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**Microemulsion Preparations (middle phase) for
Surfactant Enhancing Aquifer Remediation**

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Microemulsion Preparations (middle phase) for Surfactant Enhancing Aquifer Remediation

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Deanship of Graduate Studies
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Thesis Approval

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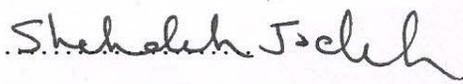
Supervisor: Dr. Ibrahim Kayali

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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

Declaration:

I certify that this thesis submitted for the degree of Master, is the result of my own research, except where otherwise acknowledged, and that is study (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signature:

Hadia Anwar"Mohammed Ameen"Inaya

Date:

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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.

.(vadose zone)

winsor type

(III)

(PluronicF127 PluronicF108 LABS CTAB)

Pluronic F108	LABS		
		4.5	3:1
3.0	1:1		
2.35	Pluronic F127	Pluronic F108	
		2.0	
			2.0

6.0

Pluronic F108 CTAB

2.0

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DEFINITION LIST OF ABBREVIATION

Abbreviation	Full word
CMC.....	Critical micelle concentration
DNAPLs.....	Dense Non Aqueous Phase Liquids
EC.....	Electrical conductivity
EOR.....	Enhancing Oil Recovery
HLB.....	Hydrophilic lipophilic balance
HLD.....	Hydrophilic Lipophilic deviation
IFT*.....	Optimum interfacial tension
LNAPLs.....	Light Non Aqueous Phase Liquids
NAPL.....	Non Aqueous Phase Liquid
NAPLs.....	Non Aqueous Phase Liquids
OWR.....	Oil-water ratio
R.....	Winsor ratio of interactions
SEAR.....	Surfactant Enhancement Aquifer Remediation
SOW	Surfactant -oil -water
SP*.....	Optimum solubility parameter
TDS.....	Total dissolved solids
γ^*	Optimum interfacial tension
γ_{mo}	Interfacial tension for oil in micelle
γ_{mw}	Interfacial tension for water in micelle

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, *et al.*, 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 – C₁₂EO₂) 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-C₁₂EO₃ 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 (Chattopadhyay, 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).

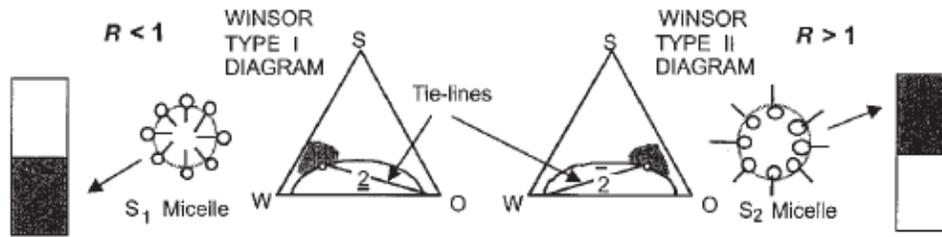


Fig.1.1 Type I and Type II of phase behavior for SOW systems according to Winsor (adopted from Ref. Winsor, P., 1954). Shading indicates the surfactant-rich phase.

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).

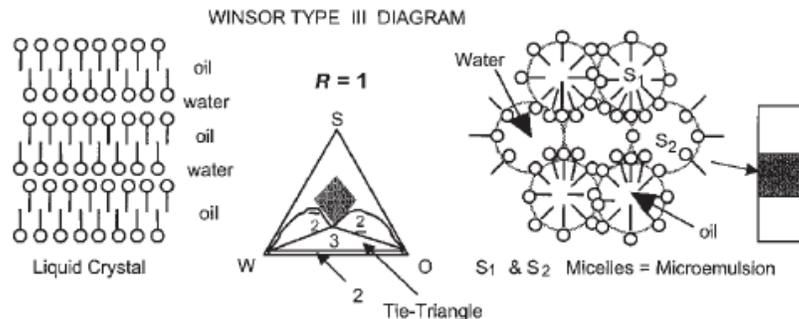


Fig.1.2. Type III, phase behavior for SOW systems according to Winsor (adopted from Winsor, P., 1954). Shading indicates the surfactant-rich phase.

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 A_{cw} 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.

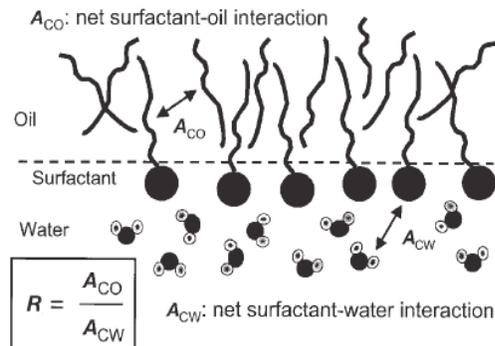


Fig.1.3. Adsorbed surfactant interactions with oil and water according to Winsor

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 $I \rightarrow III \rightarrow II$ 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 tube that is centered below the original oil-water interface. Likewise if R is just greater 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 $R = 1$).

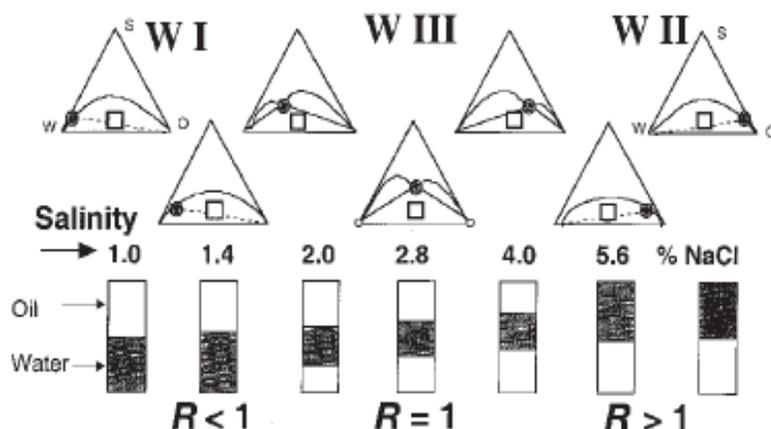


Fig.1.4. Phase behavior along a salinity scan: test tube aspect and phase diagram.

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 $v/(a \cdot l)$, 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 (Figure 1.5). 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).

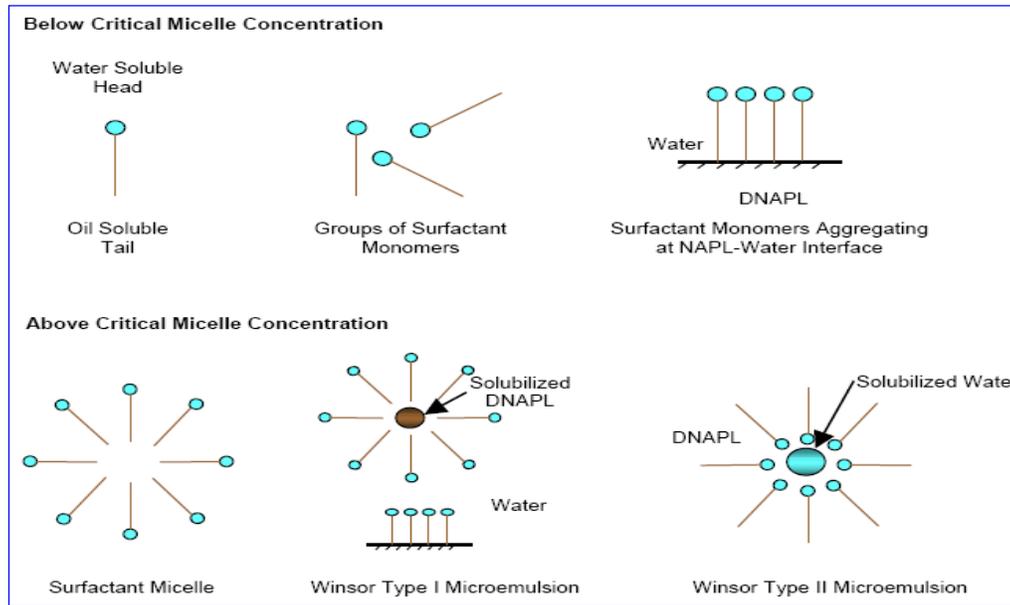


Fig.1.5. Micelle Formation Diagram (adopted from Bourrel, M., 1988)

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 Fig 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.

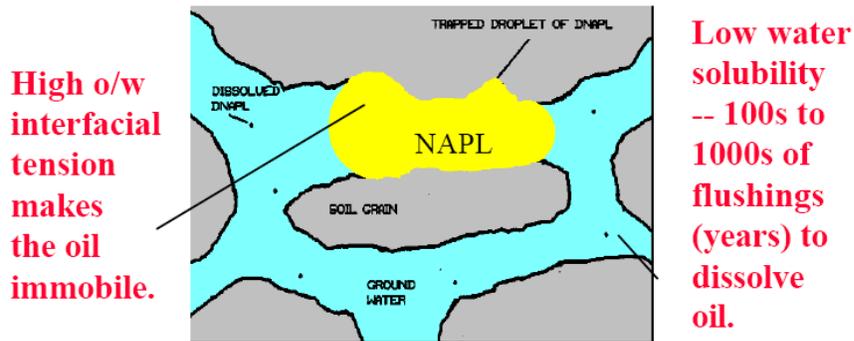


Fig.1.6. NAPL trapped by capillary forces (Adapted from Sabatini D. 1998)

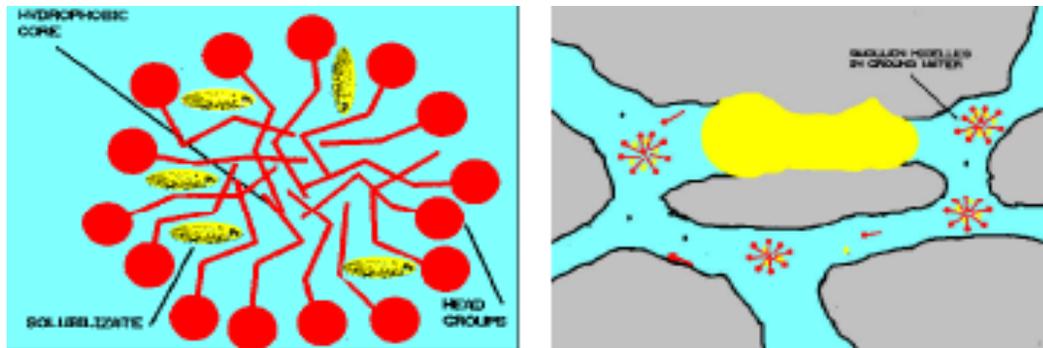


Fig.1.7. Surfactant micelles increase oil solubility (Adapted from Sabatini D. 1998)

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 and 1.9).

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.

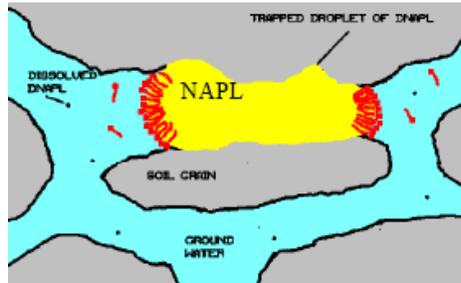


Fig.1.8. Surfactant adsorption lowers oil/water IFT (Adapted from Sabatini D, 1998)

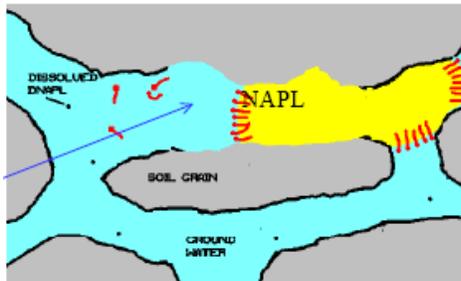


Fig.1.9. Droplet is mobilized, begins to flow (Adapted from Sabatini. D, 1998)

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 , R_2 : Radii of the curvature of the oil-water interface measured perpendicular to each other, (m).

1. 4 Hypotheses and Aims of study

Using various surfactants (ionic and/or nonionic) and varying the degree of salt concentration (in case of ionic surfactant), while varying temperature (in case of non-ionic surfactant), to reach optimum condition for Winsor type III system. Maximum solubilization will be obtained for water and oil, using a minimum amount of surfactant and obtaining ultralow IFT.

The current study aims at searching for the desired middle phase microemulsion, using different experimental methods based on different surfactants. The model will be used and tested for its efficiency, and economic value in eliminating large oil contaminant of water resources.

Chapter 2 Experimental

2.1 Chemicals and Supplies

2.1.1 Surfactants:

Anionic surfactant:

Commercial linear alkyl benzene sulphonate (LABS) with molecular formula $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ was obtained from Finkelman LTD.Chemicals.M.Wt.40, and titrated by sodium hydroxide to obtain pH around 7 with litmus paper. (1Kg LABS = 128 g NaCl).

Cationic surfactant:

Cetyl trimethyl ammonium bromide (CTAB) with molecular formula $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Br}^-$, and anhydrous mol.wt. 364.5.

Nonionic surfactant:

Pluronic surfactants were obtained from BASF Corporation. Pluronic was used as a nonionic surfactant composed of a symmetric triblock copolymer of propylene oxide (PO) and ethylene oxide (EO). The polypropylene oxide block was sandwiched between the more hydrophilic poly (ethylene oxide) blocks. The block copolymer was denoted by (EO) x (PO) y (EO) x , where x and y are the number of units of EO and PO, respectively. Being amphiphilic in nature, Pluronic aggregated in aqueous solution and formed micelles. (Jain, N. J., et al., 2000) Depending on the number of EO and PO units, various types of Pluronics are commercially available with molecular weights ranging between 1100-14600 and with the weight fraction of the hydrophilic polyethylene block ranging between 0.1 and 0.8.

Polymer with oxirane are used, as pluronic[®] F108 Prill, (chemical formula $\text{HO}(\text{C}_2\text{H}_4\text{O})_{141}(\text{C}_3\text{H}_6\text{O})_{44}(\text{C}_2\text{H}_4\text{O})_{141}\text{H}$) and pluronic[®] F127 Prill, (chemical formula $\text{HO}(\text{C}_2\text{H}_4\text{O})_{101}(\text{C}_3\text{H}_6\text{O})_{56}(\text{C}_2\text{H}_4\text{O})_{101}\text{H}$).

2.1.2 Oils:

2.1.2.1 Model oil:

Kerosene low odor [8008-20-6] (kerosene), bp. 175-325°, d. (0.800), Fp.179°F (81°C), n_D^{20} 1.4420, Merck Index (11, 5173) and R&S 1(1), was obtained from Sigma-Aldrich Chemie GmbH.

2.1.2.2 Light crude oil:

Light crude oil obtained from Ashdod refinery through Palestinian Petroleum Authority-Qalqilia.

2.1.3 Water:

Samples of distilled water were obtained from the chemistry labs; using Barnstead single distiller (by evaporation and condensation) and ground water samples were obtained from Al-Reheya ground water station in Hebron district. The sample was analyzed using Atomic Absorption Analyt 200 Atomic Absorption Spectrometer for Na^+ , K^+ , Ca^{++} and Mg^+ . Chloride (Cl^-) concentration was estimated by titration using AgNO_3 (0.1N) and K_2CrO_4 as an indicator. NO_3^- , PO_4^{3-} , F^- , NH_4^+ and SO_4^{2-} were determined using Spectrophotometer- DR 2010- HACH. The table 2.1 below shows the chemical properties of the used sample.

Table 2.1: The chemical properties of the ground water sample with $\text{EC}=649 \mu\text{S}/\text{cm}$, Total dissolved solids (TDS) = 415.36 mg/l, (4.1536×10^{-4} wt. %) and $\text{PH}=7.3$

Cations	Concentration, mg/L	Anions	Concentration, mg/L
Na^+	30.7	Cl^-	60.9
K^+	3.756	HCO_3^-	80.364
Ca^{++}	167.7	SO_4^{--}	15
Mg^{++}	43.7	NO_3^-	12.8
NH_4^+	.02	PO_3^{3-}	.06
		F^-	.36

2.1.4 Salts:

Sodium chloride NaCl was the electrolyte used for most phase behavior experiments, which contributed Na^+ and Cl^- ions to provide the required salinity gradient.

2.1.5 Alkali agent:

Sodium carbonate Na_2CO_3 with 99 % purity, was obtained from Sigma Chemical Co, also contributed additional electrolytes to solutions.

2.2 Methodology

Surfactant solutions with added ionic and salt had first been mixed at room temperature in test tubes/glass vials with screw caps, shaken with vortex for 1-2 minutes, then visually inspected for transparency and inspected under polarized microscope for anisotropy.

After that, oils were added at a specific water/oil ratio (WOR). The tubes/vials were mixed on a rotating shaker for 24 hours. Afterwards, they were put in upright position and allowed to settle. The phase behavior was inspected visually and under the polarized microscope.

The amount of electrolyte NaCl was varied (0.0-5.0%) w/w, in order to determine the optimum condition for each system. Winsor Type I representing (under optimum condition), Winsor Type II representing (over optimum), and Winsor Type III representing (optimum condition).

The same procedure can be followed when using non-ionic surfactant by varying temperature instead of salinity in order to find the balanced conditions. The use of alcohol as co-surfactant was avoided; instead mixing cationic surfactant provided a suitable alternative.

Chapter 3 Results

3. Results

3.1 Experiments with kerosene as modeling oil

3.1.1 Cationic and Nonionic blend I

Phase behavior at ambient temperature of salinity scans containing 0.25 wt. % CTAB, and 0.25 wt. % Pluronic F108 with equal weight ratios of water and oil was observed. Phase behavior was determined as a function of the concentration of added NaCl between 0.0-10.0 wt. %. No alcohol was used in any of the experiments presented in this search. Salinity scans with equal ratio of CTAB and Pluronic F108 had the appearance of conventional Winsor I, III, II microemulsion sequence with surfactants concentration at 0.5 wt.% and optimum condition (middle phase) appeared at 6.0 wt. % NaCl as shown in Figure.3.1 and Table 3.1.

3.1.2 Anionic and Nonionic blend I

Phase behavior at same circumstances of temperature and salinity scan containing 0.375 wt. %, LABS and 0.125 wt % Pluronic F108 with equal ratios of water and kerosene was observed. Salinity scans with three-quarters LABS and one-Quarter Pluronic F108 had the appearance of conventional Winsor I, III, II microemulsion sequence with surfactant concentration at 0.5 wt.% and the optimum condition (middle phase) appeared at 4.5 wt. % NaCl as shown in Figure 3.2.

The same surfactants are used with equal weight ratios of surfactants containing 0.25 wt. % LABS, and 0.25 wt. % Pluronic F108, the optimum conditions appear at low NaCl wt. % added. The middle phase appear at 3.0 wt. % NaCl as shown in Figure3.3.

Phase behavior at ambient temperature of salinity scans containing 0.25 wt. % LABS, and replace Pluronic F108 by Pluronic F127 0.25 wt. % with equal ratios of water and kerosene was observed. Salinity scans with equal ratio of LABS and Pluronic F127 had the appearance of conventional Winsor I, III, II microemulsion sequence with surfactant concentration at 0.5 wt.% and optimum condition (middle phase) appeared at 2.35 wt.% NaCl as shown in Figure.3.4.

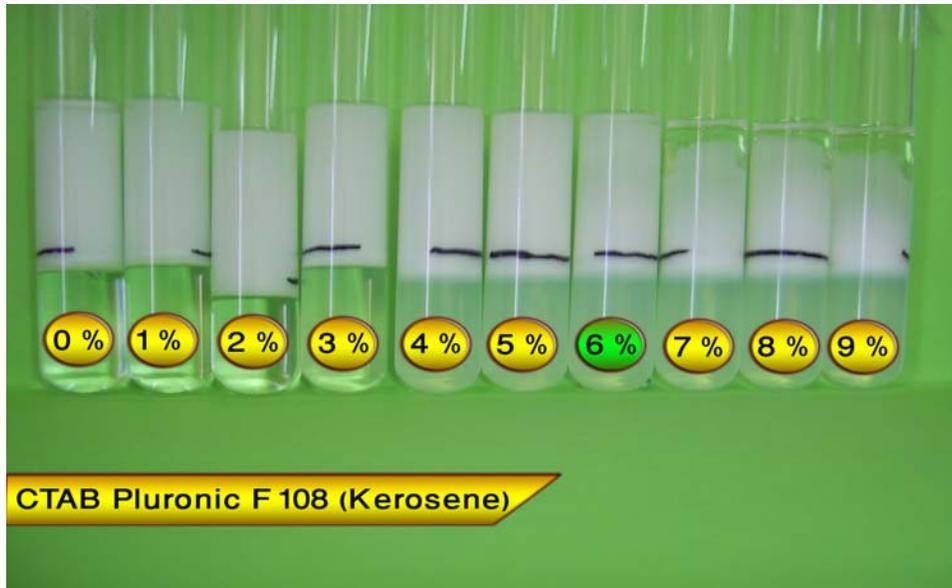


Fig.3.1. Solubilization variation along a formulation scan: CTAB and Pluronic F108 blend I (1:1)

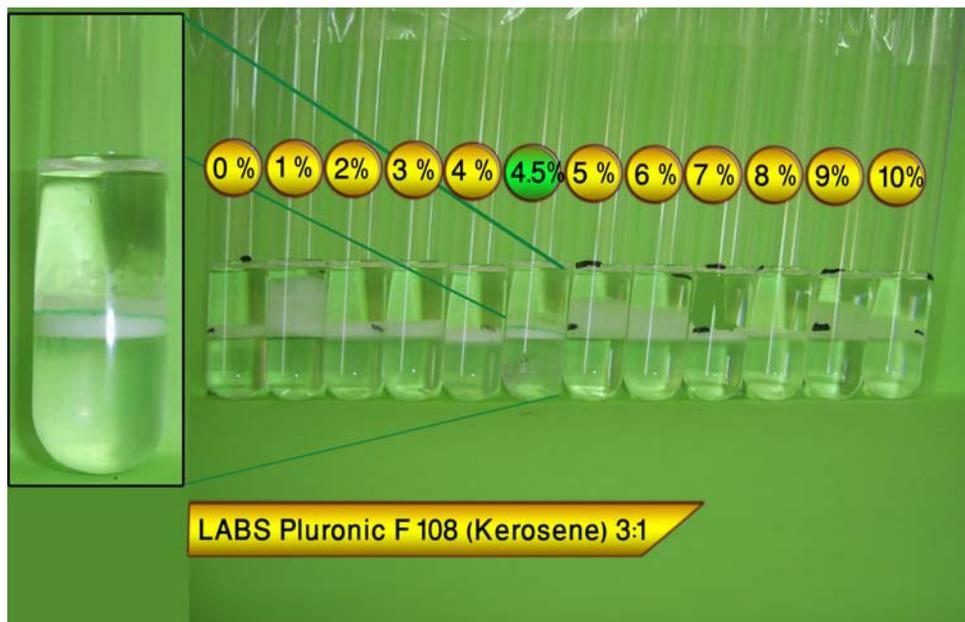


Fig.3.2. Solubilization variation along a formulation scan: LABS and Pluronic F108 blend I (3:1)

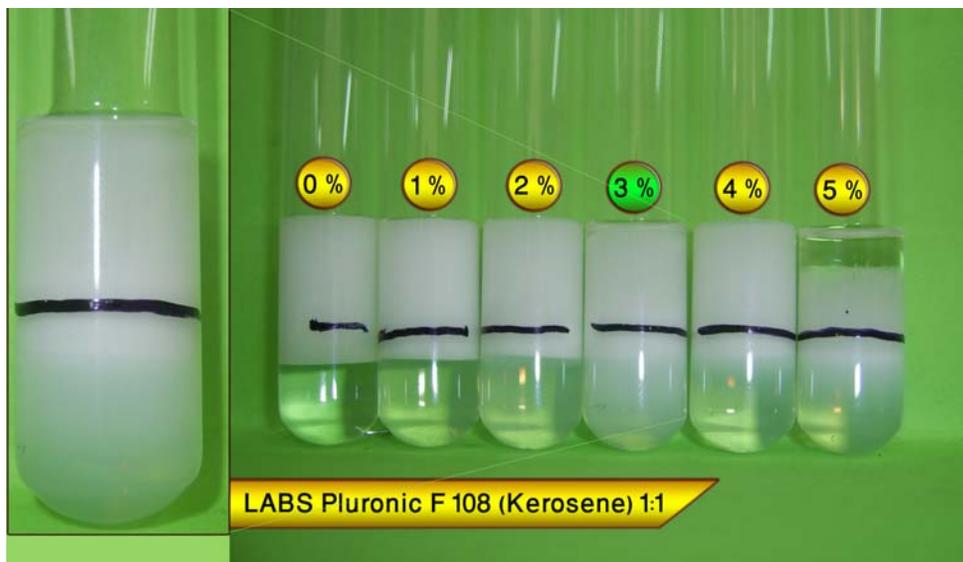


Fig.3.3. Solubilization variation along a formulation scan: LABS and Pluronic F108 blend II (1:1)



Fig.3.4. Solubilization variation along a formulation scan: LABS and Pluronic F127 blend I (1:1)

3.2 Experiments with light crude oil

3.2.1 Cationic and Nonionic blend II

Equilibrium phase behavior at ambient temperature of oil-free aqueous solutions containing 0.25 wt% of the cationic surfactant CTAB, 0.25 wt% of nonionic surfactant Pluronic F108 and 1.0 wt% Na_2CO_3 was determined as a function of the concentration of added NaCl from 0.0-5.0 wt. %. No alcohol was used in any of the experiments presented in my research. Brine phase appeared clear (homogenous phase).

After light crude oil was added and the equal ratios of CTAB and Pluronic F108 had the appearance of conventional Winsor I, III, II microemulsion sequence with surfactant concentration at 0.5 wt. % and optimum condition (middle phase) appeared at 2.0 % wt. NaCl as shown in Figure 3.5 and Table 3.2.

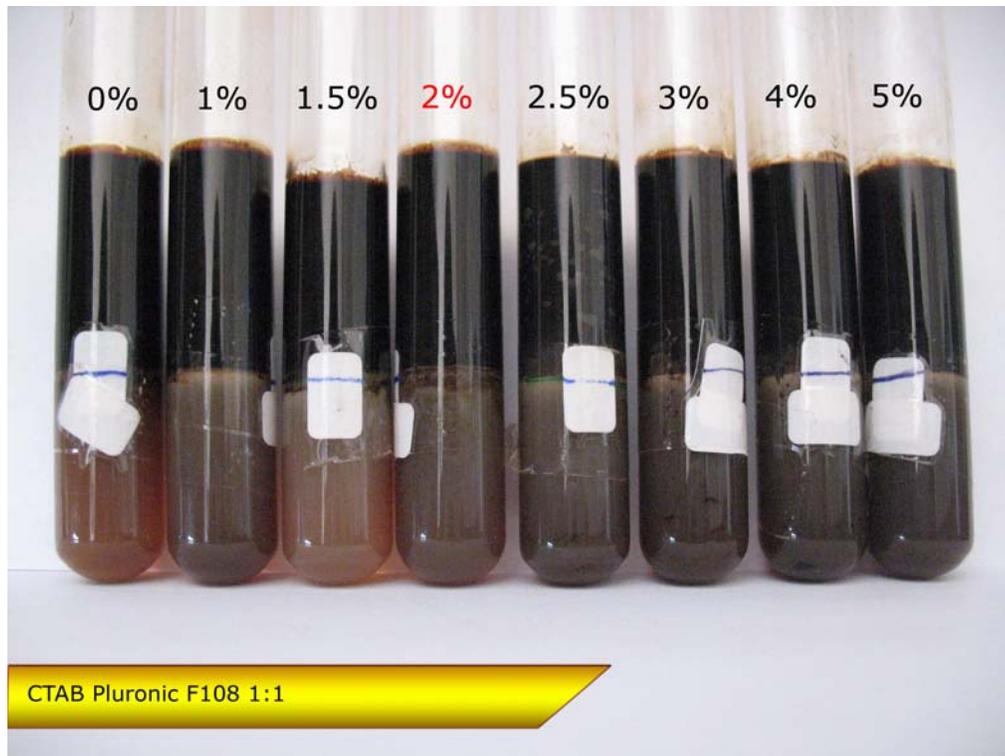


Fig.3.5. Solubilization variation along a formulation scan: CTAB and Pluronic F108 blend II (1:1)

3.2.2 Anionic and Nonionic blend II

Equilibrium phase behavior at ambient temperature of oil-free aqueous solutions containing 0.25 wt% of the anionic surfactant LABS, 0.25 wt.% of nonionic surfactant Pluronic F127 and 1 wt% Na₂CO₃ was determined as a function of the concentration of added NaCl from 0.0-5.0 wt. %. Brine phase appeared clear.

After light crude oil was added and the equal ratios of LABS and Pluronic F127 had the appearance of conventional Winsor I, III, II microemulsion sequence with surfactant concentration at 0.5 wt. % and optimum condition (middle phase) appeared at 2.0 wt. % NaCl as shown in Figure 3.6 and Table 3.2.

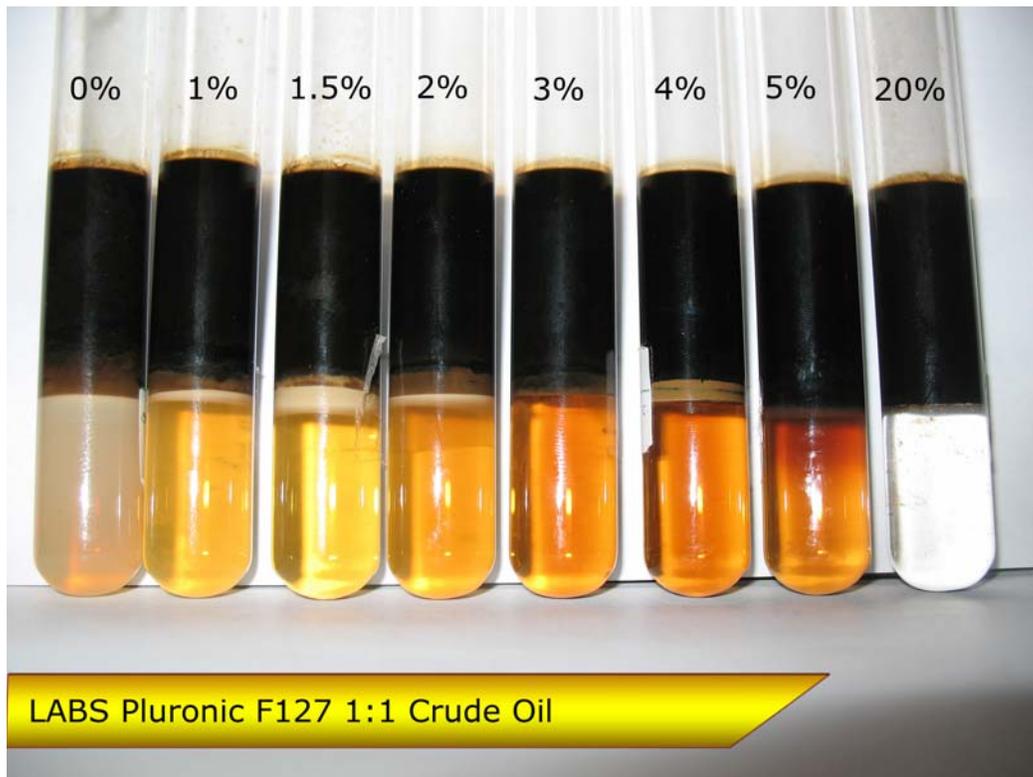


Fig.3.6. Solubilization variation along a formulation scan: LABS and Pluronic F127 blend II (1:1)

3.3 Experiments with ground water

3.3.1 Anionic and Nonionic blend III

Phase behavior at ambient temperature of salinity scans containing 0.375 wt. % LABS, and 0.125 wt. % Pluronic F127 with equal weight ratios of water and kerosene was observed. Phase behavior was determined as a function of the concentration of added NaCl between 0.0-5.0 wt. % and ground water salts. Salinity scans with equal ratio of LABS and Pluronic F127 had the appearance of conventional Winsor I, III, II microemulsion sequence with surfactant concentration at 0.5 wt.% and optimum condition (middle phase) appeared at 2.0 wt. % NaCl as shown in Figure 3.7 and Table 3.3.

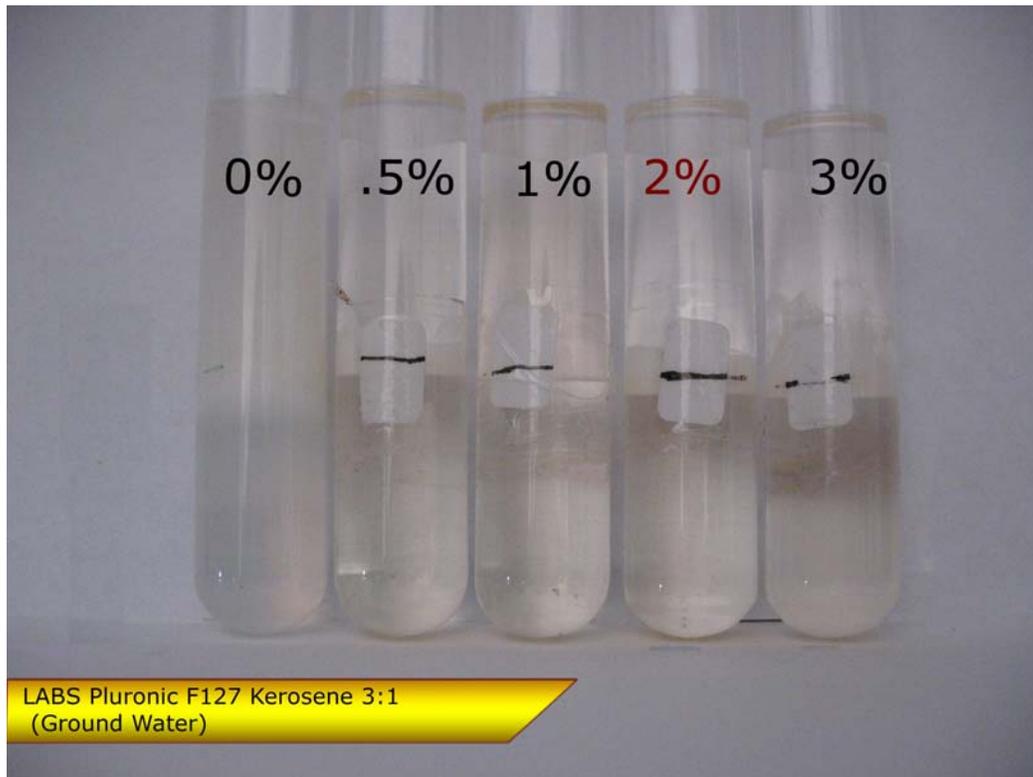


Fig.3.7. Solubilization variation along a formulation scan: LABS and Pluronic F127 blend III (3:1)

3.3.2 Cationic and Nonionic blend III

Phase behavior at ambient temperature of salinity scans containing 0.25 wt. % CTAB, 0.25 wt. % Pluronic F108 and 1.0 wt. % Na_2CO_3 with equal weight ratios of ground water and light crude oil was observed. Phase behavior was determined as a function of the concentration of added NaCl between 0.0-5.0 wt. % and ground water salts coexist. Salinity scans with equal ratio of CTAB and Pluronic F108 had the appearance of non conventional Winsor I, III, II microemulsion sequence with surfactant concentration at 0.5 wt.% and optimum condition (middle phase) appeared immediately without adding NaCl, (0.0 % NaCl) as shown in Figure 3.8 and Table 3.3.



Fig.3.8. Solubilization variation along a formulation scan: CTAB and Pluronic F108 blend III (1:1)

Table 3.1: phase behavior for surfactants blend with kerosene

samples	Surfactant		NaCl scan result (phase behavior)
	wt. %	Ratio	
CTAB+ Pluronic F 108	0.5%	1:1	0.0%-5.0 % Under optimum 6.0 % middle phase 7.0 %-10.0 % over optimum
LABS+ Pluronic F 108	0.5%	3:1	0.0 %-4.0 % Under optimum 4.5% middle phase 5.0 %-10.0 % over optimum
LABS+ Pluronic F108	0.5%	1:1	0.0 %-2.0 % Under optimum 3.0 % middle phase 4.0 %-10.0 % over optimum
LABS+ Pluronic F127	0.5%	1:1	0.0 %-2.0 % Under optimum 2.35% middle phase 2.5%-10.0 % Over optimum

Table3. 2: phase behavior for surfactants blend with light crude oil

samples	surfactant		NaCl scan result (phase behavior)					
	wt. %	Ratio	0.0%	1.0%	2.0%	3.0%	4.0%	5.0%
CTAB+ Pluronic F 108	0.5%	1:1	Under optimum	Under optimum	Middle phase	Over optimum	Over optimum	Over optimum
LABS+ Pluronic F127	0.5%	1:1	Under optimum	Under optimum	Middle phase	Over optimum	Over optimum	Over optimum

Table 3.3: phase behavior for surfactants blend with oil and ground water

Sample	Surfactant		Type of oil	NaCl scan result (phase behavior)
	wt. %	ratio		
LABS+ Pluronic F127	0.5%	3:1	kerosene	0.0 %-1.5% Under optimum 2.0 % middle phase 3.0 % Over optimum
CTAB+ Pluronic F108	0.5%	1:1	Light crude oil	0.0 % middle phase

4. Discussions

4.1 Qualitative analysis

Many different parameters become effective in surfactant enhancement aquifer remediation (SEAR), by surfactant solutions. They are mainly: (a) surfactants type, (b) interfacial tension (IFT) and solubility parameter (SP), (c) salt concentrations and (d) oil type.

4.1.1 Effect of Surfactants Types

Four different surfactants were selected as a representative of nonionic, anionic, and cationic types. Table 4.1 displays the type of surfactant used in my study and their properties.

Table 4.1: properties of surfactant

Surfactant /type	Chemical Name/formula
LABS/ Anionic	linear alkyl benzene sulphonate / $RC_6H_4SO_3^-Na^+$
CTAB/cationic	Cetyl trimethyl ammonium bromide/ $C_{16}-N(CH_3)_3Br$
Pluronic F 108/nonionic	Oxirane/ HO $(C_2H_4O)_{144} (C_3H_6O)_{44} (C_2H_4O)_{144}H$
Pluronic F 127/nonionic	Oxirane /HO $(C_2H_4O)_{101} (C_3H_6O)_{56} (C_2H_4O)_{101}H$

When LABS was mixed with Pluronic F108 oil free to get clear brine phase, (the brine phase (salinity scan) of LABS only, two phases were observed resulting from NaCl precipitation when adding NaCl more than 1 wt. %).

To avoid turbidity; LABS had been prepared with Pluronic F108 blend. This result showed LABS becoming more tolerant to salt adding with Pluronic F108 and increased salt concentration to 7 wt. % NaCl when three-quarter LABS was mixed with one quarter Pluronic F108, to 9 wt. % at equal concentration of surfactants and to 10 wt. %, when Pluronic F108 was replaced by Pluronic F 127.

All surfactant blends had clear brine phase. Thus liquid crystal formation was avoided.

4.1.2 Calculation of interfacial tension (IFT) and solubility parameter (SP)

These calculations are based on solubility parameters (SP), to determine interfacial tension for surfactants blend. The solubilization parameter (SP) is the volume of oil or water per weight of surfactant in the microemulsion phase, see Fig 4.1 for typical phase transition. For the Winsor type III system, the volume of oil and the volume of water solubilized in the middle phases are equal, this corresponds to the same composition at which IFT* is attained. At this optimum composition, SP is referred to as SP*. The interfacial tension in the region of the middle phase or Winsor type III is often as low as 10^{-3} mN/m, a so-called ultralow IFT. The lowest value of IFT, which is called the optimum interfacial tension (γ^*), is at the point where the IFT between the excess oil and the middle phase (γ_{mo}) intersects with the IFT between the middle phase and the excess brine (γ_{mw}).

According to the Chun Huh relationship for classical Winsor III behavior (Huh C, 1979), the solubilization ratios for the microemulsion phase and IFT of the microemulsion with excess oil and brine can be related as follows:

$$SP^{*2} \gamma^* = \text{constant}$$

Hence, at an optimum formulation the interfacial tension passes through a minimum (γ_{min}), whereas the solubilization parameter reaches a maximum (SP*).

And by another expression:

$$\gamma_{mo} = c / (V_o / V_s), \quad \gamma_{mw} = c / (V_w / V_s)$$

Where c is a constant for each system. When applying results available for enhancing oil recovery (EOR) systems, it was found to be consistent with the above expressions for values of c equal to 0.3 mN / m. Table 4.2, 4.3 and Fig.4.2, 4.3 show the relation between interfacial tension (IFT) and solubility parameter (SP) for surfactant used in this study.

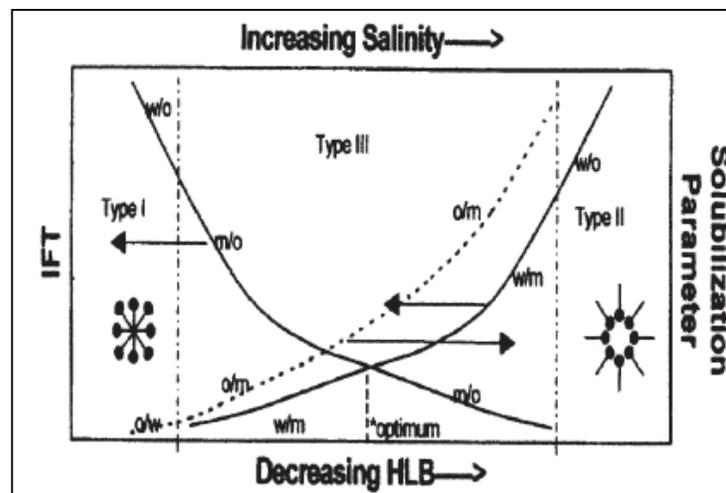


Fig 4.1: Typical phase transition, interfacial tensions (IFT), and solubilization parameter in an oil-surfactant system (adapted from Wu, B. et al.,2000).HLB, hydrophilic-lipophilic balance; w/o, water-in-oil; o/w, oil-in-water; w/m, middle-phase water-in-microemulsion; o/m, oil-in-microemulsion; m/o, microemulsion-in-oil. The term “Type” refers to Winsor Type microemulsions.

Table 4.2: The relation between IFT* and SP*, (Distilled water)

Surfactants	Ratio of surfactant	Oil type	Optimum salinity wt% NaCl	IFT* mN/m		SP* w/w	
				γ_{mw}	γ_{mo}	V_w/V_s	V_o/V_s
CTAB+ Pluronic F 108	1:1	kerosene	6.0 %	$4.12 \cdot 10^{-4}$	$4.15 \cdot 10^{-4}$	26.974	26.901
LABS+ Pluronic F127	1:1	kerosene	2.35%	$4.88 \cdot 10^{-4}$	$5.06 \cdot 10^{-4}$	24.808	24.352
LABS+ Pluronic F108	3:1	kerosene	4.5%	$3.7 \cdot 10^{-3}$	$3.53 \cdot 10^{-3}$	9.004	9.220
LABS+ Pluronic F108	1:1	kerosene	3.0 %	$3.286 \cdot 10^{-4}$	$3.287 \cdot 10^{-4}$	30.215	30.210
CTAB+ Pluronic F 108	1:1	Light crude oil	2.0 %	$1.4 \cdot 10^{-3}$	$1.34 \cdot 10^{-3}$	14.90	14.98
LABS+ Pluronic F127	1:1	Light crude oil	2.0%	$2.04 \cdot 10^{-3}$	$2.054 \cdot 10^{-3}$	12.141	12.085

Table 4.3: The relation between IFT* and SP*, (Ground water)

Surfactants	Ratio of surfactant	Oil type	Optimum salinity wt% NaCl	IFT* mN/m		SP* w/w	
				γ_{mw}	γ_{mo}	V_w/V_s	V_o/V_s
LABS+ Pluronic F127	3:1	kerosene	2.0 %	$8.2 \cdot 10^{-4}$	$8.6 \cdot 10^{-4}$	19.17	18.68
CTAB+ Pluronic F108	1:1	Crude oil	0.0 %	$1.16 \cdot 10^{-3}$	$1.24 \cdot 10^{-3}$	16.08	15.56

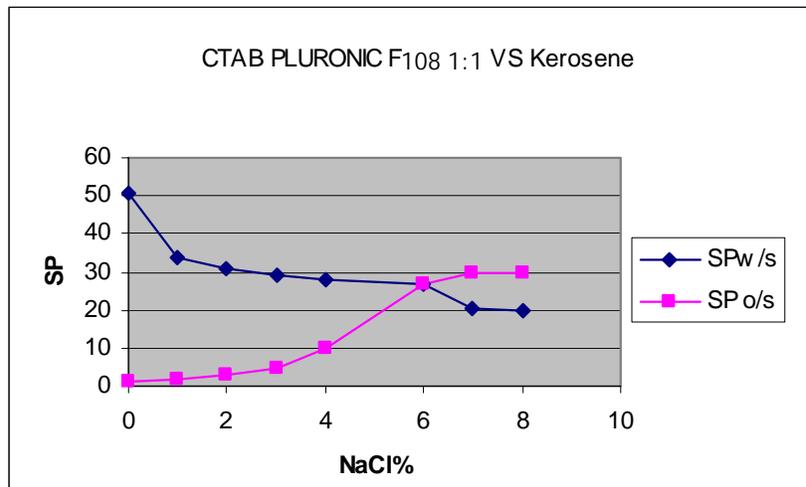


Fig 4.2- a: Correlation between SP and NaCl concentration

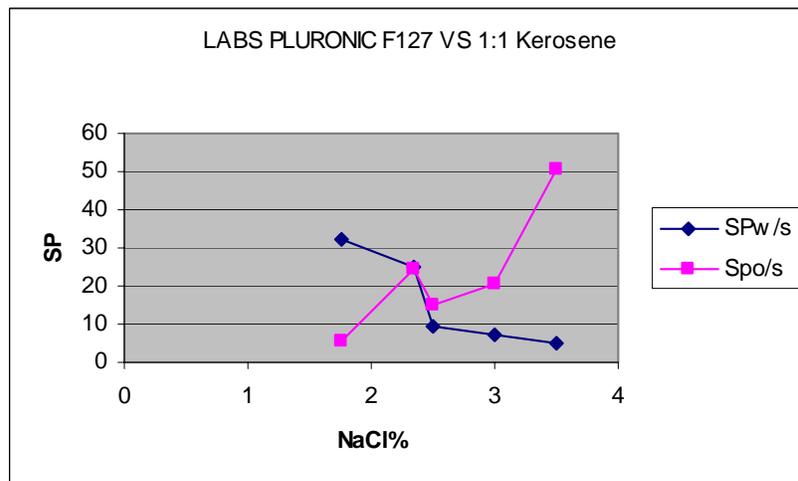


Fig 4.2-b: Correlation between SP and NaCl concentration

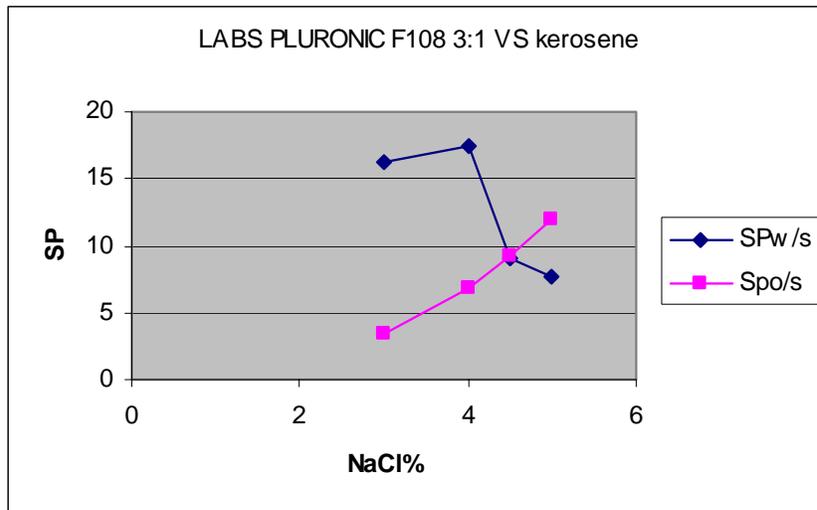


Fig 4.2-c: Correlation between SP and NaCl concentration

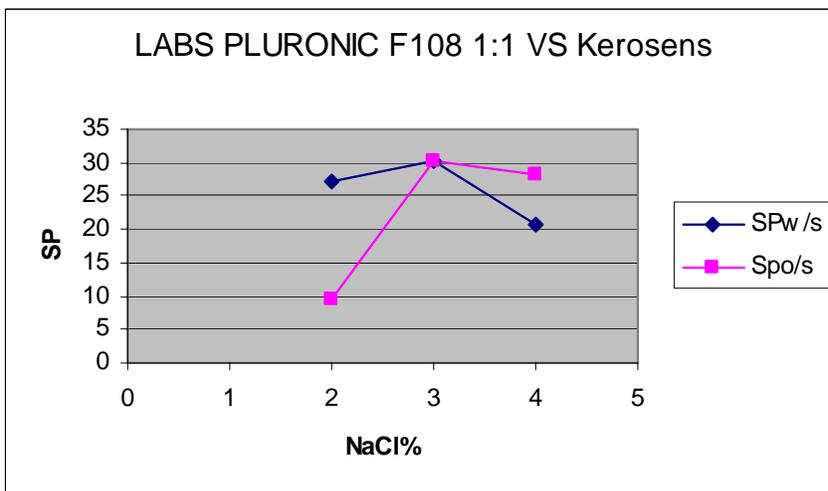


Fig 4.2-d: Correlation between SP and NaCl concentration

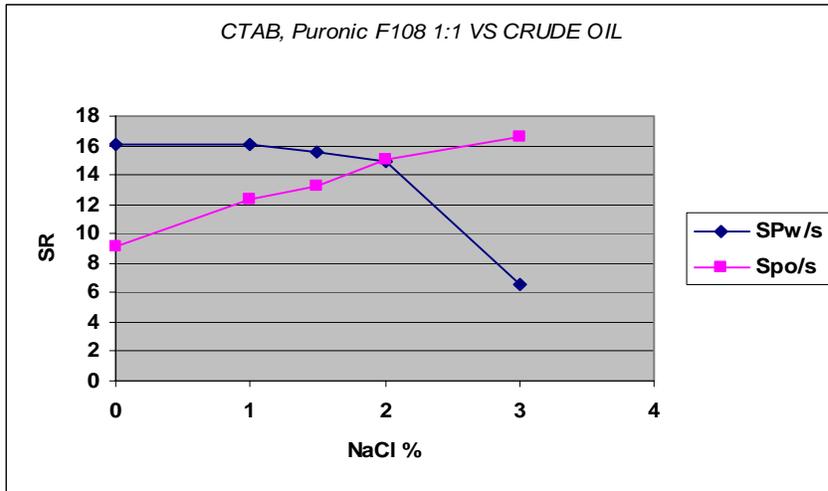


Fig 4.2-e: Correlation between SP and NaCl concentration

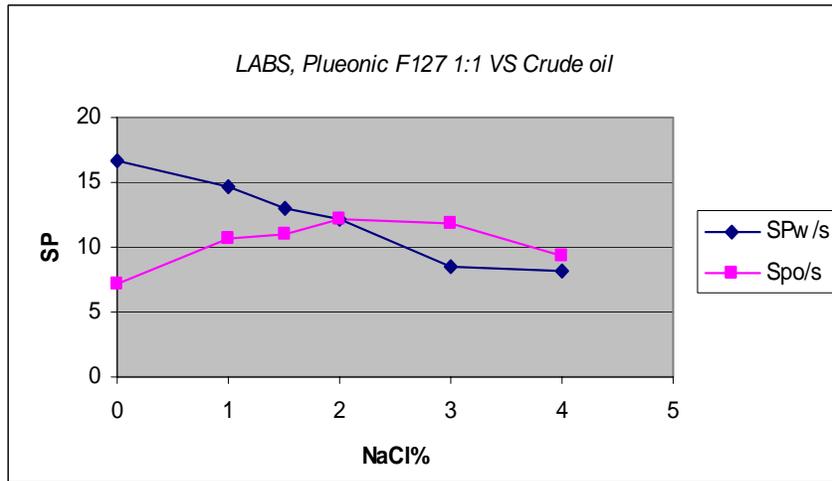


Fig 4.2-f: Correlation between SP and NaCl concentration

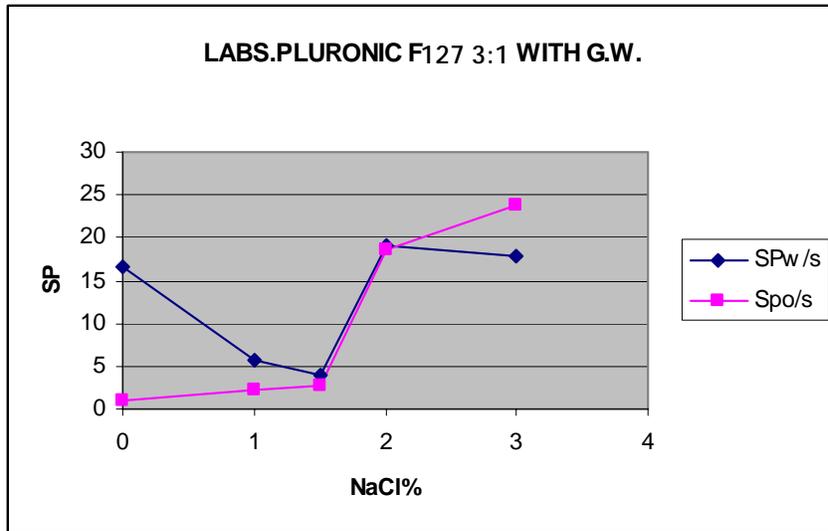


Fig 4.2-g: Correlation between SP and NaCl concentration

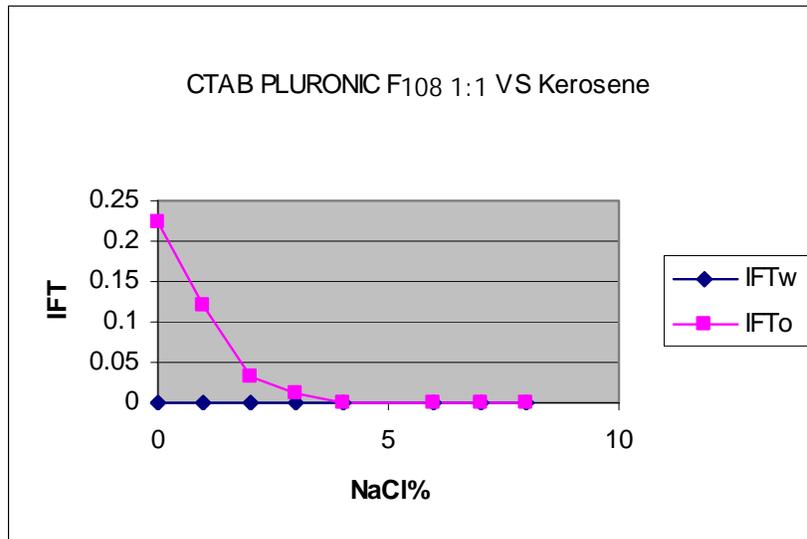


Fig 4.3-a: Correlation between IFT and NaCl concentration

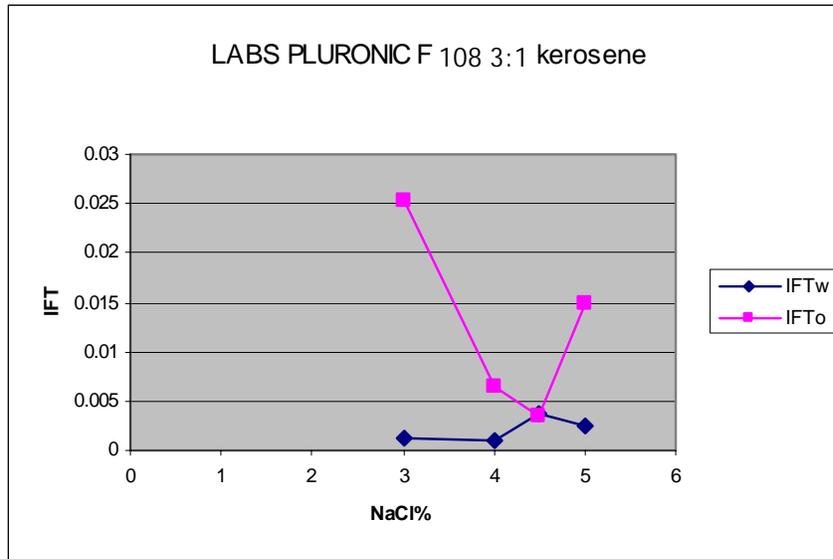


Fig 4.3-b: Correlation between IFT and NaCl concentration

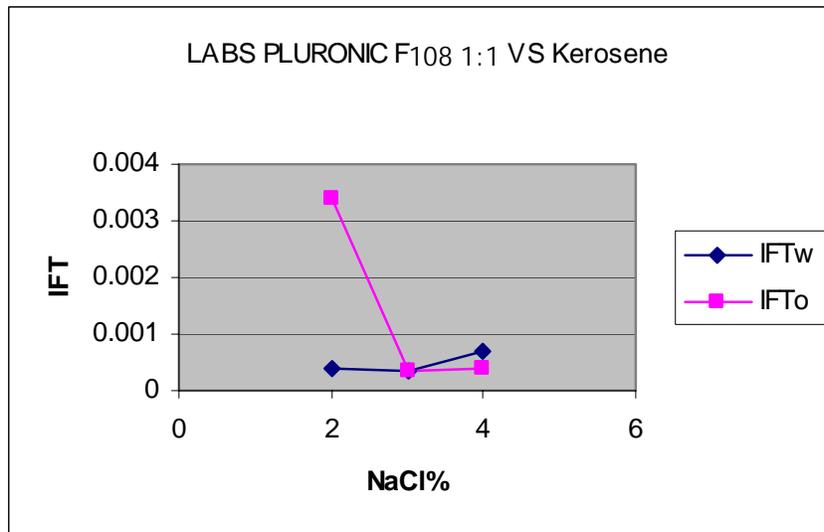


Fig 4.3-c: Correlation between IFT and NaCl concentration

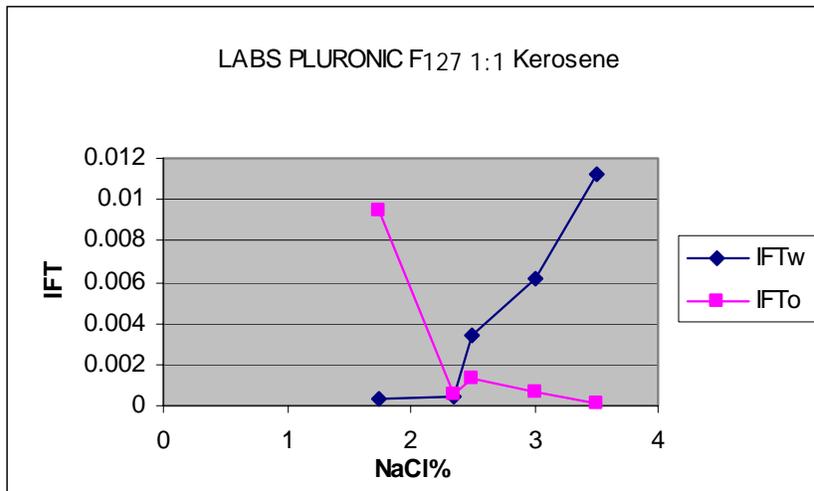


Fig 4.3-d: Correlation between IFT and NaCl concentration

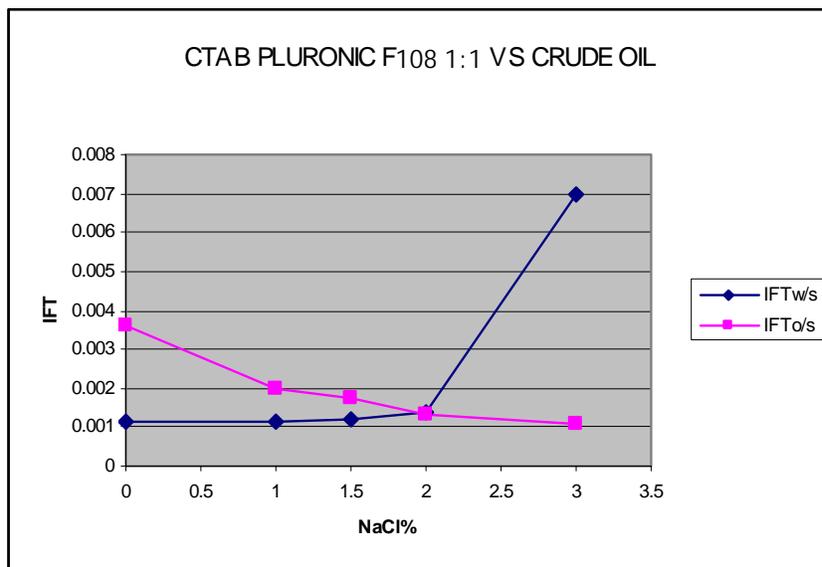


Fig 4.3-e: Correlation between IFT and NaCl concentration

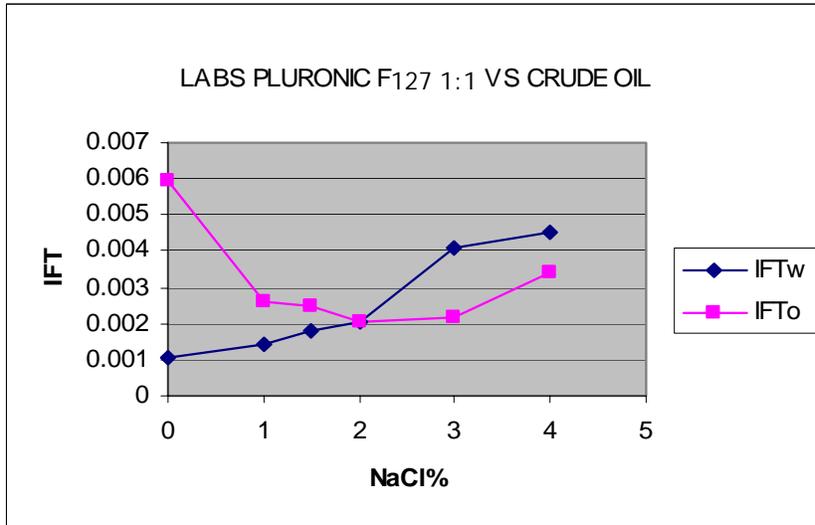


Fig 4.3-f: Correlation between IFT and NaCl concentration

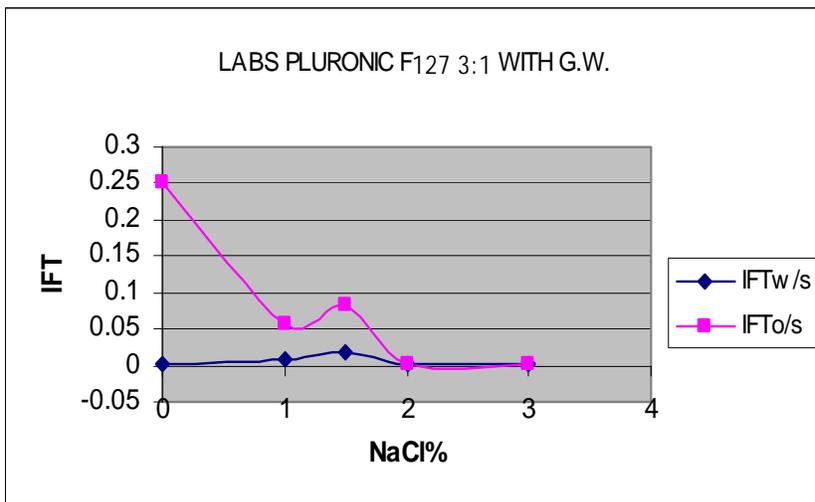


Fig 4.3-g: Correlation between IFT and NaCl concentration

4.1.3 The Effect of oil Type/ Water Type /Salt Concentration

The eight surfactant-formulations identified were tested with kerosene and light crude oil to compare the difference in phase behavior of the surfactant when the oil is changed and the formulation of light crude oil included with sodium carbonate to convert naphthenic acids to soaps, and when the water is changed from distilled water (D.W.) to ground water (G.W.). The results of these experiments will be used to correlate optimum salinity, (phase behavior), to the oil and surfactant characteristics and interfacial tensions.

For surfactant and crude oil containing naphthenic acids, optimum salinity for alkaline conditions depends on the soap -to- surfactant ratio. (Zhang, L. D., et al., 2006).

For a given crude oil Naphthenic acid is equal to 2.0 wt. %; we neutralize this acid to form 2.0 wt. % sodium naphthenate by adding Na_2CO_3 . The result was decreasing salt concentration I needed to reach the middle phase (optimum condition) in all blend with crude oil, which reveals the blend converted from hydrophilic to lipophilic.

The phase behavior of these eight surfactants as a function of salt and surfactant concentration and water to oil ratio was studied. The expected microemulsion transition from the lower to middle to upper phase was observed with increasing salt between 0.0 wt. % and 10.0 wt. % for water to oil ratio of one.

The same transition was also found upon changing kerosene to light crude oil and distill water to ground water, only one blend when mixed with ground water had the appearance of non conventional Winsor I, III, II microemulsion sequence and optimum condition (middle phase) was appeared immediately without adding NaCl, (0.0 % NaCl) as shown in Figure 3.8.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

Simple and inexpensive phase behavior experiments are very useful in identifying good surfactants for the groundwater remediation of LNAPLs such as kerosene and light crude oil. The ionic and nonionic blends were found to be highly effective in removal of the LNAPLs from contaminated ground water.

The effectiveness of this class of surfactants is illustrated by the very small amount of surfactant required to reduce the LNAPLs saturation to the very low values even without use of cosolvent (alcohol).

Middle phase microemulsion was formulated in all blends with kerosene as modeling oil and light crude oil. Salinity scans with light crude oil, ground water and CTAB with Pluronic F108 did not follow the conventional Winsor I, III, II sequence. The middle phase appeared at 0.0 wt. % NaCl. LABS become more tolerant to salt added when mixed to nonionic block copolymer surfactant.

Solubilization ratios for the middle phase microemulsion were measured. When applying Chun Huh equation, such ratios produces ultra low interfacial tensions with kerosene. LABS and Pluronic F108 blend have the smallest IFT (3.28×10^{-4}) that reveals solubility ratio was the highest value.

5.2 Recommendations

In the light of study findings, the researcher recommends the following:

- The same theory procedure can be followed when using non-ionic surfactant by varying temperature instead of salinity in order to find the balanced conditions.
- The effect of ground water salts, which is changed from place to another, should be studied to find the optimal conditions.
- Scale-up from the laboratory to the field is necessary part for developing SEAR process. A reservoir simulator can be used as a tool for such a scale-up which contains dolomite and calcite rocks, that are polluted with crude oil and kerosene, and test the hypothesis using the same method.

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