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Thesis Approval

Microemulsion Preparations (middle phase) for Surfactant Enhancing Aquifer Remediation

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Dedication:

First of all, my full thanks to Allah. With proud and honor I would like to dedicate this work to my beloved parents Mr. Anwar Inaya and Ms.Sanaa Inaya in recognition of their unlimited moral and all kind support and loyalty to me, and Introduce step-down to my brothers Ameen, Ahmad and Mohammed, and sisters Rana, Suha and Nesreen for their help all over the time.

Here by I consider this thesis as a drop of science in the way of grounding.

Hadia Anwar" Mohammad Ameen" Inaya

Abstract:

Nonaqueous phase liquids NAPLs., such as kerosene and light crude oil, pose a significant threat to the environment, specifically to our drinking water present in aquifers. In many instances, a NAPL will become trapped and form pools on top of confining layers while migrating through the vadose zone. Residual NAPL sources of long term contamination is difficult to remove by classical pump-and-treat remediation.

Surfactant enhanced aquifer remediation (SEAR) involves the injection of a surfactant solution consisting of surfactant and electrolyte. The aim was to observe optimum condition (Winsor III) with minimum surfactant's concentration. Surfactants increase the aqueous solubility of NAPLs by reducing their surface/interfacial tension at water–oil interfaces. As the interfacial tension is reduced and the aqueous surfactant concentration increased, the monomers aggregate to form micelles.

The ability of aqueous surfactant solutions (CTAB, LABS, PluronicF108 and Pluronic F127) for applications in removal of kerosene and crude oil from contaminated aquifer was carried out. The surfactants behavior in water–oil system (such as solubilization ratio and interfacial tension) was measured as a function of salt concentration at ambient temperature. Visual inspection as well as cross polarizers were used to detect anisotropy. The phase behavior of surfactants solution was determined for alcohol-free system.

Results showed that the middle phase of LABS and Pluronic F108 with ratio 3:1 appeared at 4.5 wt. % NaCl with kerosene. This percentage decreased when surfactants have equal ratios 1:1 to 3 wt. %. When replacing Pluronic F108 with Pluronic F 127, the middle phase appeared at 2.35 wt. % with distilled water and 2.0 wt. % with ground water. Meanwhile it appeared at 2.0 wt. % when kerosene was replaced by crude oil.

The middle phase of CTAB and Pluronic F 108 with the same ratios appeared at 6.0 wt. % with kerosene, 2.0 wt. % with crude oil and 0.0 wt. % with ground water.

The solubility ratios of all surfactant solutions were measured, approximately the same values of oil and water were solubilized in the middle phase. Ultra low interfacial tension values were calculated for the systems containing kerosene as model oil and low IFT values were predicted for the system containing crude oil.

الملخص

السوائل العضوية مثل الكيروسين والنفط الخام الخفيف ، تشكل خطرا كبيرا على البيئة ، على وجه الخصوص مياه الشرب الموجودة في طبقات المياه الجوفية. وفي كثير من الحالات ، السوائل العضوية تعلق و تصبح على شكل تجمعات طافية أعلى طبقات المياه الجوفية في حين تنتقل عبر الشقوق إلى منطقة بين القشرة الأرضية وخزان المياه الجوفية تعرف باسم (vadose zone).
السوائل العضوية الآتية من مصادر التلوث تبقى عالقة على المدى الطويل ، والتي يصعب إزالتها بالطرق الكلاسيكية عن طريق الضخ والمعالجة.

المركبات النشطة سطحيا تعزز معالجه المياه الجوفية عن طريق إدخال المركبات النشطة سطحياً والمركبات الأيونية كملح كلوريد الصوديوم. الهدف هو الوصول إلى الحالة المثلى winsor type (III) بأقل كميه مضافة من المركبات النشطة سطحياً. المركبات النشطة سطحياً تعمل على زيادة الذائبية للسوائل العضوية عن طريق تقليل التوتر السطحي الداخلي بين مزيج الماء والزيت. قلة التوتر السطحي بين الماء والزيت وزيادة تركيز محاليل المركبات النشطة سطحياً يؤدي إلى تجمع جزيئات الماء والزيت لتشكل محلول متجانس.

محاليل المركبات النشطة سطحياً(CTAB وLABS وPluronicF108 وPluronicF127)، قادرة على إزالة الكيروسين والنفط الخام الملوثة للمياه الجوفية. سلوك المركبات النشطة سطحياً لنظام الماء والزيت قيست أخذاً بعين الإعتبار تركيز الملح المستخدم في درجة حرارة الغرفة العادية. كما وقد تم استخدام المجهر المستقطب للكشف عن وجود الخواص المتباينة لمحاليل المركبات النشطة سطحياً. سلوك محاليل المركبات النشطة سطحياً حدد مع تجنب استخدام الكحول.

أظهرت النتائج أن الحالة المثلى لهذين المركبين LABS و Pluronic F108 بنسبه 3:1 ظهرت عند 4.5 من الوزن المئوي من ملح كلوريد الصوديوم مع الكيروسين. وهذه النسبة انخفضت عندما أصبحت المركبات النشطة سطحياً بنسب متساوية 1:1 وظهرت عند 3.0 من الوزن المئوي بينما عند استبدال Pluronic F108 ب Pluronic F127 ظهرت عند 2.35 من الوزن المئوي مع الماء المقطر و2.0 من الوزن المئوي مع المياه الجوفية. وفي الوقت نفسه ظهرت عند 2.0 من الوزن المئوي عندما تمت الاستعاضة عن الكيروسين بالنفط الخام.

الحالة المثلى للمركبين CTAB و Pluronic F108 بنفس نسب الخلط ظهرت عند 6.0 من الوزن المئوي مع إضافة الكيروسين و2.0 من الوزن المئوي عند إضافة النفط الخام وصفر من الوزن المئوي بإضافة المياه الجوفية. نسب الذائبية لجميع محاليل المركبات النشطة سطحيا قيست، وسجلت تقريبا نفس القيم للزيت والماء الذائبين في الحالة المثلى .وقد تم حساب قيم التوتر السطحي الداخلي للأنظمة المحتوية على الكيروسين والنفط الخام وقد كانت هذه القيم منخفضة بإضافة النفط الخام ومنخفضة جداً عند اضافة الكيروسين.

Chapter 1 Introduction

1. Introduction

1. 1 Remediation Options for Contaminated groundwater with NAPLs

Contamination of groundwater by nonaqueous phase liquids (NAPLs) is a widespread problem. The NAPL moves through subsurface due to gravity forces and the trapped NAPL can persist in the soil for many decades (Mackay, D. M. and Cherry, J. A., 1989). Organic liquids such as gasoline and diesel fuel are lighter than water and referred to as light non-aqueous phase liquids (LNAPLs). LNAPLs tend to accumulate above and slightly below the water table (consistent with a fluctuating water table). Organic liquids that are heavier than water such as, chlorinated solvents and polychlorinated biphenyl (PCB) oils are referred to as dense non-aqueous phase liquids (DNAPLs). Due to their high density, DNAPLs have the potential to migrate to depths well below water table, and thus, pose special cleanup challenges.

The conventional remediation method of pump and treat involves pumping of contaminated water followed by treatment of the surface by air stripping, activated carbon filtration and various other means. The hydraulic force imposed upon the NAPL as a result of pumping alone is usually insufficient to lower the residual NAPL saturation to acceptable levels. The pump and treat method is limited in its remediation effects (Mackay, D. M. and Cherry, J.A., 1989).

In-situ soil flushing with surfactants and co-solvents proven to be an effective strategy for solubilization and subsequent removal of NAPLs. (Brusseau, *at el.,* 1999; Lowe, *et al.,* 1999; Wood, A. L., and Enfield, C. A., 1999).

Aramaki, K. *et al.,* (1997), studied the effect of temperature on the phase behavior of ionic and nonionic microemulsions using different surfactants (sodium dodecyl sulfate-SDS; polyoxyethylene dodecyl ether – $C_{12}EO_2$) in decane system. The study showed that microemulsions are formed over a wide range of temperatures under different experimental conditions. The change in the hydrophilic lipophilic balance (HLB) composition with temperature is well described with increasing the monomeric solubility and decreasing the mixing fraction of nonionic surfactant in the surfactant layer. As a result, temperature-*insensitive microemulsions are formed in the* SDS-$C_{12}EO_3$ system.

Balcan, M. *et al.,* (2003) investigated the phase behavior of systems consisting of water / n-hexane / polyethoxylated nonionic surfactants with a normal distribution of ethylene oxide (EO) chain length. The study showed that in both the binary and the ternary systems containing the ethoxylated nonionic surfactants, anisotropic phase's specific to lamellar mesophases (liquid crystals) are present. The anisotropic zone disappears on increasing the temperature and its area on the phase diagram shrinks with surfactant hydrophilicity.

1.2 Microemulsions

Microemulsions are thermodynamically stable mixtures of oil and water that are stabilized by surfactants (Chattopadhay, A.K., *at el.,* 1996). They are typically classified into three main categories, or Winsor-type systems (Winsor, P., 1954). Winsor's Type I microemulsion consist of oil-swollen micelles in a water continuum; whereas a Type II consists of water-swollen reverse micelles in an oil continuum. Type III can be understood as an accumulation of swollen micelles so numerous that they touch one another, forming either some kind of percolated dispersion or a perfectly bicontinuous structure (Scriven, S., 1979) in which all water domains are connected and all oil domains are likewise connected. Because microemulsions are not dispersions, the boundary between the oil and water domains does not exhibit a strong curvature. In fact, as far as solubilization is concerned, the best microemulsions are found to have a zero net-curvature condition for the surfactant layer between the oil and water domains.

Formulation of microemulsions effective for enhanced oil recovery is often based on identification of state variables that lead to the so-called "middle-phase" microemulsion (or micellar solution) having the special property that it is in equilibrium with both excess oil and excess brine.

It is well established that interfacial tension between phases, and hence solubilization of oil and brine into the surfactant-rich phase, play important roles in the oil displacement process. A middle-phase microemulsion model is introduced that consists of alternating thin layers of oil and brine containing surfactant molecules oriented at each planar interface according to their amphiphilic character. Equilibrium is considered by the following interactions: van der Waals' attraction, electrostatic repulsion, and entropy decrease attendant surfactant orientation. The microstructure of a middle-phase microemulsion may have an essentially lamellar character, in large (Huh, C., 1979). The ternary-phase diagram surfactant, oil, and water (SOW), is helpful in understanding the role of the surfactant in microemulsion systems.

In the case of Types I and II, microemulsion systems shown in Figure 1, the dome in the lower part of the triangle represents a two-phase (polyphasic) region. A SOW mixture inside the dome will separate into two phases, as indicated by the tie lines. In the case of Type I microemulsions, the separation occurs in such a way that an excess oil phase is produced along with a surfactant-rich aqueous phase; the composition of each phase can be determined by locating where the tie line intersects with the dome frontier, i.e., the so-called binodal curve. The intersection point of the tie line and binodal curve closest to the water vertex is the surfactant-rich water phase, whereas, the other intersection point is the excess oil, excess water. The lower layer (aqueous phase) indicate the surfactant-rich microemulsion, which is generally more dense (Bennet, K., C., *et al.,* 1981). Conversely, in a Winsor Type II two-phase behavior region, the tie-line slope is in the opposite direction, and a surfactant-rich microemulsion (oil) phase is in an excess aqueous phase as shown in fig (1.1).

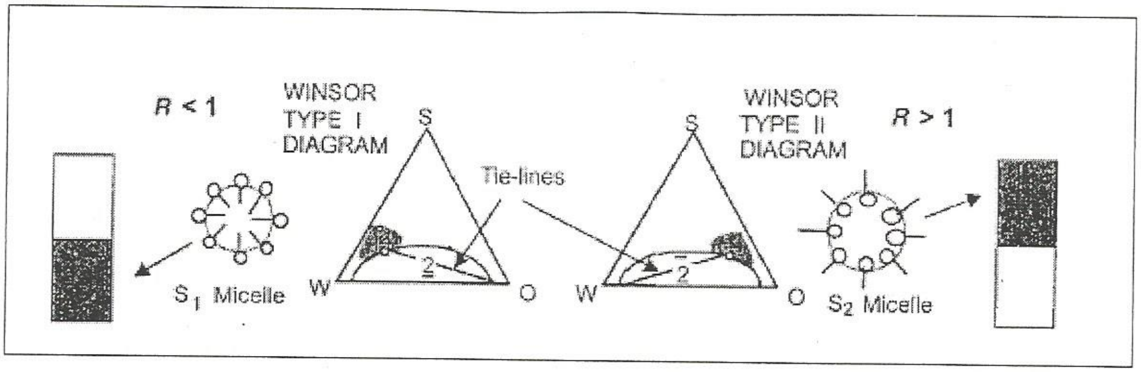


Fig.1.1 Type I and Type II of phase behavior for SOW systems according to Winsor (adopted from Ref. Winsor, P., 1954). Shading indicates the surfactant-rich phase.

Winsor Type III system contains a region in which three phases are in equilibrium: a surfactant-rich microemulsion, a so-called middle phase because of its intermediate location in the test tube, and two excess phases (oil and water). For the simplest Type III systems, the three phases can be represented by a tie triangle (excess oil, excess water, and a bicontinuous microemulsion), and any point in the triangle will separate into three phases, as represented by the vertices of the triangle (Shown the ternary diagram in fig 1.2).

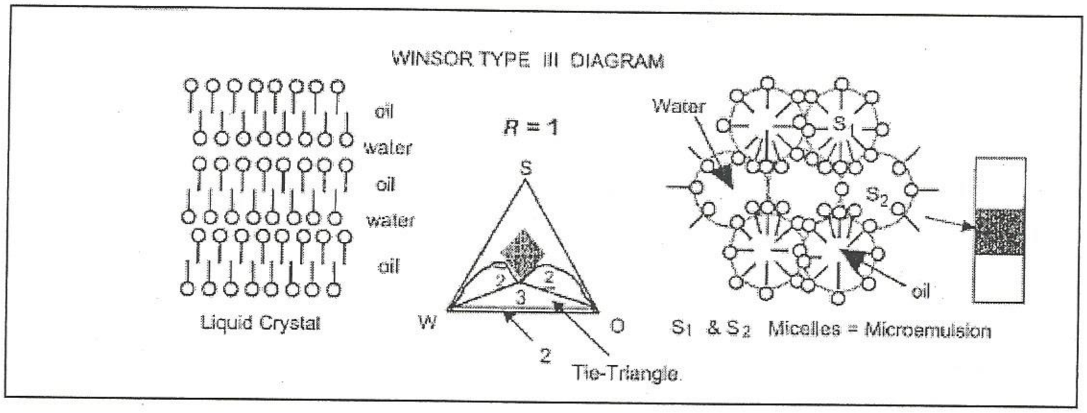


Fig.1.2. Type III, phase behavior for SOW systems according to Winsor (adopted from Winsor, P., 1954). Shading indicates the surfactant-rich phase.

1.2.1 Winsor ratio of interactions (R)

To interpret the different cases of phase behavior, Winsor introduced the following ratio of interactions (R) between the surfactant, oil, and water phases:

$R=A_{co}/A_{cw}$

Where A_{co} indicates the interaction between the surfactant adsorbed at the interface and the oil phase per unit area of interface, and where Acw does likewise for the water phase. Figure 1.3 shows a schematic for these interactions at the oil-water interface. In this simplified form, the Winsor R ratio is a handy tool to interpret the phase behavior changes. By definition, $R = 1$ when a middle-phase microemulsion contains equal volumes of oil and water (the tie triangle shown in Fig1.2). When the temperature, salinity or pressure changes the interaction changes. For instance, if the aqueous-phase salinity (electrolyte concentration) increases, the interaction A_{cw} will decrease and R will increase, resulting in an uptake of oil by the middle phase. Hence, a change in R from $R < 1$ to $R > 1$, or vice versa, will produce a change in diagram type, which is easily detectable through a change in the phase behavior.

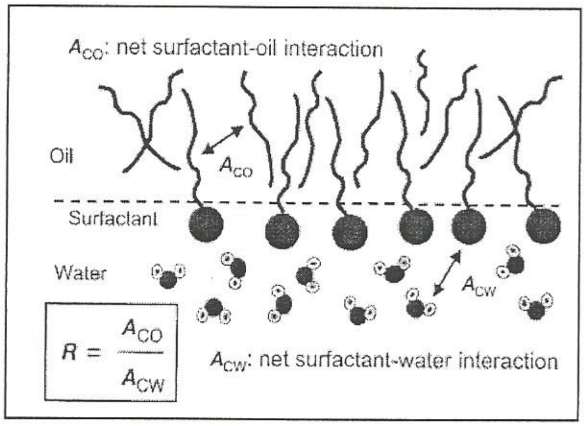


Fig.1.3. Adsorbed surfactant interactions with oil and water according to Winsor

Figure 1.4 illustrates this transition by a series of test tubes in which the SOW systems have a constant composition of surfactant, oil, and water, as indicated by the square dot in the ternary diagrams, but in which the salinity of the aqueous phase varies from one system to the next (increasing from left to right). The surfactant-rich phase is indicated as the shaded phase in the test tubes. Provided that the composition of the systems is properly selected to be located in the multiphasic region, observing the phase behavior in the test tube allows one to deduce the type of Winsor diagram that applies to the system. Such a series of systems, in which a single formulation variable such as salinity is varied in a continuous way, is called a formulation scan. Most often, changing the formulation variable produces I →III →II transition of the phase behavior if the change increases R, or vice versa. The formulation scan is the basic technique to pinpoint experimentally the case in which $R = 1$, a very special situation in which extraordinary phenomena take place (Noronha, J.C., *et al.,* 1982).

Specifically, the interfacial tension goes through a very low minimum and the solubilization reaches a maximum when $R = 1$. For this reason, the formulation with equal oil and water uptake is known as the optimum formulation, but is still less than unity; a three-phase system appears that has more water than oil in the middle phase. This is an "under-optimum" system, e.g., where $S = 2.0$ in Figure 4, one that exhibits a tie triangle slanted to the left (toward the water corner) and a middle phase (shaded) region in the test than unity, e.g., case S = 4.0 in Figure 1.4, the tie triangle slants toward the oil corner and the center of the shaded area of the test tube moves just above the original oil-water interface. As described before, for the optimum system both the tie triangle and the shaded region of the test tube are centered, and the interaction of the surfactant with oil and water is exactly balanced ($A_{CO} = A_{CW}$ and R = 1).

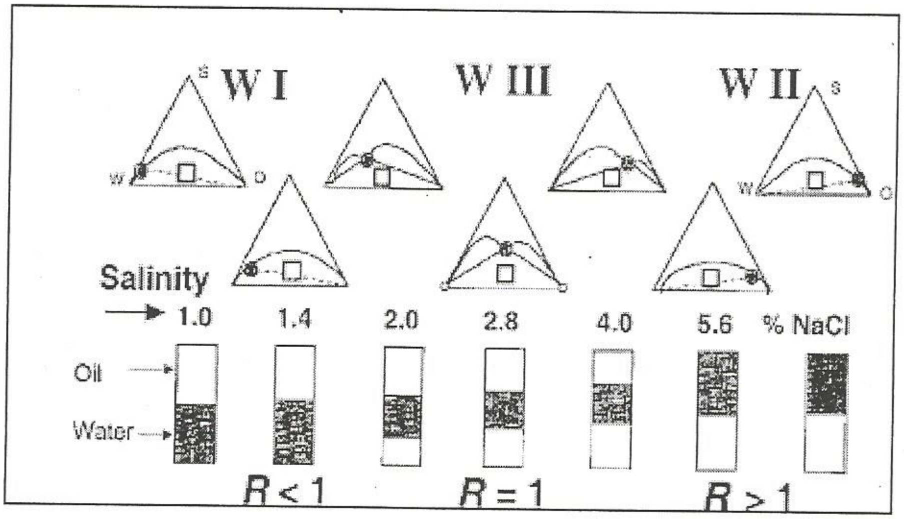


Fig.1.4. Phase behavior along a salinity scan: test tube aspect and phase diagram.

1.2.2 Surfactant Critical Packing Factor

To demonstrate another concept helpful in understanding microemulsion phase transition: the surfactant critical packing factor (Barakat, Y. *et al.,* 1983) which is expressed as $v/(a*l)$, where v is the volume of the surfactant tail, a is the surfactant area per molecule, and l is the length of the surfactant hydrophobe. Critical packing factors less than 1:3 suggest spherical micelles (Type I); whereas packing factors near 1 suggest that the surfactant molecule has the tendency to form zero-curvature surfactant membranes (Type III). Critical packing factors much larger than 1 form negatively curved (Type II) microemulsions (Hyde, S.T., 1992). Thus, increasing the critical packing factor by decreasing the area per head group (e.g., increasing salinity, shielding the ionically charged head groups) or increasing the volume of the tail group (e.g., using branched surfactants) predicts a transition from Type I to Type III to Type II, in keeping with the formulation experience. The importance of a balanced surfactant system is that increased interactions on both sides of the interface would enhance the affinity of the surfactant for both phases, and would thus improve the solubilization while maintaining optimum behavior. Since the maximum solubilization of a scan takes place when the interactions are equal, i.e., when $R = 1$, it was a matter of comparing various ways to attain $R = 1$, e.g., $R = 2{:}2$ or $5{:}5$, or to reach HLD = 0, e.g., HLD = 2 – 2 or 5 – 5.

Hydrophilic-Lipophilic deviation (HLD) concept is useful also, in model aggregate sizes, solubilization, phase volumes, phase transitions, and interfacial tension of microemulsion systems (Types I, II, III). This has recently been done by using the HLD concept in a critical scaling/statistical modeling approach to microemulsions, and is known as the net-average curvature model (Acosta, E., *et al.*, 2003).

1.3 Surfactant Enhanced Aquifer Remediation (SEAR)

The goal of surfactant-enhanced subsurface remediation is to maximize the contaminant extraction efficiency while optimizing system economics. Since middle phase microemulsions maximize the solubilization while minimizing oil–water interfacial tension, these systems are highly desirable for LNAPLs (Childs, J. D. *et al.,* 2004).

Surfactants, such as common household detergents, are chemical agents that enhance the effective solubility of organic compounds in the water or aqueous phase. Anionic surfactants have been more frequently used for SEAR application in recent years because soil surfaces are generally negatively charged, and a negatively charged surfactant will be repelled, rather than attracted to the soil surface.

Surfactant enhanced aquifer remediation (SEAR) involves the injection of a surfactant solution consisting of surfactant, electrolyte (for an anionic surfactant), water and often co-solvent (i.e., alcohol). Commonly used anionic surfactants for SEAR include alcohol ether sulfates, alkane sulfonates and sulfosuccinates. The addition of electrolytes and co-solvents helps to improve contaminant mass recovery and to prevent the formation of gels in the subsurface. Sodium chloride and calcium chloride are examples of commonly used electrolytes.

Surfactants increase the aqueous solubility of nonaqueous phase liquids (NAPLs) by reducing their surface/interfacial tension at air–water and water–oil interfaces. As the interfacial tension is reduced and the aqueous surfactant concentration increased, the monomers aggregate to form micelles. The concentration at which micelles first begin to form is known as the critical micelle concentration (CMC). This concentration corresponds to the point where the surfactant first shows the lowest surface tension (Figure1.5). Many physical properties used to characterize surfactants depending on the CMC such as; emulsion formation, oil solubilization, foaming and detergency, interfacial and surface tensions. These properties may be used to assess surfactant suitability for environmental remediation such as soil washing (Jawitz .J.W. *et al.,* 1998).

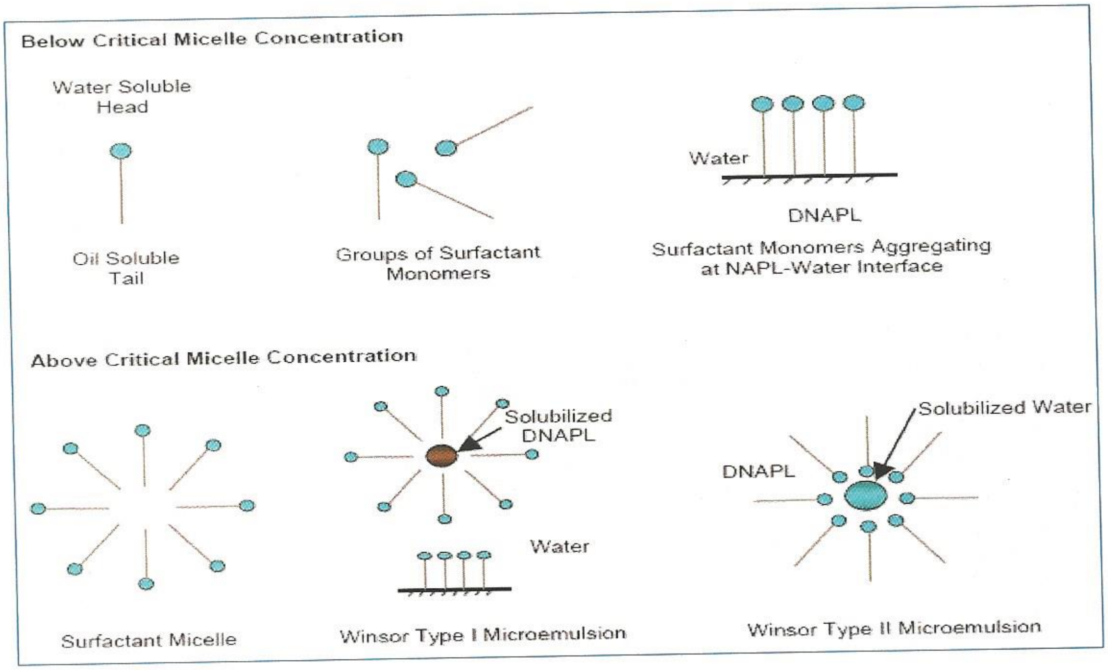


Fig.1.5. Micelle Formation Diagram (adopted from Bourrel, M., 1988)

1.3.1 Surfactant Dissolution and Mobilization of LNAPLs Contaminants in Aquifers

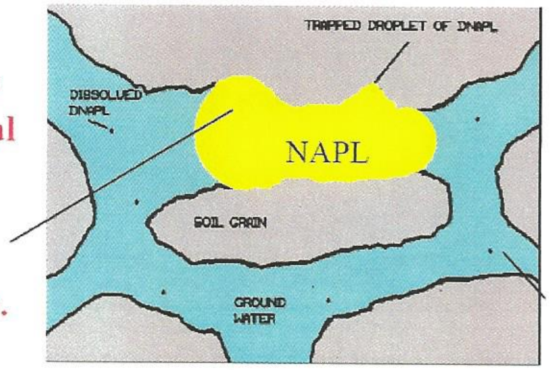
Surfactants work to enhance contaminant mass recovery in the subsurface by reducing the interfacial tension of the fluid phases contacting the residual NAPL. The extent of interfacial tension reduction will determine whether the primary mechanism of contaminant removal is via:

1- Solubilization of the residual DNAPLs into the surfactant solution, or
2- Mobilization of entrapped DNAPLs as free product:

1.3.2 LNAPLs Solubilization with SEAR

Low interfacial tension (IFT) reduction resulting in a single aqueous-phase solubilization system, also known as a Winsor Type III solubilization regime, is the preferred mode of SEAR application at locations where no capillary barrier exists or where it has been determined that the capillary barrier is fractured or otherwise not competent. Higher IFT reduction that increases the likelihood of an unsolubilized NAPL moving front typically provides more rapid NAPL removal, but may increase the potential for NAPL migration, if no competent barrier to downward movement exists as shown in Figure 1.6.

A surfactant solution designed to maximize solubilization significantly increases the total aqueous solubility of organic contaminants. The solubility increase allows residual DNAPLs mass to be recovered much more rapidly than by pump and treat which relies upon the much less efficient process of dissolution into groundwater. The solubility enhancement under ideal laboratory conditions, where surfactant is completely saturated with NAPL is on the order of 100 to 1,000-fold. Under field conditions, the solubility enhancement will vary with the quantity of NAPL contacted by surfactant. Surfactants reduce interfacial tension (IFT) by accumulating at the interface between the NAPL and water phases. At low concentrations, surfactants will exist as single molecules or monomers, at higher concentration they will begin to accumulate to form structures called micelles as shown in Figure 1.7.



High o/w interfacial tension makes the oil immobile.

Low water solubility -- 100s to 1000s of flushings (years) to dissolve oil.

Fig.1.6. NAPL trapped by capillary forces (Adapted from Sabatini D. 1998)

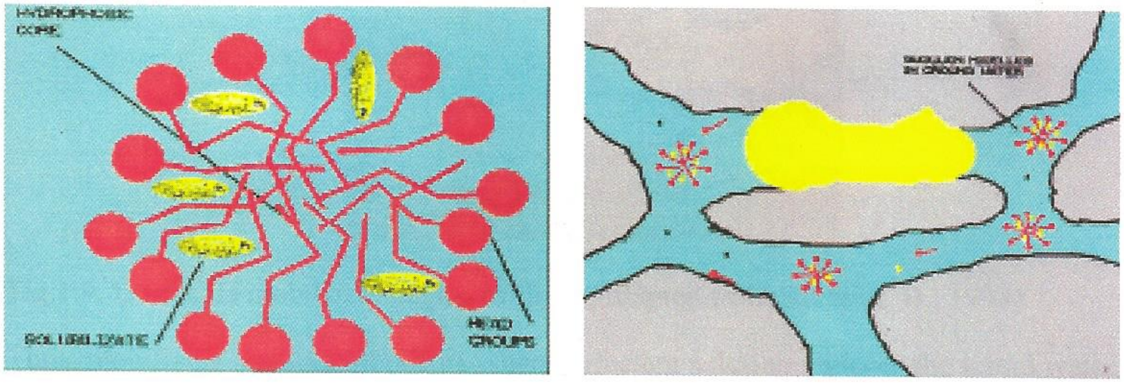


Fig.1.7. Surfactant micelles increase oil solubility (Adapted from Sabatini D. 1998)

1.3.3 LNAPLs mobilization with SEAR

Mobilization should be used only at sites with minimal potential for further vertical migration of the NAPL. A competent capillary barrier is needed to allow successful implementation of NAPL mobilization with SEAR. Surfactants mobilize NAPL by lowering the IFT sufficiently for the capillary forces holding the NAPL in place to be overwhelmed by gravity and viscous forces. The trapping number is a dimensionless quantity which considers the viscous and gravity forces that must be overcome to mobilize the NAPL, and is dependent upon parameters such as the interfacial tension, NAPL density and soil permeability. Capillary forces are inversely proportional to the soil permeability; the higher the soil permeability or the larger the pore size, the lower the capillary forces or pressure and the more easily mobilization will occur for a given IFT reduction. The lower soil permeability, the greater the IFT reduction, or the lower the IFT value necessary to induce mobilization (Figs 1.8 and1.9.).

Although an IFT of 0.001 dynes/cm will generally cause mobilization, the IFT value that induces mobilization must be computed on a site-by-site basis. While all surfactants have an effect on IFT, only certain surfactants can be used to achieve the ultralow IFTs needed to successfully mobilize residual NAPL. However, ultralow IFT surfactant systems can also lead to the undesirable Winsor Type II solubilization systems where surfactants will begin to partition (i.e. be lost) into the NAPL phase.

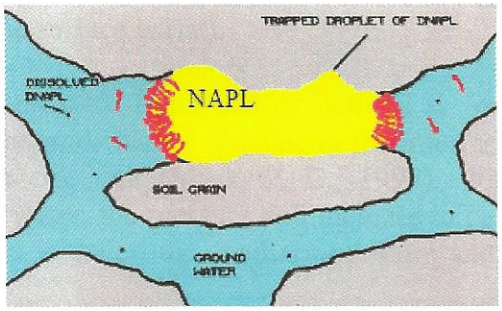


Fig.1.8. Surfactant adsorption lowers oil/water IFT (Adapted from Sabatini, D., 1998)

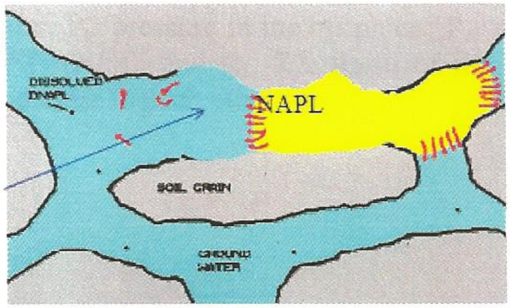


Fig.1.9. Droplet is mobilized, begins to flow (Adapted from Sabatini, D., 1998)

Thus, mobilizing residual oil occurs when surfactant solution replaces the initial water, and reduces the IFT between the residual oil and aqueous phase. Well performing surfactants commonly lower the IFT to 10^{-3} mN/m. An IFT of 10^{-3} mN/m nearly eliminates capillary pressure that originally trapped the residual oil, causing the oil to mobilize. The capillary number, N_c, is a non-dimensional parameter relating viscous forces to capillary forces, and is expressed as:

$$N_c = k\nabla\ |\Phi| / \gamma$$

The capillary forces are represented by the interfacial tension, γ, and the viscous forces are represented by $k\nabla\ |\Phi|$ (which includes the viscous potential gradient). Empirical data for different porous media have shown the reduction of residual to correlate to an increase in capillary number (Delshad, M., 1986). A critical capillary number describes the lower limit where residual oil can become nearly zero when capillary number increases a few orders of magnitude greater. A surfactant-based chemical flood reducing IFT to 10^{-3}mN/m commonly achieves capillary numbers representing zero residual oil (Shen, P., et al., 2006).

The work required to increase the surface area provides evidence for the existence of a pressure difference between the two sides of a curved surface. Its value for a spherical surface was deduced in 1805 independently by Thomas Young and by Pierre Simon de Laplace, and is given by

$$P_\alpha - P_\beta = 2\gamma\, r$$

Where P_α and P_β are the internal and external pressures of the spherical surface and r is its radius. The Young-Laplace equation shows that the pressure inside a spherical surface is always greater than the pressure outside, but the difference decreases to zero as the radius becomes infinite (when the surface is flat).

The IFT between two immiscible fluids can be defined as force per unit distance acting parallel to the interface perpendicular to any line in the interface, or as the work needed to increase the surface area one unit (Mørk, P. C., 1997). When passing over a curved interface between oil and water, the pressure will increase to balance the interfacial tension forces. The pressure jump is called the capillary pressure and it is given by the Laplace equation (1806),

$$P_c = P_o - P_w = \gamma_{ow}\,(1/R_1 + 1/R_2)$$

Where P_c: capillary pressure, P_o: pressure in the oil phase, P_w: pressure in the water phase (N/m^2), γ_{ow}: Oil-Water IFT, (N/m), and R_1, R2: Radii of the curvature of the oil-water interface measured perpendicular to each other, (m).