

# EFFECT OF ALCOHOL AND OIL TYPE ON MINIMUM INTERFACIAL TENSIONS AND PHASE BEHAVIOR OF THE BRINE/ SURFACTANT/ ALCOHOL/OIL SYSTEMS

Truong Hong TIEN<sup>1</sup>, Mehdi BETTAHAR<sup>2</sup> and Uichiro MATSUBAYASHI<sup>3</sup>

<sup>1</sup> Member of JSCE, Graduate Student, Dept. of Civil Eng., Nagoya University  
(Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan)

<sup>2</sup> Dr. of Eng., Visiting Professor, Research Center for Advanced Waste and Emission Management, Nagoya University

<sup>3</sup> Former Member of JSCE, Dr. of Eng., Professor, Research Center for Advanced Waste and Emission Management, Nagoya University

The middle-phase microemulsion potentially for oil recovery is often produced by using alcohol as a co-surfactant. The objective of this study is to connect the changes of this middle-phase with the resulting minimum interfacial tensions upon adding the alcohol to the systems containing brine, an anionic surfactant and different alkanes. The results demonstrated a reduction in the interfacial tensions with either increasing alcohol concentration or decreasing the alkane carbon number. The observed trends were expressed by a simple correlation between the minimum interfacial tensions and optimal salinities. This correlation can be used to select the optimum surfactant/alcohol formulations for soil remediation.

*Key Words : surfactant, minimum interfacial tension, optimal salinity, optimum middle-phase microemulsion*

## 1. INTRODUCTION

Organic solvents and other petroleum products have become a major threat of groundwater contamination in many countries. Such liquids are often called non-aqueous phase liquids (NAPLs) as they are immiscible in water. NAPLs with the densities greater than water are classified as dense non-aqueous phase liquids (DNAPLs), whereas NAPLs with the densities less than water are referred to light non-aqueous phase liquids (LNAPLs). Once released to the subsurface, NAPLs will transport downward due to the gravitational forces, but a portion of the organic liquids may be retained within the soil pores as discrete globules or ganglia due to the capillary forces. Under normal flow regimes, this residual NAPL phase is immobile and often represents a long-term source of aquifer contamination<sup>1</sup>.

Soil and groundwater remediation methods rely on partitioning of the contaminants into water known as pump- and treat<sup>2,3</sup> or for volatile compounds, into the gaseous phase - soil vapor extraction<sup>4,5,6,7</sup>. However, these methods are found to be neither an effective nor economical means for recovering semi-volatile and non-volatile compounds with low solubility, such as crudes and

diesel oils. To overcome these limitations, different innovative technologies such as surfactant flushing<sup>8,9,10</sup>, alcohol flushing<sup>11,12,13</sup> or combination of both<sup>14,15,16</sup> have been developed. In most cases, the systems using the mixture of surfactant/alcohol have shown high efficiency than that with the use of surfactants or alcohols, separately. This latter technique is based on the ability of surfactant/alcohol mixture to form a middle-phase microemulsion coexisting with both water- and oil rich phases. With the presence of this middle-phase, the water-oil interfacial tension can be decreased to several order of magnitudes<sup>17</sup>. Because the water-oil interfacial tension is zero when the nature of two phases are identical, the best formulation from the technical point of view is one which produces one-phase microemulsion (all oil and water are dissolved in the middle-phase microemulsion). However, to create such conditions, it may need very high concentrations of surfactants and alcohols. Obviously, this is not economical and desirable approach. Therefore, for practical purposes, it is better to find the composition of surfactant/alcohol mixture necessary to obtain the middle-phase microemulsion which will produce a desirable value of interfacial tension. For displacement of the residual oils from the porous

media, the value of this interfacial tension less than about  $10^{-2}$  dyn/cm and preferably less than  $10^{-3}$  dyn/cm is generally required<sup>18),19)</sup>.

During the past several decades, a number of the research groups<sup>20),21),22)</sup> had attempted to find the conditions of forming the three phase behavior. Salager et al<sup>20)</sup> had found an empirical correlation to link the variables of optimum formulation containing anionic surfactants, alkanes, and various alcohols with the function of optimal salinity ( $S^*$ ) (a more precise definition is given in a subsequent section). Although the correlation allows identifying those formulations that yield optimum middle-phase microemulsions, it does not provide any information on the water-oil interfacial tension which quantifies its efficiency for oil recovery. Other groups<sup>23),24)</sup> were devoted to clarifying the mechanism of the ultralow interfacial tension. They used a pure nonionic alkylpolyglycoether and temperature as adjustable variable to form the middle-phase microemulsion. Huh<sup>25)</sup> had developed a theoretical model to relate the water-oil interfacial tensions with solubilizations of the water and oil phases in microemulsion. Because the measurement of the solubilization parameters is generally easier than measurement of interfacial tension, the model can be used for approximate evaluation of surfactant performance. However, the screening process to obtain the best formulation is still time-consuming, and it will be virtually impossible to conduct the screening process for all possible contaminant compositions. In this context, a special interest is to find a correlation between minimum interfacial tensions and other variables of middle-phase microemulsions. If viable, this correlation will significantly reduce laboratory works and thus the cost associated with design of surfactant formulation suitable for aquifer remediation.

The objective of this study is to connect the three-phase behavior and minimum interfacial tension as criteria for optimum brine/surfactant/alcohol systems and to understand the factors influencing on the reduction of the minimum interfacial tension. Other objective is to relate the observed trends of minimum interfacial tensions with other variables of optimum formulations through the optimal salinities.

## 2. BACKGROUND

### (1) Mechanism of NAPL entrapment

The entrapment of NAPLs within porous media occurs when capillary forces are sufficiently strong to overcome viscous and gravity or buoyancy forces<sup>26),27)</sup>. The displacement of these entrapped

NAPLs by groundwater flow depends on the ratio of the viscous and buoyancy forces to the capillary forces. A dimensionless expression for these ratios needed for the displacement of oil globules by water flowing through a porous medium is shown in Eq.(1)<sup>1)</sup>

$$\frac{v_w \mu_w}{\gamma_{wo} \cos \theta} + \frac{\Delta \rho g k k_{rw}}{\gamma_{wo} \cos \theta} \sin \alpha \geq \frac{2 \beta k k_{rw}}{\Delta l r_n} \quad (1)$$

where  $v_w$  and  $\mu_w$  are the velocity and the viscosity of the displacing fluid (water), respectively;  $\gamma_{wo}$  is the water-oil interfacial tension;  $\theta$  is the contact angle;  $\Delta \rho = \rho_w - \rho_o$ ,  $\rho_w$  and  $\rho_o$  are the densities of water and oil, respectively;  $g$  is the specific gravity;  $\alpha$  is the angle between groundwater flow direction and horizontal axis;  $\beta = 1 - r_n/r_p$ ,  $r_n$  and  $r_p$  are the radii of the pore neck and pore body, respectively;  $k$  and  $k_{rw}$  are the intrinsic and relative permeabilities of the porous medium and water, respectively;  $\Delta l$  is the average length of the oil globule.

It can be seen from Eq.(1) that both pore structure of a porous medium and fluid properties control the manner by which NAPL is whether trapped or mobilized. In order to improve the rate of recovering the residual oil, the left hand side of Eq.(1) should be increased in two or more orders of magnitudes<sup>28)</sup>. This can be done by either increase of  $v_w \mu_w$  or decrease of  $\gamma_{wo}$  or both. However, in soil treatment  $v_w \mu_w$  can not be acted to a great extent because of risk of soil disruption<sup>29),30)</sup>. Thus, the reduction of  $\gamma_{wo}$  between oil and injected fluid would be the main strategy for oil recovery process. Surfactant and alcohol are added to the solution to achieve this goal.

### (2) Surfactant in water-oil system

A surfactant molecule (monomer) contains one water-soluble and one water insoluble moieties which are referred to hydrophilic (or head) and hydrophobic (or tail) groups (Fig.1). Due to the dual structure, a surfactant molecule in solution is attracted to hydrophobic (NAPL) phase while remaining soluble in the hydrophilic (water) phase<sup>31)</sup>. Depending on the nature of hydrophilic portion of the molecules, surfactants are classified into 4 groups: anionic, cationic, nonionic and zwitterionic<sup>32)</sup>. At very dilute surfactant concentration, the surfactant molecules exist as separate monomers. As the surfactant concentration in solution increases, aggregates of monomers, called micelles<sup>33)</sup>, begin to form. This is defined as critical micelle concentration (CMC). The formation of the micelles will increase the solubilization of the oil in aqueous phase, whereas the adsorption of

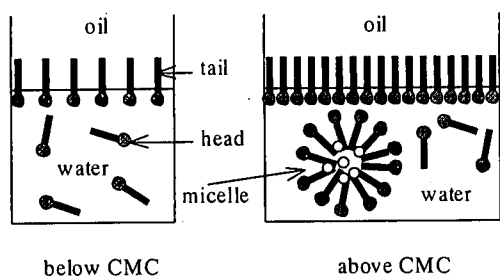


Fig.1 Surfactant molecules in water-oil system

surfactant molecules at the interface will reduce the water-oil interfacial tension.

### (3) Winsor system

In order to attain ultra-low interfacial tension between aqueous and nonaqueous phases, the materials on both sides of interface must be very similar in nature. This happens only when both sides of the interface have similar concentration of surfactant, oil and water<sup>18</sup>). A systematic approach designed to create such situation is the observed relationship between interfacial tension and the formation of a middle-phase microemulsion with varying only the salinity while keeping other variables constant (Fig.2). When mixing oil and surfactant solution, the preferential partitioning of the surfactant in water results in the formation of the two phase system, which is referred to o/w microemulsion (or Winsor I), e.g. oil droplet in water coexisting with an excess oil phase. In case of ionic surfactants, the addition of salinity decreases the repulsion between surfactant head groups, thereby increasing the packing degree of surfactant molecules and resulting in the decrease of the interfacial tension at water-oil interface ( $\gamma_{wo}$ ). On the other hand, the addition of salinity with its consequent reduction of the electrical interactions of the ionic head groups can cause the surfactant to change from hydrophilic to hydrophobic. Therefore, with increasing the salinity concentration, the surfactant molecules have tendency to move to the oil phase. For an intermediate affinity, when balance between hydrophilic and hydrophobic characters takes place, the surfactant molecules will move from aqueous phase to the interface and form the middle-phase microemulsion (or Winsor III) in equilibrium with both water and oil phases. The water-oil interface is now replaced by microemulsion/water and microemulsion/oil interfaces having the interfacial tensions of  $\gamma_{mw}$  and  $\gamma_{mo}$ , respectively. With further increase in salinity, the surfactant molecules become more hydrophobic and consequently move to the oil phase forming w/o microemulsion (or

Winsor II), e.g. water droplet in oil. This is accompanied by the increase of the water-oil interfacial tension. The middle-phase microemulsion contains almost all of the surfactant and large quantities of water and oil.

In the Fig.2, boundaries between two-phase and three-phase systems are marked by vertical dotted lines passing through two critical values of salinities ( $S_L$  and  $S_U$ ), which correspond to the points of appearance and disappearance of the middle-phase microemulsions, respectively. The difference between these two critical salinities is called as salinity range ( $L_S$ ) of the three-phase region.

The volume of water or oil per unit weight of the surfactant in the middle phase is called the solubilization parameter<sup>30,34</sup>). The water-oil interfacial tension reaches to extremely low values when the middle-phase is formed. It is minimized at salinity taken at the midst of the three-phase region, i.e.  $S^* = (S_L + S_U)/2$ <sup>20,22</sup>). This point of water-oil minimum interfacial tension is also characterized by approximately equal volumes of water and oil solubilized in middle phase<sup>22,35</sup>). Thus, the  $S^*$  values can be determined by either minimum interfacial tension, or midst of the three-phase region, or equal volumes of water and oil phases in the microemulsion.

The salinity change in ionic surfactant systems is not the only method for producing the phase changes and ultralow interfacial tension. The addition of hydrophilic or hydrophobic co-surfactants can also change the hydrophilic or hydrophobic character of the system. As a result, this will change the phase behavior and interfacial tension. For nonionic surfactants, with increasing the temperature, the hydrophilic head group will be more dehydrated, which increases the hydrophobic character of surfactants.

### (4) Optimum surfactant formulation

Similar to the surfactant-enhanced oil recovery, surfactant-enhanced aquifer remediation is primarily based on low interfacial tension and high solubilizing power of the middle-phase microemulsion. The lower the water-oil interfacial tension, the less energy would be required to push the residual oil from the pores, and consequently the higher the efficiency of the surfactant formulation. From the relationship  $\gamma$ - $S$  (Fig.2), for the constant conditions of surfactant/alcohol concentrations, oil type and temperature, the system is defined as optimum, when water-oil reaches to its minimum value ( $\gamma_{min}$ ). The salinity associated with that formulation is called as optimal salinity ( $S^*$ )<sup>20,22</sup>). As the variables of the formulation are changed, the system will move to another optimum state with its

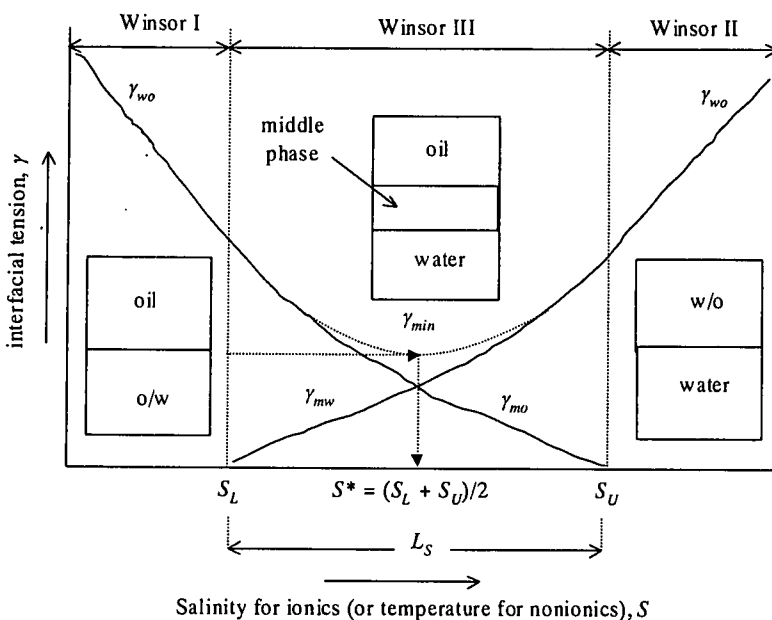


Fig.2 Relationship between phase behavior and interfacial tension

new optimum parameters ( $S^*$ ,  $\gamma_{min}$ ). Thus, both  $\gamma_{min}$  and  $S^*$  are function of surfactant, alcohol, oil and temperature.

By considering the effect of these variables independently, Salager et al<sup>20</sup> found that the  $S^*$  can be expressed by the following empirical correlation

$$\ln S^* = K(ACN) + f(A) - \sigma + a_T(T - 25) \quad (2)$$

where  $K$  is constant depending on the surfactant type;  $f(A)$  is a function of heavy alcohol and its concentration in aqueous solution;  $\sigma$  is a parameter characteristic of surfactant;  $ACN$  is alkane carbon number, e.g. the number of carbons in the hydrocarbon chain;  $a_T$  is the temperature coefficient;  $T$  is the current temperature. At 25°C, the graphical representation of the Eq.(2) can be shown as in Fig.3.

For crude oil and mixture of pure hydrocarbons, an equivalent alkane carbon number ( $EACN$ )<sub>m</sub> for the oil mixture can be assigned as in Eq.(3)<sup>22</sup>.

$$(EACN)_m = \sum X_i (EACN)_i \quad (3)$$

where ( $EACN$ )<sub>i</sub> are the equivalent alkane carbon number for the oil component  $i$ ;  $X_i$  is the mole fraction of the component  $i$  in the mixed oil phase; that is,  $\sum X_i = 1$ . Thus, ( $EACN$ )<sub>m</sub> can be substitute into Eq.(2), resulting in

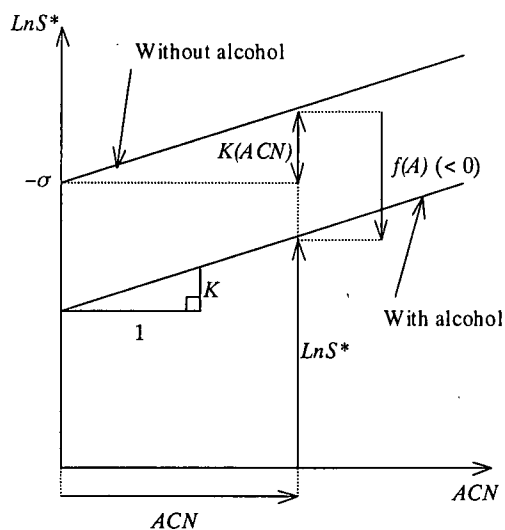
$$\ln S_m^* = K(EACN)_m + f(A) - \sigma + a_T(T - 25) \quad (4)$$

The significance of Eq.(2) and Eq.(4) is that these correlations indicate the value of salinity for each formulation, at which the water-oil interfacial tension is minimum. However, the correlations do not provide the values of interfacial tension, which is the main criterion to evaluate the performance of the surfactant/alcohol mixture.

The experiments described below were designed to tie together the optimum formulations and minimum water-oil interfacial tensions and to relate the observed trend of these minimum interfacial tensions with the optimal salinities. Since the surfactant/alcohol formulations will then be applied to the subsurface, it is therefore necessary to conduct all the research works at temperature, which is similar to the groundwater temperature.

### 3. EXPERIMENTAL SECTION

Two steps of experimental works were implemented. In the first step, a series of batch experiments were conducted to study the phase behavior and to determine the optimal salinities for systems containing different compositions of surfactant, alcohol and oils. The second step involved measurement of water-oil interfacial tension at the selected samples having the salinities equal to the optimal values.



**Fig.3** Relationship between variables of optimum surfactant/alcohol mixtures and minimum interfacial tension

## (1) Materials

Sodium Dodecyl BenzeneSulfonate (SDBS) with purity of 95% was selected as a surfactant. *n*-pentanol or *iso*-pentanol with purity > 99% was used as a co-surfactants for producing middle-phase microemulsions. 2-butanol with purity > 99% was used for determining the characteristics of the surfactant. Four saturated hydrocarbons (alkanes): *n*-octane, *n*-decane, *n*-dodecane and *n*-tetradecane with purity > 99% were used as contaminants. The contaminants were dyed with Oil-Red-O (0.5 g/l), so that appearance of the different phases could be observed quantitatively. All these chemicals were purchased from Tokyo Kasei Kogyo Company and used without further purification. Sodium chloride with purity of 99% was used as an electrolyte and water was distilled for preparation of aqueous solution. The selective properties of these chemical are given in Table 1.

## (2) Methodology

### a) Determination of optimal salinity

Batch experiments were conducted in 100ml-bottles capped to prevent volatilization losses. In each bottle, a 50 ml/12.5 ml water/oil ratio was used. Different hydrocarbons were utilized, with a constant concentration of SDBS (10 g/l) and variable concentrations of *n*-pentanol. For each composition of the surfactant system, the classical Winsor type I-III-II transitions were obtained by varying the salinity concentration while maintaining

**Table 1** Selected properties of the chemicals used in this study

Chemical name	Chemical formula	Molecular weight	Density (g/cm <sup>3</sup> )
SDBS	C <sub>12</sub> H <sub>25</sub> C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> Na	348.49	1.190
2-butanol	C <sub>4</sub> H <sub>9</sub> OH	74.12	0.800
<i>n</i> -pentanol	C <sub>5</sub> H <sub>11</sub> OH	88.15	0.815
<i>iso</i> -pentanol	C <sub>5</sub> H <sub>11</sub> OH	88.15	0.812
<i>n</i> -octane	C <sub>8</sub> H <sub>18</sub>	114.23	0.704
<i>n</i> -decane	C <sub>10</sub> H <sub>22</sub>	142.28	0.731
<i>n</i> -dodecane	C <sub>12</sub> H <sub>26</sub>	170.33	0.750
<i>n</i> -tetradecane	C <sub>14</sub> H <sub>30</sub>	198.39	0.763

other variables constant. All bottles were shaken multiple times, and were equilibrated for at least one week at 15°C in a temperature controlled room. This temperature was selected for the experiment because it is close to the groundwater temperature range<sup>35</sup>. The occurrence and disappearance of middle phase microemulsions were verified by visual observation and marking the values of the critical salinities ( $S_L$  and  $S_U$ ). The  $S^*$  were then determined as the average value of these salinities, i.e. the midpoint of the three-phase region.

### b) Interfacial tension measurements

The samples with the salinities equal to optimal values were selected for measuring the water/oil interfacial tension. Their phases were separated carefully by a small pipette into different bottles and densities of the phases were measured by an electronic density meter (DA-110, Kyoto Densi Kogyo). The spinning drop tension meter (SITE 04, Kruss, Hamburg) was used to measure extremely low interfacial tensions (from 10<sup>-6</sup> up to 10 dyn/cm).

The principle of measurement is based on the fact that gravitational acceleration has little effect on the shape of a droplet rotating at sufficient speed around its longitudinal axis. A droplet located along the axis of a rotating capillary filled with denser fluid will form a cylindrical shape. With the appropriate drop volume and rotation speed, drop diameter depends solely on interfacial tension. The droplet stabilizes in the axis of rotation, while the surrounding fluid is forced outward owing to its higher density.

Prior to measurement, the system was brought to the 15°C. The denser fluid (aqueous phase) was poured into the elevated glass reservoir. Valves were opened, and the denser fluid flushed through the capillary. The valves were then closed and the capillary was set in rotation. Generally, best results were obtained with setting the speed of rotation between 2000-4000 rpm. A droplet of the lighter fluid (oil) of approximately 1 μl in volume was

injected into a rotating capillary through a septum by a micro-syringe. After a few seconds, the droplet appeared in the field of vision. Its diameter was then measured using a built-in microscope. It is often necessary to allow a few minutes for the two phases to equilibrate before measurement.

Usually, first droplet only served for adjustment of the instrument, so repetition of measurement was needed to obtain an accurate value of interfacial tension. For doing this, the valve controlling the flow of the dense phase was opened and the droplet was removed by heavy phase flowing through the capillary. Afterwards, a new droplet could be injected.

Knowing the radius of droplet ( $r$ ), difference of densities between phases ( $\Delta\rho$ ), speed of rotation ( $\omega$ ), the values of interfacial tension ( $\gamma$ ) were found by Eq.(5)<sup>24</sup>.

$$\gamma = \frac{1}{4} r^3 \Delta\rho \omega^2 \quad (5)$$

## 4. RESULTS AND DISCUSSION

### (1) Phase behavior diagram and parameter estimation for correlation of optimal salinity

#### a) Phase behavior diagram

The phase behavior diagrams of the systems containing brine, surfactant,  $n$ -pentanol and different alkanes were developed at fixed conditions of SDBS concentration of 10g/l, water/oil ratio of 4 and temperature of 15°C. At each  $n$ -pentanol concentration ranging from 10 g/l to 120 g/l, the experiments were carried out with varying the salinity concentration (called salinity scan). Here, the term 'concentration' was defined as the weight of the substance per liter of the aqueous phase which is the mixture of water, salinity, surfactant and alcohol. The changes of the phases were recognized by visual observation and two critical salinities ( $S_L$  and  $S_U$ ), i.e. the points of occurring and disappearing the three-phase systems were marked. The optimal salinities were then obtained by taking the values at the midst of the salinity range which equals to the average of two critical salinities values. For example, at concentration of  $n$ -pentanol,  $C_{alc} = 20$  g/l, the results of observing the phase changes of the system with  $n$ -dodecane were that the three-phase behavior appeared at salinity,  $S_L = 14.5$  g/l and disappeared at salinity  $S_U = 19.7$  g/l. The optimal salinity was then  $S^* = (S_L + S_U)/2 = 17.13$  g/l. At the salinities lower than  $S_L$  or higher than  $S_U$ , the two-phase system (Winsor I or Winsor II) was observed. At the salinities within these limits, the systems exhibited three-phase behavior (Winsor III).

Increasing the  $n$ -pentanol concentration leads to the increase in solubilizing power of the surfactant for both water and oil phases. As a result, the volume of the middle phases is increased. Thus, at sufficient high concentration of  $n$ -pentanol, when all the water and oil phases are completely solubilized in the middle-phase and the system contains only one-phase microemulsion. This means that instead of observing the three-phase behavior, one could see only one-phase microemulsion. At this point, the interfacial tension between water and  $n$ -dodecane equals to zero.

Fig.4 shows an example of the phase diagram constructed from the experimental data for brine/surfactant/ $n$ -pentanol/ $n$ -dodecane system. The dashed curves that run from upper left to lower right are the boundaries between Winsor I or Winsor II and Winsor III systems. The solid line through the center of the three-phase region connects the points, at which the water- $n$ -dodecane interfacial tensions are minimum. The intersection of the curves is the point at which only one phase is present. Because the upper and lower boundaries between the Winsor systems tend to converge at the point of one-phase microemulsion, the salinity range of the three-phase system shrinks upon increasing  $n$ -pentanol concentration.

Fig.4 also allows one to observe the phase changes of the system when the concentration of  $n$ -pentanol is varied but keeping the salinity constant. It is seen that the effects of salt and  $n$ -pentanol act in the same direction. At fixed salinity concentration, upon increasing  $n$ -pentanol concentration, the phase behavior of the system is also changed from Winsor I  $\rightarrow$  Winsor III  $\rightarrow$  Winsor II.

The reason of using alcohol in this study is that SDBS is a single-tailed ionic surfactant which is too hydrophilic to be salted out even into oils of low carbon numbers such as aromatic oil<sup>36,37</sup>. To make it easier to separate into three phases, one therefore has to make the surfactant more hydrophobic, for which reason alcohol was added. The long chain alcohols (pentanol or heavier) can be considered as hydrophobic nonionic co-surfactants as well as polar co-oil<sup>33</sup>. As they distribute between the interfacial layers and the oil-rich phase, thereby making the amphiphilic layers become effectively less nonpolar, both of which decrease the amount of salt required for traversing the three-phase interval. Because for the fixed conditions of oil type, surfactant concentration, temperature and water/oil ratio, the effects of salt and co-surfactant act in the same direction, so  $S^*$  decreased with increasing  $n$ -pentanol concentration.

The plot of  $LnS^*$  versus  $ACN$  shown in Fig.5

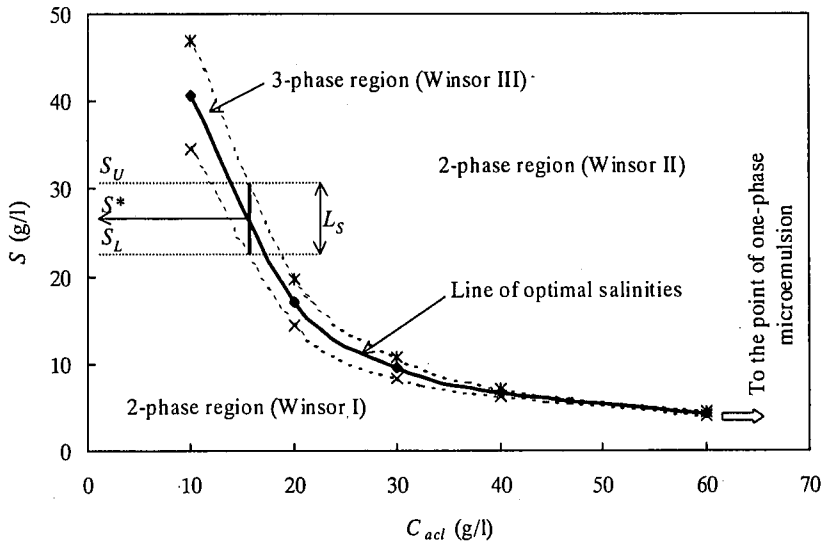


Fig.4 Phase diagram of brine/surfactant/*n*-pentanol/*n*-dodecane system

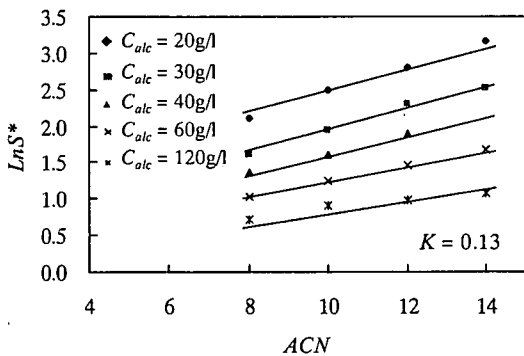


Fig.5  $LnS^*$  versus  $ACN$  for different *n*-pentanol concentrations

allows one to understand the effect of the oil chain length on values of optimal salinities. The results obtained in this study were similar to those found by Salager et al<sup>20</sup>. The  $LnS^*$  was increasing linearly with increasing  $ACN$ , but decreasing with increasing *n*-pentanol concentration. Since hydrocarbons with longer chain are more hydrophobic than those with shorter chain, more salinity is required to salt out the surfactant into the middle-phase.

#### b) Parameter estimation of the correlation for $S^*$

The Eq.(2) seems to be a good correlation to link all variables of optimum middle-phase microemulsions. Because the parameters of this correlation are determined at 15°C, the modified form of Eq.(2) will be

$$LnS^* = K(ACN) + f(A) - \sigma + a_T(T - 15) \quad (6)$$

The method to estimate the model parameters can be summarized as follows:

Because  $K$  is a constant depending on only surfactant type, it can be determined by taking the slope of the straight lines shown in Fig.5. From Fig.3, if  $S^*$  of any brine/surfactant/oil system is known, the position of the free- (without) alcohol line and the corresponding value  $\sigma$  can be determined. Since the solubilization power of SDBS for both water and oil phases is low in absence of alcohol, the middle-phase is not visible to the naked eye. For these reasons, the optimal salinity of the free-alcohol system can not be determined by the method as described in the §3.2a. In stead, one should construct the  $\gamma - S$  curve by measuring the water-oil interfacial tensions at different salinities. The salinity at which the interfacial tension becomes minimum is the optimal salinity.

The  $f(A)$  function is determined by taking the vertical distance from position of the free-alcohol system to that of the alcohol systems (Fig.3) or by Eq.(7)

$$f(A) = LnS^* - K(ACN) + \sigma \quad (7)$$

$\sigma$  also can be determined by another method recommended by Salager et al<sup>20</sup>. Basing on the  $f(A)-C_{alc}$  relationship developed previously for any alcohol, if only one value of  $S^*$  for the system containing any concentration of that alcohol is known, the value of  $\sigma$  can be found by Eq.(7). Because this method is rather easier for determining the  $\sigma$  value than the first one, it was adapted for this

study.

From the experimental data shown in Fig.5, the  $K$  values were determined by taking the slopes of the straight lines and found to be almost 0.13 for different  $n$ -pentanol concentrations. Next, the experiment was carried out to determine  $S^*$  value for a system containing brine, surfactant,  $n$ -decane with 30 g/l of 2-butanol. Two critical salinities, at which the three-phase system appeared and disappeared were  $S_L = 69$  g/l and  $S_U = 128$  g/l, respectively. Thus,  $S^* = 98.5$  g/l. On the other hand, the  $f(A)$  value for 30 g/l of 2-butanol given by Salager et al<sup>20</sup> is  $-0.16$ . From the Eq.(7) the characteristic parameter  $\sigma$  of SDBS was found to be  $-3.45$ . Therefore, the position of the 'without alcohol' line is determined by following equation

$$\text{Ln}S^* = 0.13(\text{ACN}) - 3.45 \quad (8)$$

Following this, the values of  $f(A)$  function were calculated from the Eq.(7) for each  $n$ -pentanol concentration using  $S^*$  values which were obtained experimentally from the systems containing brine, SDBS,  $n$ -pentanol and different alkanes. The results of plotting the  $f(A)$  versus  $C_{alc}$  shown in Fig.6 indicates that the absolute value of  $f(A)$  function is increased with increasing  $n$ -pentanol concentration. This trend can also be seen from Fig.5. The downward (or right) movement of the straight line upon increasing  $n$ -pentanol concentration leads to the increase in vertical distance of that line from the position of the free-alcohol line. Fig.6 also shows that  $f(A)$  is independent on the oil type. These findings are in agreement with the previous work done by Salager et al<sup>20</sup> for other type of alcohols (2-butanol, *iso*-pentanol and  $n$ -hexanol). They found that  $f(A)$  is not only the function of alcohol concentrations, but also the function of alcohol types. Thus, each alcohol has its own  $f(A)$ - $C_{alc}$  relationship.

Finally, the experiments were carried out to find the  $S^*$  of the systems at different temperatures ranging from 15°C to 25°C and the average value of the temperature coefficient was found as

$$a_T = \frac{\partial \text{Ln}S^*}{\partial T} = 0.0073 \quad (9)$$

which is compatible with the value of 0.01 reported earlier<sup>20</sup>.

## (2) Minimum interfacial tension

### a) Effect of ACN and alcohol concentration on minimum interfacial tension.

In order to investigate the effect of ACN and alcohol concentration on minimum interfacial

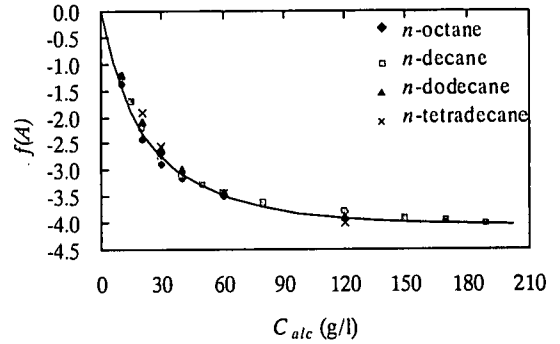


Fig.6  $f(A)$  function versus  $n$ -pentanol concentrations

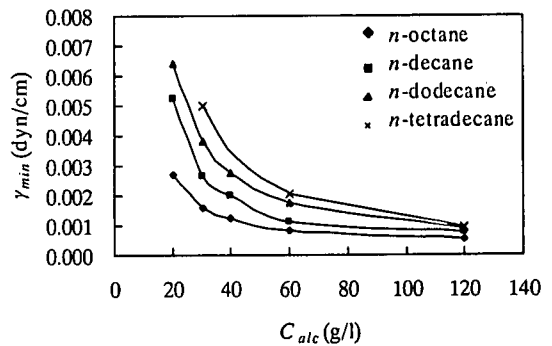


Fig.7  $\gamma_{min}$  versus  $n$ -pentanol concentrations for different alkanes

tension, at each alcohol concentration, the minimum interfacial tensions between aqueous and non-aqueous phases were measured at the optimal salinities (the midst of the three phase region) for a series of alkanes. The concentration of SDBS, water/oil ratio and temperature were kept constant as 10 g/l, 4:1, and 15°C, respectively. The plotting results between minimum interfacial tensions and  $n$ -pentanol concentrations for different alkanes were shown in Fig.7. It appeared that for all alkanes, the minimum interfacial tensions decreased with increasing  $n$ -pentanol concentration. Because increasing  $n$ -pentanol concentration led to shrinkage of the salinity range ( $L_S$ ) of the three-phase region (Fig.4), so the narrower the salinity range of the three phase region, the lower the minimum IFT. The behavior of the systems with nonionic surfactant upon increasing the temperature is similar to that with anionic surfactant upon increasing the salinity (Fig.2). Defining the temperature range of the three-phase region for system with nonionic surfactant the same as the salinity range of the three phase region for system with anionic surfactant, Kunieda and Shinoda<sup>23</sup> found that increasing the temperature also causes the decrease of the



minimum IFT and temperature range. For this reason, they concluded that the narrower the temperature range of the three-phase region, the lower the minimum interfacial tension.

The reduction of interfacial tension upon adding the alcohol to the system is due to the fact that SDBS is highly purified surfactant, it produces interfacial films that are not close packed and hence not strong to reduce the interfacial tension. A mixture of SDBS (water-soluble) and *n*-pentanol (oil-soluble) could overcome this disadvantage. Because of greater interaction of the SDBS with the aqueous phase, its hydrophilic group extends further into water than *n*-pentanol, and this is believed to permit the hydrophobic group of two materials to approach each other more closely in the interfacial film and to interact more strongly than when each amphiphilic in presence by itself. Furthermore, because *n*-pentanol dissolves mainly in the oil phase and performs as co-oil to decrease its hydrophobicity, an increase of *n*-pentanol concentration will make oil less hydrophobic or in other words to make the nature of oil more similar to that of aqueous phase. As a result, the interfacial tension will decrease with increasing *n*-pentanol concentration.

The relationship between minimum interfacial tension and *n*-pentanol concentration was nonlinear. Initially, the minimum interfacial tension was sharply decreased with increasing *n*-pentanol concentration and then gradually decreased and approached to an asymptote with horizontal axis. At sufficiently high concentration of *n*-pentanol, all excess phases were dissolved in the middle phases, the microemulsion became as one phase and interfacial tension equaled zero. The same trends were observed when only alcohol was used as interfacial reducing agent<sup>13</sup>. Their study was only a specific case when the surfactant and electrolyte were excluded from the system and the interfacial tension between oil and aqueous phase was therefore unique for each alcohol concentration.

It also can be seen from the Fig.7 that at fixed concentration of surfactant and *n*-pentanol, water/oil ratio and temperature, the minimum interfacial tension increases with increasing *ACN*. This is because the hydrophobicity of oil increases with increasing *ACN*, which makes the nature of the oil more different from that of the aqueous phase. Thus, the longer the chain length of oil, the greater the dissimilarity of the two phases and greater the interfacial tension between them.

It is important to recognize that, even both water and oil phases contain very small amount of surfactant after removing the middle-phase microemulsion, the water-oil interfacial tension is

still very small. This is because that the water/oil interface can be regarded as a thin film of the middle phase microemulsion after its removal<sup>23</sup>. Therefore, in principle, low surfactant concentrations could be used to obtain the ultralow water-oil interfacial tension without lowering the efficiency. But in practice, the interfacial tensions may become rapidly large due to the adsorption, precipitation and dilution of the surfactant. It is then necessary to use high surfactant concentrations to form the microemulsions in between the oil and water, which play the role of surfactant reservoir.

#### b) Correlation between $\gamma_{min}$ and $S^*$

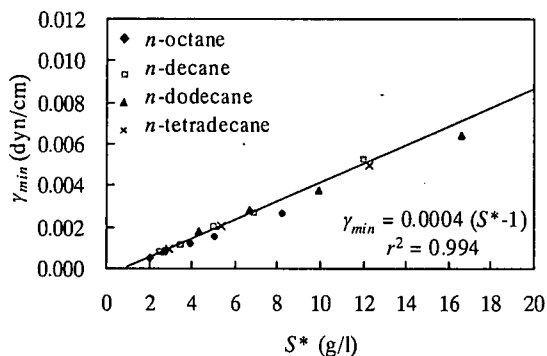
It is apparent from the above discussion that both  $S^*$  and  $\gamma_{min}$  were affected by other variables in the same direction. They decreased with increasing alcohol concentration and increased with increasing *ACN*. Thus, the minimum interfacial tension could be correlated with other variables of optimum formulation by the same method as Salager et al<sup>20</sup> have used to link those variables to the function of optimal salinity. However, the measurement of interfacial tension is very difficult and time-consuming compared with the screening process for obtaining the  $S^*$ , it is sometime impossible to conduct the interfacial tension measurements for all possible contaminant compositions. Alternatively,  $\gamma_{min}$  can be correlated with  $S^*$  since both parameters are the function of the variables of optimum formulation.

The plot of  $\gamma_{min}$  versus  $S^*$  was shown in Fig.8. Interestingly, the results showed a linear relationship between these two parameters. The Fig.8 shows that the  $\gamma_{min}$ - $S^*$  relation can be assumed to be of the form

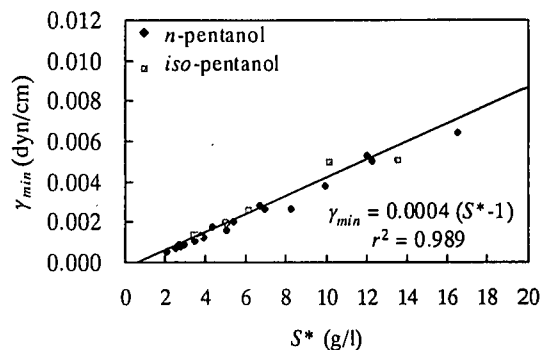
$$\gamma_{min} = K_S (S^* - b) \quad (10)$$

where,  $K_S$  is the slope of the straight line;  $b$  is the abscissa of the intersection between this line and horizontal axis.  $b$  value represents the optimal salinity at which the system becomes one-phase microemulsion ( $\gamma_{min} = 0$ ). The relation was fitted with the results obtained from the systems with different alkanes. It was found that  $K_S$  and  $b$  are essentially independent of the oil type and are almost 0.0004 and 1, respectively, when  $\gamma_{min}$  is expressed in dyn/cm and  $S^*$  in g/l. Fig.8 also shows that these two parameters are independent of the concentration of *n*-pentanol. The minimum interfacial tension decreased with decreasing the salinity and equaled to zero as salinity equaled to  $b$ .

In order to investigate the dependence of  $K_S$  and  $b$  on another form of pentanol, the experiment was carried out by using *iso*-pentanol (in stead of *n*-pentanol) as a co-surfactant to produce the middle-



**Fig.8**  $\gamma_{min}$  versus  $S^*$  for different systems with  $n$ -pentanol as co-surfactant

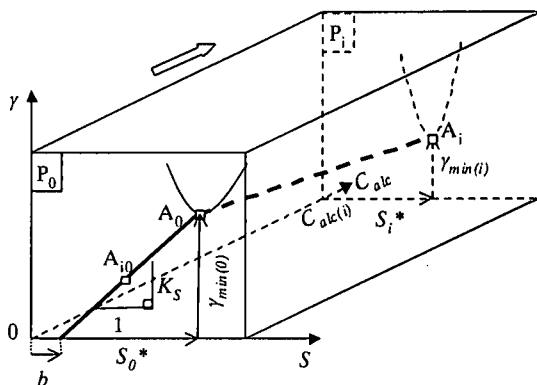


**Fig.9**  $\gamma_{min}$  versus  $S^*$  for different systems with  $n$ -pentanol or iso-pentanol as co-surfactant

phase microemulsion with  $n$ -decane and  $n$ -dodecane. These two alcohols contain the same number of carbon atoms i.e. the same molecular weight but have different position of the carbon to which the hydroxyl group  $-OH$  is attached. For different  $iso$ -pentanol concentrations ranging from 20 g/l to 40 g/l, the optimal salinities were obtained experimentally by the same methods as described for the case of  $n$ -pentanol. The interfacial tensions between water and  $n$ -decane or  $n$ -dodecane were then measured at the optimal salinities. From the experimental results, it was found that in order to bring the systems containing the surfactant concentration of 10 g/l,  $iso$ -pentanol concentration of 30 g/l, water/ $n$ -decane ratio of 4 and temperature of 15°C to the optimum state (minimum interfacial tension), 10.2 g/l of salinity is needed. To create the same situation, it requires however, less salinity ( $S^* = 6.93$  g/l) if using  $n$ -pentanol as co-surfactant. The interfacial tensions measured at these optimal salinities were 0.00492 dyn/cm and 0.00263 dyn/cm for the cases of  $iso$ -pentanol and  $n$ -pentanol, respectively. These results indicate that  $n$ -pentanol is more hydrophobic than  $iso$ -pentanol (less salinity required to bring the system to the optimum state) and more effective in reduction of interfacial tension. However, replacement of  $n$ -pentanol by  $iso$ -pentanol does not affect the values of  $K_S$  and  $b$  (Fig.9).

### c) Geometrical interpretation

Consider a three dimensional space, the axes of which correspond to  $X = S$ ,  $Y = C_{alc}$ , and  $Z = \gamma$ , and the origin is at  $(0, 0, 0)$  (Fig.10). In such a space, at fixed surfactant concentration, oil type, water/oil ratio and temperature, a set of  $\gamma = \gamma_{min(t)}$  and  $S^* = S_0^*$  determining the position of point  $A_0$  on plane  $P_0$ , will characterize an optimum formulation for free-alcohol system ( $C_{alc} = 0$ ). Upon increasing the alcohol concentration in aqueous solution ( $C_{alc} = C_{alc(t)}$ ), the point  $A_0$  (on plane  $P_0$ ) will move to a new



**Fig.10** Geometrical interpretation of the correlation

position  $A_i$  (on plane  $P_i$ ). The ordinates of point  $A_i$  ( $\gamma = \gamma_{min(t)}$ ,  $S^* = S_i^*$ ) will characterize a new optimum formulation for the alcohol concentration of  $C_{alc(t)}$ . A dashed line connecting points  $A_0$  and  $A_i$  is the trace of all optimum formulations. A projection of the line  $A_0A_i$  on the  $\gamma$ - $S$  plane will form a straight line  $A_0A_i$ , which expresses the relationship the minimum interfacial tensions and optimal salinities,  $\gamma_{min} = K_S(S^*-b)$ . The parameters ( $K_S$  and  $b$ ) of this correlation are also shown in the Fig.10.

A transition corresponding to an oil scan would be interpreted as the change of relative position of the point representing the system ( $\gamma_{min(t)}$ ,  $S_i^*$ ,  $C_{alc(t)}$ ). However the projections of all these points on  $\gamma$ - $S$  plane (not shown in the figure) are also located on the line  $\gamma_{min} = K_S(S^*-b)$ .

### d) Application of the correlation

The main advantage of the correlation over other model<sup>25)</sup> is that in absence of the measured data, the minimum interfacial tensions between aqueous and oil phases can be estimated directly from the compositions of the surfactant/alcohol mixtures. The use of the correlation is rather simple and this

correlation can be used to help select surfactant/alcohol formulations potentially effective for soil remediation. Because the measurement of the ultralow interfacial tension is extremely difficult and time-consuming, the correlation significantly reduces the laboratory works, thus the cost associated with the optimization of the surfactant/alcohol formulation.

Although the correlation developed in this study is applied to the particular surfactant (SDBS), *n*-pentanol or *iso*-pentanol as co-surfactants, NaCl as electrolyte, alkanes as oil. However, whatever the values of  $K_s$ , and  $b$  the use of the correlation is the same. In practice, for displacement of a particular residual oil from the porous media, it is not economical to create zero interfacial tension between aqueous phase and that oil by forming one-phase microemulsion, since it needs very high concentration of alcohol (Fig.4 and Fig.7). In stead, one can find an efficient mixture of surfactant and alcohol, that can produce a desired value of water-oil interfacial tension sufficient to induce mobilization of the residual oil. This value less than about  $10^{-3} + 10^{-2}$  dyn/cm is generally required<sup>18),19)</sup>.

From the desired value of interfacial tension, the concentration of salinity needed to produce the middle-phase microemulsion can be computed using Eq.(10). The correlation of  $S^*$  with other variables shown in Eq.(6) is used to estimate the value of the adjustable variable,  $f(A)$  for a particular oil ( $ACN$ ). Based on  $f(A)$  value, the concentration of either *n*-pentanol or *iso*-pentanol can be selected. In reality, because the contaminants existing in the subsurface are usually a mixture of pure compounds, the  $ACN$  term in Eq.(6) must be replaced by the equivalent alkane carbon number ( $EACN$ )<sub>*m*</sub> as described in Eq.(3).

As mentioned in §2.4, the lower the water-oil interfacial tension, the less energy would be required to push the residual oil from the pores, and consequently the higher the efficiency of the surfactant formulation. However, this will also increase the amount of alcohol, i.e. the cost of remediation. Therefore, the selection of the optimum surfactant/alcohol formulation will be likely based on the criteria of minimum cost needed to reduce the residual oil to the target level.

It is important to note that the correlations discussed here were developed with considering only the liquid-liquid interactions, i.e. the change of phase behavior and the lowering of interfacial tensions. In these conditions, 100% of alcohol and surfactant in the system were assumed to be effective in contributing to the efficiency of the formulation. However, upon injecting the solution to the subsurface, there is a liquid-solid interactions

(adsorption) causing the losses of surfactant and alcohol. The surfactant can also be precipitated due to the low temperature of groundwater. If these losses are significant, the effective concentrations of the surfactant and alcohol in injecting solution will be reduced. This will cause a rapid increase in water-oil interfacial tension which becomes a threat to the success of soil remediation. Due to these reasons, the Eq.(10) can be applied directly only to the sites, where the adsorption and precipitation of surfactant and alcohol are minimized (or negligible). For the sites, where these factors are significant, the concentrations of surfactant and alcohol calculated from the correlation must be increased in an amount equal to their losses due to the adsorption and precipitation. The sandy aquifers are usually less susceptible to the adsorption of the surfactant and alcohol<sup>38)</sup>, but it becomes significant in case of soils rich with clay minerals. Since the extend of adsorption and precipitation of surfactant and alcohol will be site specific, their values should be determined in the laboratory tests at groundwater temperature using representative soil samples from the site.

## 5. CONCLUSIONS

In this research, results of batch experiments have been presented which were conducted to investigate the the relationship between minimum interfacial tensions and optimum middle-phase microemulsions. Different systems containing anionic surfactant (SDBS), sodium chloride, water, alkanes and alcohols were used to produce the optimum middle-phase microemulsions. The measurements of interfacial tension were then made at the optimal salinities taken at the midst of the three-phase regions. The results have demonstrated that the minimum interfacial tension is highly dependent on the chain length of hydrocarbon, alcohol type and its concentration. At fixed surfactant concentration, temperature and water/oil ratio, the logarithm of minimum interfacial tension increases linearly with increasing  $ACN$ , but decreases with increasing the concentration of alcohol. These factors affected on the optimal salinity and minimum interfacial tension in the same direction. Based on this fact, a correlation between minimum interfacial tension and optimal salinity was developed which can describe the relationship between the former parameter with other variables of optimum formulation. The main feature of that correlation is that minimum interfacial tension increased linearly with increasing  $S^*$  and slope of the straight line was independent with alcohol concentration and type of

the oils. Replacement of *n*-pentanol by *iso*-pentanol containing the same number of carbon atoms i.e. the same molecular weight but having different position of the carbon to which the hydroxyl group –OH is attached, does not affect the parameters of the correlation. However, this replacement leads to lower efficiency of surfactant/alcohol mixture to reduce the water-oil interfacial tensions. The dependence of these parameters on the type of surfactant and molecular weight of alcohol needs further investigation. Associating with the correlation of  $S^{*20}$ , this correlation provides an useful guide for designing the optimum surfactant formulation suitable for remediation of the contaminated soils.

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## 界面張力の最小値及び塩/界面活性剤/アルコール/オイル溶液の相挙動に及ぼす アルコール及びオイルの種類の影響

Truong Hong TIEN · Mehdi BETTAHAR · 松林宇一郎

オイル回収のためのミドル相マイクロエマルションは、アルコールを補助剤として用いることによって得られる。本研究では、塩、アニオン系界面活性剤及び異なる種類のアルカンを含む溶液にアルコールを加え、界面張力が最小となるミドル相マイクロエマルションの相挙動について検討している。その結果、界面張力は、アルコール濃度の増加、あるいは炭化水素基の炭素数の減少に伴って減少する。この現象は、界面張力の最小値と最適塩濃度の関係式で表される。この関係式を用いて、汚染土壌の修復のための界面活性剤とアルコールの最適調合を決定することが可能である。