.


46. , R. E. Williams and P. A. Kolodzie 1974 "Oil recovery by alkaline waterflooding". JPT 26, 1365.


55. and W. Wade 1977 "Linear alkyl benzene sulfonates and low interfacial tensions". To be published.


64. Ehrlich, R. 1974a "Wettability alteration during displacement of oil by water from petroleum reservoir rock". 48th Natl. Colloid Symposium ACS preprints, 139, Austin.


78. Geffen, T. M. 1973a "Oil production to expect from known technology". Oil and Gas J., May, 66.

79. 1973b "Improved Oil Recovery could help ease energy shortage". World Oil, October, 84.

80. 1975 "Here's what's needed to get tertiary recovery going". World Oil 180 (4) 53.


84. Gogarty, W. B. 1967a "Mobility Control with Polymer Solutions". SPE J., 7, 161.

85. 1967b "Rheological properties of pseudoplastic fluids in porous media". SPE J., 7, 149.


surfactant or micellar methods". JPT, January, 93.


112. Houston, C. A. and Ass 1976 "MS surfactant forecast to 1985". Chemical Week, February 18, 63.


on Enhanced Oil and Gas Recovery, September.


149. 1965 "Wettability as related to capillary action in porous media". SPE J., 5, 259.


161. 1973b "Oil-in-water Emulsions and their flow properties in porous media". JPT, June, 727.


178. PCC (Petroleum Publishing Company) 1976 Enhanced Recovery Methods are Worldwide: monograph compiled from articles published in Oil and Gas J.


184. . and T. H. Doscher 1956 Publication No: 75, Shell Development Co., presented at Dallas Meeting of ACS.


190. Ruschak, K. J. and C. A. Miller 1972 "Spontaneous Emulsification in ternary systems with mass transfer'. I & EC. Fundamentals, 11 (4) 534


205. Shah, D. O. 1974 "On distinguishing microemulsions from cosolubilized systems".
   48th National Colloid Symposium ACS Preprints, Austin, june.

206. A. Tamjeedi, J. W. Falco and R. D. Walker 1972 "Interfacial instability and
   spontaneous formation of microemulsion". AIChE J., 18 (6) 1116

207. R. D. Walker Improved Oil Recovery Research Program, semi-annual
   report, june. See also D. O. Shah et al., in Improved Oil Recovery by Surfactant
   and Polymer Flooding, D. O. Shah and R. S. Schechter Eds., Academic Press,
   1977.

208. Sharp, J. M. and J. R. Crump 1976 "ERDA microemulsion chemical study". Gulf
   Universities Research Consortium, Houston, June 27.

209. Shinoda, K. 1954 "The effect of alcohols on the CMC of fatty acid soaps and the
   CMC of soap mixtures". J. Phys. Chem., 58, 1136

210. S. Friberg 1975 Advances Colloid Int. Sci., 4, 281
211. and H. Kunieda 1973 Conditions to produce so-called microemulsions. Factors to increase the mutual solubility of oil and water by solubilizers". J. Colloid. Int. Sci., 42 (2) 381


214. Snyder, R. E. 1974 "60 billion-barrel tertiary recovery potential claimed". World Oil, june, 70

215. Sperling, R. 1948 "Sulfonation products of mineral oil"., I & EC., 890


217. and 1972b "Experiments in coalescence by flow through fibrous mats". I & EC Fundamentals, 11 (1) 73

218. and Y. P. Su "Coalescence of liquid-liquid dispersions by flow through porous media". 48th National Colloid Symposium ACS Preprints, 94, Austin, june.


224. Taber, J. J. 1969 "Dynamic and static forces required to remove a discontinuous oil phase from porous media containing both oil and water". SPE J., 9 (1) 3


232. 1977c "Equilibrium and Non-equilibrium Adsorption of Amphiphilic compounds". Ph.D. dissertation, University of Texas.


239. Vasquez, E. Ortiz de 1977 Private communication. MSc thesis to be completed, University of Texas


246. Weinaug, C. F. et al., Eds. 1965 Thermal Recovery Processes., SPE Reprints Series R-7
247.1966 Miscible Processes. SPE Reprints Series R-8 1972

248. Thermal Recovery Techniques. SPE Reprints Series R-10


252. Whiteley, R. C. and J. W. Ware 1976 "Low tension waterflood pilot at the Salem unit, Marion County, Ill., part I." Paper SPE 5832 presented at the Improved Oil Recovery Symposium of SPE, Tulsa, March

253. Widmyer, R. H. et al. 1976 "Low tension waterflood pilot at the Salem unit, Marion County, Ill., part II." Paper SPE 5833 presented at the Improved Oil Recovery Symposium of SPE, Tulsa, March
