OPTIMUM SURFACTANT FORMULATIONS FOR REMOVAL OF RESIDUAL OIL FROM THE CONTAMINATED POROUS MEDIA

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The objective of this work is to investigate the effect of oil fraction (θ_O) on optimal salinity (S^*) and minimum water-oil interfacial tension (γ_{min}). The results reveal that S^* and γ_{min} are changing upon changing θ_O. These results are in agreement with that of the column experiments. The formulation optimized at θ_O equal to degree of oil saturation present in the column shows highest efficiency for oil recovery. The change of S^* with θ_O is described through the coefficient of oil fraction (k_a), however, this change does not affect the parameters of the correlation between S^* and γ_{min} found in our previous study. These findings provide an useful tool for the selection of surfactant formulations for soil remediation.

Key Words: surfactant, microemulsion, oil fraction, contamination, soil remediation

1. INTRODUCTION

Recently, our laboratory has applied the knowledge gained about surfactants for aquifer restoration, in which nonaqueous phase liquids (NAPLs) are considered as major contaminants of the aquifers. The applied technique referred as surfactant flushing, is usually implemented after pumping free mobile part of NAPLs. In this technique, an aqueous surfactant solution is injected into contaminated formations to recover almost all entrapped organic compounds. The remaining part of contaminants should be eliminated by a biodegradation techniques[1].

The success of the surfactant flushing depends primarily on the selection of surfactant formulations. In order to displace or mobilize the residual NAPLs from the porous media under normal flow regimes, ultralow interfacial tensions (IFTs) (< 0.001 – 0.01 dyn/cm) between aqueous and organic phases[2),3),4)] are generally required. These ultralow IFTs can be achieved by the presence of middle-phase microemulsion. In our previous study[5)], we have attempted to find out a correlation between this parameter and other variables of the optimum formulations through the function of optimal salinity (S^*). The significance of this correlation is that in the absence of the measured data, the minimum water-oil IFT (γ_{min}) can be estimated from the compositions of the surfactant/alcohol mixture. However these correlations were developed under constant water/oil ratio ($WOR = 4$) or volumetric oil fraction ($\theta_O = 0.2$). The term θ_O here, is defined as ratio between volume of oil phase and total volume of the system. Based on this definition, θ_O is equivalent with the degree of oil saturation (S_O), i.e. ratio between volume of oil entrapped in the porous medium and total volume of the pore space[6)]. In saturated zone, S_O is different from site to site depending on the amount of entrapped NAPL, which may occupy between 5 and 40% of the pore volumes[7),8)]. The remaining part of the pore is occupied by water. Thus, the degrees of both water and oil saturation and their ratio are the function of pore structure and nature of contaminants. The question arises here is whether the effect of θ_O on the characteristics of the optimum formulations is significant. If so, the value of S_O should be taken into account during the optimization process.

To date, no attention was made on the relationship between the θ_O taken for the batches and S_O present inside the porous media. Ducreux et al[1)] used a surfactant formulation optimized at $\theta_O = 0.2$ to remediate the soil contaminated with NAPL at $S_O = 0.128$ only. Other studies concerning with the phase

behavior of the system were also carried out under the constant θ_O[9),10),11),12)]. The constant value of θ_O adapted by many researchers[13),14),15)] during the optimization of the surfactant formulation for aquifer remediation, implies that the effect of θ_O on the phase behavior of the system is negligible. This may be valid only for the cases, when the partitioning coefficient of surfactant or alcohol between oil and aqueous phase is small. But in the systems containing heavy alcohols, which are dissolved mainly in the oil phase, changing the θ_O tends to change the alcohol concentrations in both oil and water rich phases, which in turn can change the type of the systems.

The focuses of the present work are therefore to investigate the effect of the θ_O on the phase behavior of the brine/surfactant/alcohol/oil systems in the batches and to incorporate it into the functions of S^* and γ_{min}. The compatibility between the θ_O taken for the batches and S_O present inside the porous media are then verified through the column experiments.

2. EXPERIMENTAL SECTION

Two steps of the experimental works were conducted to investigate the effect of θ_O on S^* and γ_{min} and to verify these results for soil remediation purposes. The first step involved measurements of S^* and γ_{min} for several systems at different θ_O. Various alkanes and diesel oil were used as contaminants. In the second step, one-dimensional column apparatus was used to compare the efficiency of three surfactant/alcohol formulations for removal of residual n-dodecane from the glass-beads medium. These formulations contained the same concentrations of surfactant (10 g/l) and alcohol (30 g/l), but different salinities, which were obtained by optimizing the formulations for three cases: $\theta_O < S_O$, $\theta_O = S_O$ and $\theta_O > S_O$, respectively.

(1) Materials

Sodium Dodecyl BenzeneSulfonate (SDBS) with purity of 95% was selected as surfactant, while n-pentanol with purity > 99% was used as co-surfactant for producing middle-phase microemulsions. Three saturated hydrocarbons (alkanes): n-decane, n-dodecane and n-tetradecane with purity > 99%, and diesel oil representing a mixture of hydrocarbons were used as contaminants. All contaminants were used for the batch experiments, but only n-dodecane – a representative of the saturated hydrocarbons found in gasoline and jet fuel[7] - was selected as a testing contaminant for column experiments. n-dodecane has a density of 0.75 g/cm³, an aqueous solubility of 3.7 μg/l and a dynamic viscosity of 1.6 kg/ms[7),16)]. The surface tension of n-dodecane is 24.9 dyn/cm, while the IFT between n-dodecane and water is 52.8 dyn/cm[16)]. The contaminants were dyed with oil-red-O, so that appearance of the different phases could be observed quantitatively. All these chemicals were purchased from Tokyo Kasei Kogyo Company, except the diesel oil which was purchased from a gasoline station. Their selective properties are given in the **Table 1**. Sodium chloride with purity of 99% was used as electrolyte and water was distilled for preparation of the aqueous solutions.

The porous medium is composed of 0.5-mm glass beads, which have a bulk density of 1.53 g/cm³, a porosity of 0.373 and a hydraulic conductivity of 0.023 cm/s. The glass beads were washed several times by distilled water prior to use. The reason of using the glass beads in this study is that the adsorption of the surfactant and alcohol onto solid surface is negligible or practically zero[17)]. This means that, 100% of surfactant and alcohol are contributed to the efficiency of the formulation. This allows one to study the effect of θ_O independently on the efficiency of the optimum surfactant formulations for oil recovery.

(2) Methodology
a) Batch experiments

Studies on phase behavior of the brine/surfactant/alcohol/oil systems were conducted in 110-ml glass bottles capped to prevent volatilization losses. In each bottle, 50 ml of an aqueous phase containing brine, surfactant and n-pentanol was contacted with an oil phase with variable volumes by shaking and allowed to stand until phase volumes became time-independent for at least one week in a 15°C room. This temperature was selected for the experiment because it is close to the groundwater temperature range[9)]. All concentrations are expressed in gram per liter (g/l) of aqueous phase. Different types of oil were used as contaminants, with a constant concentration of SDBS (10 g/l) and variable n-pentanol concentrations (C_{alc}). For each θ_O, the classical Winsor type I-III-II transitions were obtained by varying the salinity concentration (S) with keeping other variables constant. The appearance and disappearance of middle phases were verified by visual observation. The S^* were then determined as the midpoints of the three-phase regions.

The selective samples with optimal salinities obtained for different θ_O were taken for IFT measurements. The method of measurement is spinning drop technique, which has been described by details in our previous study[5)]. The experimental data were then used to incorporate θ_O into the

Table 1 Selected properties of the chemicals used in this study

Chemical name	Chemical formula	Molecular weight	Density (g/cm^3)
SDBS	$C_{12}H_{25}C_6H_4$ $-SO_3Na$	348.49	1.190
n-pentanol	$C_5H_{11}OH$	88.15	0.815
n-decane	$C_{10}H_{22}$	142.28	0.731
n-dodecane	$C_{12}H_{26}$	170.33	0.750
n-tetradecane	$C_{14}H_{30}$	198.39	0.763
diesel oil	mixture	-	0.818

functions of S^* and γ_{min}.

In order to gain more understanding on the mechanism of oil displacement process by an aqueous phase, the viscosities of the aqueous and oil phases were measured by using a viscometer (Sibata, Scientific Technology Ltd, Japan).

b) Column experiments

The column apparatus was made by glass (length, L = 50 cm, inside diameter, ID = 10 cm) equipped with two removable end caps (**Fig.1**). Both end caps were fitted with the steel support meshes to avoid the flow of glass beads from the column.

The experiment began by contaminating the glass beads with n-dodecane. The process was the same as described by Bettahar et al[13]. To create the natural condition, initially the glass beads were wetted with water and then were mixed with an amount of n-dodecane equal to 10% of pore volume (or S_O = 0.1). This value is the maximum residual saturation of n-dodecane entrapped in the glass beads due to capillary forces. The mixture of water-wetted glass beads and n-dodecane was then mixed gently until a homogeneous mixture was obtained. The homogeneity of the system was confirmed by gravitational method.

The column was then packed with the contaminated glass beads under vibration and fitting the column with the top end cap containing a steel mesh. At the start of the experiment, approximately 10 pore volumes of distilled water were pumped through the bottom of column to ensure that the glass beads were completely saturated and no free mobile n-dodecane was displaced from the column. Following the water flow, the surfactant solution – a mixture of water, sodium chloride, surfactant and alcohol was pumped in upward mode with a flow rate of about 30 ml/min to displace the entrapped n-dodecane. The column effluent was collected in glass bottles and immediately capped.

The homogeneous brine/surfactant/n-pentanol/n-dodecane mixtures obtained by shaking effluent samples multiple times, were diluted in a solvent (*iso*-propanol) and analyzed by gas chromatography (GC-14B, Shimadzu Corporation, Kyoto, Japan) equipped with a packed column (SE-30) and flame ionization detector (FID). The presence of n-dodecane in the sample was recognized by occurrence of a peak, the area of which indicated the concentration of n-dodecane. The results were then converted into grams of n-dodecane present in each effluent bottle.

3. RESULTS AND DISCUSSION

(1) Batch experiments

a) Effect of θ_O on the phase behavior

In order to investigate the effect of θ_O on the system phase behavior, salinity scans were conducted for a range of θ_O, maintaining all other variables constant. The maximum θ_O was selected not greater than 0.5 since the typical residual saturation of NAPL may occupy only between 5 and 40% of the pore volume[7],[8]. The typical results for the systems with n-decane at n-pentanol concentration of 20 g/l are shown in **Fig.2**. The dashed curves run from lower left to upper 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 connecting the points, at which the water-oil interfacial tensions are minimum, is called as the line of optimal salinity.

As seen from **Fig.2**, the effect of θ_O on system phase behavior is significant. With increasing the θ_O, the system changes from Winsor II→ Winsor III → Winsor I and this leads to increase also the salinity needed to produce the three-phase system. The observed phenomena could be explained as follows: let K_C be the distribution coefficient of n-pentanol between oil and aqueous phases

$$K_C = C_O / C_A \qquad (1)$$

where C_O and C_A are the equilibrium concentrations of n-pentanol in oil and aqueous phases.

Upon increasing θ_O i.e. the oil volume of the system, while keeping the aqueous volume constant, the C_A will be decreased due to the additional partition of n-pentanol into the oil phase. Since K_C is constant for a given temperature, the C_O is also decreased. The n-pentanol can be considered as both co-surfactant to increase the hydrophobic nature of aqueous phase and co-oil to decrease hydophobicity of the oil phase[11],[18]. Thus, a decrease in concentration of n-pentanol in both phases creates more dissimilarity between them, which in turn promotes the system to become o/w microemulsion
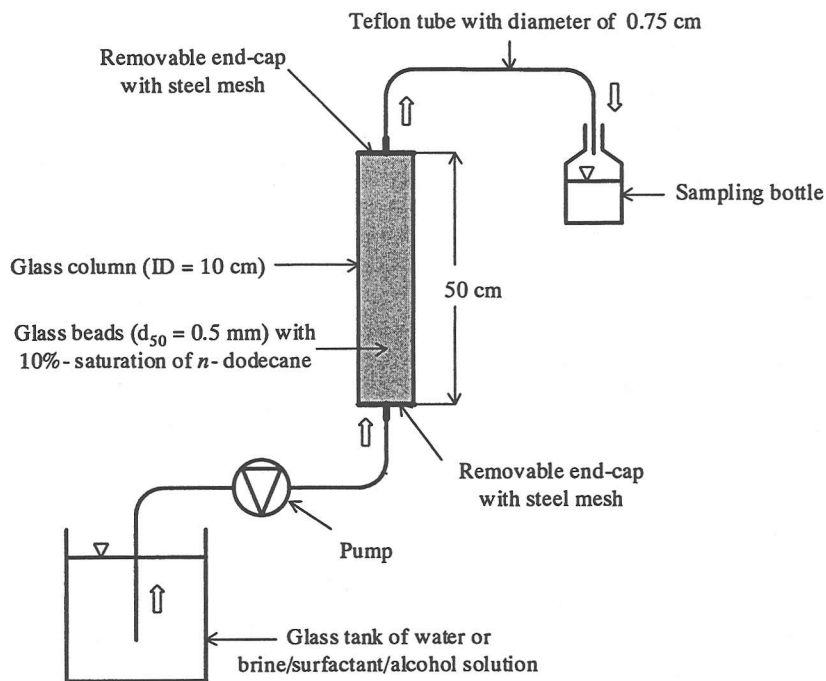
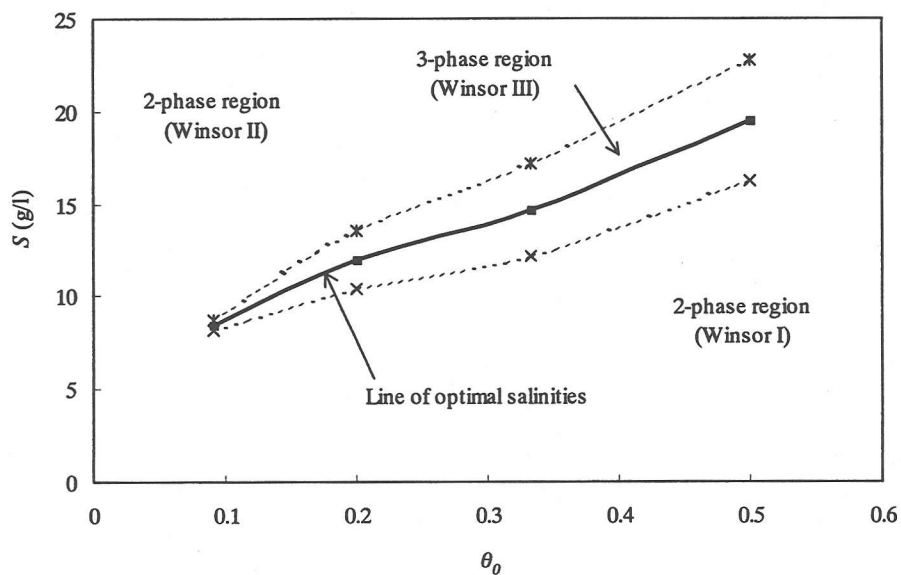**Fig.1** Set up for surfactant flushing experiments

Fig.2 Phase diagram S - θ_O for n-dodecane at C_{alc} = 20 g/l

(or Winsor I). This also means that with increasing θ_O, the salinity required to produce the middle-phase microemulsion is also increased.

b) Incorporation of θ_O into the function of $S*$

For pure hydrocarbon, the correlation between $S*$ and other variables of the optimum middle-phase microemulsion at $\theta_O = 0.2$ and $T = 15^0C$ can be written as follows[14].

$$LnS^{\bullet} = K(ACN) + f(A) - \sigma + a_T(T - 15) \qquad (2)$$

where K is a constant depending on the surfactant type; $f(A)$ is a function of heavy alcohol (n-pentanol or heavier) and its concentration in aqueous solution; σ is a parameter characteristic of surfactant, ACN is the *alkane carbon number*, e.g. the number of carbons in the hydrocarbon chain; a_T is the temperature coefficient; T is the current temperature.

For crude oil and mixture of pure hydrocarbons, the Eq.(2) will be[15].

$$LnS^{\bullet}_m = K(EACN)_m + f(A) - \sigma + a_T(T - 15) \qquad (3)$$

where

$$(EACN)_m = \Sigma X_i (EACN)_i \qquad (4)$$

here, $(EACN)_m$ and $(EACN)_i$ are the equivalent alkane carbon numbers for the oil mixture and component i, respectively; X_i is the mole fraction of the component i in the mixed oil phase; that is, $\Sigma X_i = 1$.

The methods and results of determining the parameters K, σ, $f(A)$ and a_T were provided in details in our previous work[5]. It is apparent from the Eq.(2) and (3) that the term θ_O has not been included in the function of $S*$. Thus additional attempt is needed to link this term to that function.

Fig.3 shows the logarithm of the $S*$ as a function of θ_O for different types of oil. Interestingly, all curves are straight but not parallel lines. Upon increasing n-pentanol concentration, the straight lines shift downward (or right) with increased magnitudes of the slope angle.

The optimal salinity, S_x* at any oil fraction, $\theta_O = x$ can be related with $S_{0.2}*$ at $\theta_O = 0.2$ as in Eq.(5)

$$LnS^{\bullet}_x = LnS^{\bullet}_{0.2} + \frac{\Delta LnS^*}{x - 0.2}(x - 0.2) \qquad (5)$$

Setting $k_a = \Delta lnS^*/(x-0.2)$ (called as coefficient of oil fraction) and substituting it into the Eq.(2) and (3), results in

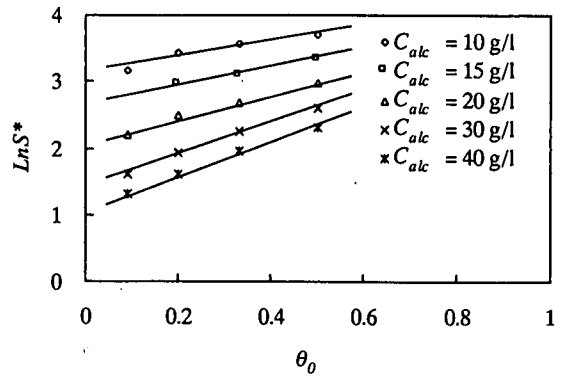Fig.3 $LnS*$ - θ_O for n-decane with different C_{alc}

$$LnS^{\bullet} = K(ACN) + f(A) - \sigma + a_T(T - 15) + \\ + k_a(x - 0.2) \qquad (6)$$

$$LnS^{\bullet}_m = K(EACN)_m + f(A) - \sigma + a_T(T - 15) + \\ + k_a(x - 0.2) \qquad (7)$$

From **Fig.3**, k_a is the slope of the straight lines, which is the function of n-pentanol concentration. In a free n-pentanol system, changing the WOR does not change the system behavior, so k_a is equal to zero. This results from hydrophilic nature of the surfactant. The plots of k_a versus concentrations of n-pentanol shown in **Fig.4** indicates that k_a is increased with increasing n-pentanol concentration and is essentially independent of the oil type.

c) Incorporation of θ_O into the function of γ_{min}

In our previous study[5], we have found an empirical correlation between γ_{min} and $S*$ of the optimum surfactant formulations at $\theta_O = 0.2$ as follows

$$\gamma_{min} = K_S(S^* - b) \qquad (8)$$

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 ($\gamma_{min} = 0$). Both K_S and b are independent of the oil type and n-pentanol concentration. It was also found that with the conditions of this study K_S and b are almost 0.0004 and 1, respectively, when γ_{min} is expressed in dyn/cm and $S*$ in g/l.

As mentioned in 3.(1)a) that with changing θ_O, the $S*$ needed to produce the three-phase system is also changed. This in turn can lead to the change of the minimum IFT between aqueous and oil phase.
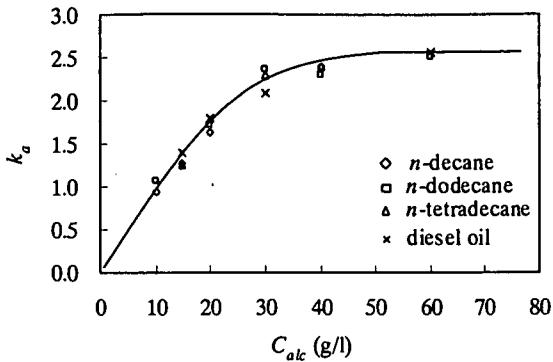
Fig.4 $k_a - C_{alc}$ for different types of oil

Fig.5 Verification of the correlation $\gamma_{min} = f(S^*)$

It is then assumed that whatever value of θ_O, the correlation between γ_{min} and S^* will still obey the Eq.(8). This assumption needs to be verified by the experimental data. For doing this, at each n-pentanol concentration, the minimum IFTs were measured experimentally ($\gamma_{min(exp)}$) at the optimal salinities obtained for different θ_O values (ranging from 0.1-0.5). The experiment was carried out for various types of oil under constant concentration of SDBS and temperature, which were as 10 g/l and 15^0C, respectively.

Based on the values of S^*, the minimum IFTs were then estimated ($\gamma_{min(est)}$) by using Eq.(8). The relationship between estimated and experimental values of γ_{min} is shown in Fig.5. Only a small difference between estimated and experimental values of the IFTs is obtained. On average, the estimated γ_{min} are 0.95 times less than experimental values. Thus, the Eq.(8) established for θ_O = 0.2 provides reasonable estimates of γ_{min} between aqueous and nonaqueous phases for other values of θ_O. This means that for the conditions of these experiments, the parameters K_S and b are independent of the volumetric oil fraction.

Since the conditions applied in the batches (in absence of the porous media and under equilibrium and static regimes) are somewhat different from the actual situations occured in the porous media (under dynamic and nonequilibrium conditions), the Eq.(6), (7) and (8) need to be verified through the column experiments before one can use to select an optimum surfactant formulation for oil recovery. The section described below will address to this concern.

(2) Column experiments
a) Verification of the developed correlations
Three surfactant/alcohol formulations (I, II and III) optimized at different θ_O (less, equal and higher
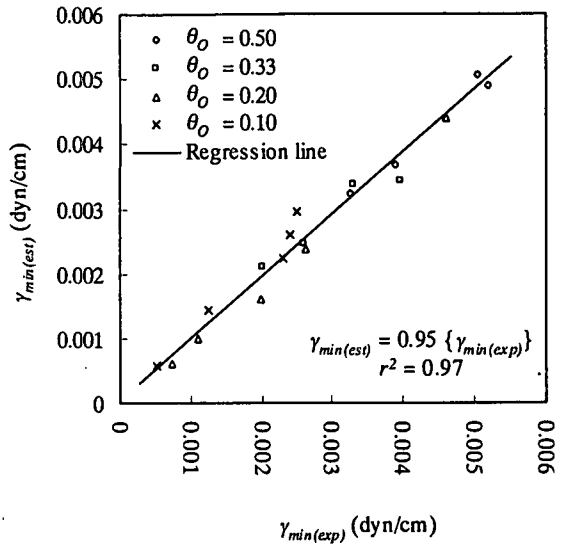
than S_O present inside the porous media) were used to compare their efficiency for oil recovery. The optimal salinities corresponding to these three n-dodecane fractions are given in Table 2.

Fig.6(a) represents a plot of total n-dodecane recovery (M_T is expressed in percentage of n-dodecane amount initially present in the column) versus number of washing (V/Vp), i.e. the ratio between the discharged volume of surfactant solution (V) and the total pore volume (Vp) of the porous medium. Here, the total recovery is obtained by successive addition of all n-dodecane amounts removed from the glass beads column from the first sample to the sample of consideration.

As seen from the Fig.6(a), more than 90% of entrapped n-dodecane could be removed after injection of only 1.77 Vp, 1.05 Vp and 1.37 Vp of the formulations I, II and III, respectively. In order to remove this amount of n-dodecane by using conventional pump and treat method, at least 20×10^6 Vp of water is needed. However, among these three formulations, the formulation III is less suitable since it needs highest salt concentration, but yields lowest efficiency. Although the final recovery (96.8% at 1.82 Vp) of n-dodecane obtained by using the formulation I is higher than that (93.8% at 1.15 Vp) obtained by the formulation II, the amount of surfactant/alcohol solution needed to remove this additional 3% of n-dodecane is increased in 0.67 Vp (or 52.8%). This will increase the cost of remediation significantly. Furthermore, when more than 90% of n-dodecane could be recovered, the final residual saturation of n-dodecane is only 1.82 grams per kilogram of the glass beads: this is an

Table 2 The values of S^* obtained at different θ_O

Formulation	θ_O	S^* (g/l)
I	$0.02 < S_O$	3.0
II	$0.10 = S_O$	6.6
III	$0.20 > S_O$	8.55

Table 3 Physical properties of the aqueous phase at $\theta_O = S_O$

Formulation	Salinity (g/l)	Dynamic viscosity (kg/ms)	Water-oil IFT (dyn/cm)
I	3.0	1.43	0.0790
II	6.6	1.22	0.0023
III	8.55	1.23	0.0179
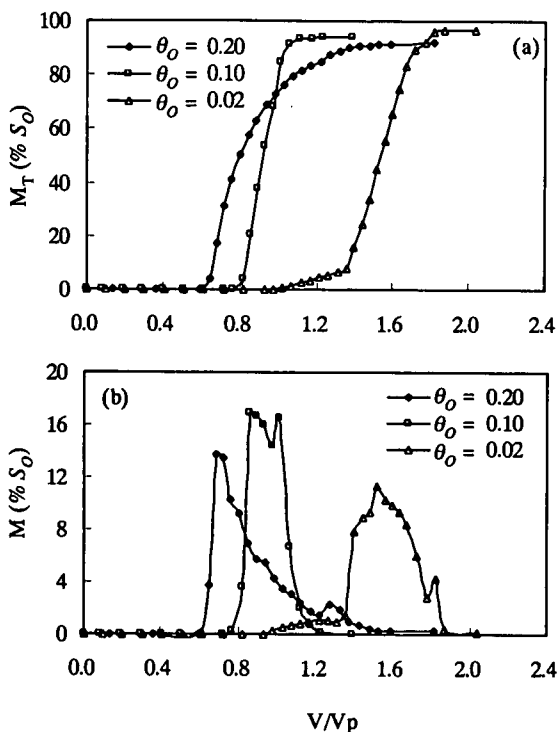
Fig.6 Total n-dodecane recovery (a) and mass of n-dodecane displaced (b) from the column versus number of washing

appropriate situation for implementing the biodegradation stage[19]. Given this, the formulation II with $\theta_O = S_O$ would be the optimum one among these three formulations. This means that the results of the batch experiments are in agreement with that of the column experiments.

The difference between the potentials for oil recovery of the surfactant formulations can be explained based on the values of water-oil IFTs. The results of measuring the IFTs at $\theta_O = 0.1$ are shown in Table 3. As the formulation II with the salinity of 6.6 g/l, yields lowest IFT, it is the best one among others. The formulations I and III have salinities less and higher than 6.6 g/l, respectively, but both produce greater IFTs than the formulation II. As a result, they are less efficient to recover n-dodecane.

For these reasons, the formulation II is called as optimum, whereas the formulations I and III as under-optimized and over-optimized formulations[19], respectively.

b) Understanding the mechanism of oil displacement process

Fig.6(b) shows a mass of n-dodecane (M) removed from the column during the flushing process versus V/Vp. This figure reveals that the volumes of the surfactant/alcohol solution needed to reach the points, at which the n-dodecane appeared in the column effluent, are different for the three formulations. Although the initially saturated water in the column prior to surfactant flushing was 0.9 Vp, measurable quantities of n-dodecane appeared in the effluent after only 0.75 Vp and 0.6 Vp for the formulations II and III, respectively. These data indicate that the mobilized n-dodecane formed a bank of free product that was displaced from the column prior to surfactant breakthrough[20],[21]. It was also observed during the experiments that there was a preferential flow of the aqueous phase through the n-dodecane bank. This allows the surfactant/alcohol solution together with solubilized n-dodecane to reach the column effluent before complete displacement of water. The break of the n-dodecane bank may be due to the lower viscosity of the aqueous phase (Table 3) than that of the n-dodecane phase (1.6 kg/m s). With the formulation I, the n-dodecane appeared in the effluent after nearly 0.9 Vp of the surfactant/alcohol solution had passed through the column indicating that at the moment of n-dodecane appearance in the effluent, almost all initially saturated water was displaced by the surfactant/alcohol solution. A small difference in the viscosities of the aqueous phase (1.43 kg/ms) and of the n-dodecane, allows the aqueous phase to move with approximately the same velocity with the n-dodecane. This leads to displace almost all initially saturated water from the column before the appearance of n-dodecane in the effluent.

The viscosity of the aqueous phase at salinity of 3 g/l is greater than that at other salinities. This is because of the presence of surfactant in the aqueous phase at low salinity concentration, i.e. the system is Winsor I type. At the salinities of 6.6 g/l and 8.55

g/l, the surfactant resides from the aqueous phase to the water/n-dodecane interface (Winsor III) or to n-dodecane phase (Winsor II), respectively, leaving very small amount of surfactant molecules in the aqueous phase. This creates the similarity in viscosity of the aqueous phase in these cases, but less than that in the previous case.

Both mobilization and solubilization processes occurred simultaneously during the main displacement period, in which 96.8%, 93.8% and 91.8% of the initially entrapped amount of n-dodecane were removed from the column after flushing ~ 1.82 Vp, 1.15 Vp and 1.6 Vp of the formulations I, II and III, respectively. However, the mobilization process was dominant because most of the displaced n-dodecane at the effluent was found in the form of separate phase (or free product). Thus, in comparison with the formulation III, the formulations I and II were able to displace more 5% and 2% of initially entrapped amount of n-dodecane as free product, respectively. It is due to the fact that behind the n-dodecane bank, there still remains very small amount of n-dodecane, which is much less than initial S_O. Obviously, the formulations with lower salinities would have greater potentials to mobilize this remaining n-dodecane, because they make the system closer to the optimum state.

The mobilization process ceased after the main displacement period, but the solubilization still continued. However, the amount of n-dodecane removed by this solubilization process was very small. For this reason, the curves of total n-dodecane recovery reach almost constant values after the main period.

(3) Application of the correlations

For remediation of a site contaminated with a particular contaminant (ACN) at a certain S_O, the correlations can be used to select an optimum formulation, which can produce ultralow IFT needed to displace the oil from the soil. From the desired value of IFT, the S^* required to bring the system to the optimum state, can be computed by Eq.(8). Eq.(6) is then used to estimate the values of the adjustable variables $(f(A)$ and $k_a)$, based on which the concentration of alcohol can be calculated. In reality, the contaminants usually exist as a mixture of pure compounds, so the term ACN in Eq.(6) must be replaced by $(EACN)_m$ as in Eq.(4).

Because the screening process for obtaining the optimum system is extremely time-consuming, these correlations will significantly reduce the laboratory works, thus the cost associated with the optimization of the surfactant formulations for soil remediation.

It is noted that the correlations were developed in this study with considering only liquid-liquid interactions, in which 100% of surfactant and alcohol were contributing to the efficiency of the formulation. However, with presence of the soil, surfactant and alcohol may partition into the solid phase (adsorption) causing a decrease of their concentrations in the liquid phases[3]. Because only the surfactant and alcohol present in the liquid phases are contributing to the decrease of water-oil IFT, the reduction of their effective concentrations will diverge the system from the optimum state and thus, decrease the efficiency of the formulation[22]. Therefore, in order to maintain the system at or near the optimum state, the surfactant and alcohol concentrations calculated from the correlations should be added in an amount equal to their losses. Since the extent of soil adsorption by surfactant and alcohol is site specific, the selection of the surfactant formulation should be determined in laboratory tests using representative soil samples from the site.

4. CONCLUSIONS

(1) The effect of θ_O on phase behavior of the brine/surfactant/alcohol/oil systems is significant. As θ_O increases, the system changes from Winsor II→ Winsor III → Winsor I.

(2) The change of θ_O leads to the change of S^*. This dependency of S^* on θ_O is described through the coefficient k_a, which is a function of alcohol concentration.

(3) As S^* changes with θ_O, the γ_{min} is also changed. However, their correlation is still the same as that developed for $\theta_O = 0.2$.

(4) The agreement between the results obtained from the batches and that from the column experiments indicates that the Eq.(6), (7) and (8) can be used to select the optimum surfactant formulations for soil remediation.

(5) The success of the soil remediation depends also on the method of injecting and recovering the surfactant solution. The optimization of the hydraulic systems for this purpose needs further investigation.

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汚染土壌から石油系炭化水素を除去するための最適な界面活性剤溶液の調整

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本研究では，汚染土壌修復のために調製した界面活性剤溶液の最適塩濃度(S^*)及び水－油界面張力(γ_{min})の最小値に及ぼす油分率の影響について検討した．その結果，最適塩濃度と界面張力の最小値は，油分率の変化に伴い変化することが確認された．又，この結果がカラム実験の結果と一致していることを確認した．カラム中の油分率を考慮して調製した界面活性剤溶液が最も高い回収率を示した．この油分率の変化に伴う最適塩濃度の変化は，油分率係数(ka)によって表される．しかしながら，この変化は，最適塩濃度と界面張力の最小値との関係に影響しないことが前報の中で確認された．以上の結果から，汚染土壌修復のために最適な界面活性剤溶液を調製するための有用な指標を提供した．