

Salinity-Alkane Carbon Number (ACN) Relationship of Some Anionic Nonionic Surfactant Mixtures

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Abstract

Salinity scans were performed for petroleum sulphonate/eugenol ethoxyate mixtures having the same composition (0.75 mole fraction of witco TRS 10-80 petroleum sulphonate + 0.25 mole fraction of any of the prepared eugenol ethoxylates). Widths of the obtained three-phase (3Φ) microemulsion regions, were determined and the optimum salinity (S^*) values of these anionic/nonionic systems, were calculated at different oil phase alkane carbon numbers (ACN). Phase behaviour diagrams, of the investigated systems, were constructed by plotting the width of the 3Φ region against oil phase ACN. From the obtained phase maps, the areas of the 3Φ regions, bounded between the upper and lower phase boundaries (UPB & LPB), were located. Also, the areas bounded between the UPB and LPB fitted curves for the whole ACN range (from hexane to hexadecane, $3\Phi_{6-16}$) and that for the preferred ACN (from hexane to nonane, $3\Phi_{6-9}$), were determined through computational approach. Linear and polynomial equations were developed to describe the S^* -ACN relationship of the investigated systems. Results obtained reveal that more pronounced shift, in the 3Φ region, to higher ACN was observed when nonionic having longer polyoxyethylene chain was employed. Sulphonate/eugenol ethoxyate mixtures gave $3\Phi_{6-9}$ regions at a relatively higher salinity ranges if compared with that of sulphonate alone. Such mixtures are more beneficial in surfactant flooding for high salinity reservoirs.

Keywords : Eugenol ethoxylates, Petroleum sulphonates, Phase behaviour, Phase map, Surfactant flooding formulation systems.

INTRODUCTION

"Traditional" surfactant flooding involves the injection of a chemical solution that consists of, water, surfactant, co-surfactant, and salt. Polymer is added to these formulations to maintain favourable mobility control and hence to achieve good sweep efficiency. However, the overall economics of this process was not sufficient to warrant wide implementation by the industry (Goddard et al., 2004; Shuler et al., 1989, 1987).

One of the lower cost methods for improved oil recovery via surfactant flooding design is to add alkali to the surfactant formulation. The process is known as ASP (alkaline-surfactant-polymer) flooding (Shuler et al., 1989; Mayers, 1992). ASP process has been designed to reduce adsorption of anionic surfactants onto reservoir rock. Significant ASP projects have been constructed in China and Indonesia but only small ASP flooding process are found in U.S. and Canada (Pitts, 2001). One other approach to reduce the cost of chemical flooding process by using low concentrations of surfactant without any added polymer (Berger and Lee, 2002; Austad, 1993). The process is less efficient in oil recovery than conventional one. Dilute solutions of ethoxylated anionic surfactants were attempted for this EOR in sea water (Skauge and Palgren, 1989). The development, of anionic surfactant formulations that include a small amount of cationic surfactant, is another laboratory scale process for EOR (Wellington, 1993; Jayanti, 2001; Kayali et al., 2010). Significant oil recovery is achieved with much less surfactant concentration than that used in formulations developed up to the mid 1980's.

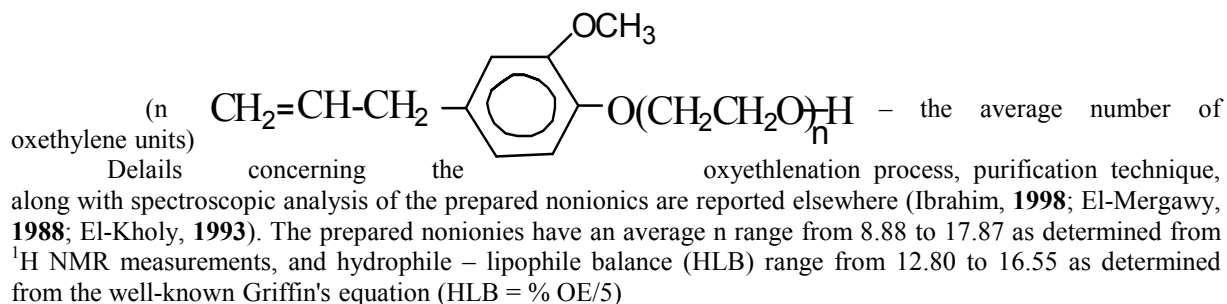
In a similar vein, there is the suggestion for the addition of a so-called linker molecule to the surfactant formulation. Linker molecules are amphiphiles that segregate near the microemulsion region, near the surfactant tail (lipophilic linkers) or near the surfactant head group (hydrophilic linkers). The concept of lipophilic linkers was first introduced by Graciaa et al., 1993, the state of art and linker-modified microemulsions have been reported by Acosta et al., 2002, Sabatini et al., 2003 and Salager et al., 2005. In three-phase (3Φ) microemulsion formulated by polyoxyethylenated alkylphenols. Nonionics and iso-octane oil phase, Graciaa et al., (1993) have observed that alkylphenol with one or two ethoxy groups did not participate at the interface, but rather segregated near the oil/water interface and between the tails of alkylphenol surfactants with a higher number of ethoxy groups. These components are "linking" the oil molecules and the surfactant tails (lipophilic linkers) which promote better solubilization of the excess oil by the main surfactant. Also, shorter alkyl chain surfactants

are discussed as hydrophilic linkers (Sabbatini et al., 2003; Acosta, 2002) and thought to adsorb at the oil/water interface, thereby promoting the surfactant-water interaction, but have a poor interaction with the oil phase. They observed a synergistic effect when combining the lipophilic and hydrophilic linkers, which further allows an increase in oil solubilization by the surfactant.

EXPERIMENTAL :

I- SURFACTANTS :-

I.1- Polyoxyethylenated Eugenol. (4-allyl-2-methoxyphenol), was prepared through the reaction of ethylene oxide with eugenol. The prepared nonionic surfactants have the general formula:-



I.2- Witco TRS 10-80 : commercially available petroleum sulphonate manufactured by Witco Chemical Corporation- Sonneborn Division. Specifications of this anionic surfactant are given in Table 1 as received from the manufacturer. Witco TRS 10-80 was used after de-oiling and de-salting steps (Ibrahim, 1998; El-Mergawy, 1988). The purified petroleum sulphonate obtained is a pale yellow hygroscopic powder which was kept in a stoppered container under dry conditions.

II- PROCEDURES AND TECHNIQUES

II.1- Surface Tension (γ) and cmc :-

Surface tension measurements, of aqueous surfactant solutions, were carried using Dagnon-Abribat Tensiometer – prolabo (ElKholy, 1993; Ibrahim, 1998). The cell temperature was controlled by circulation of thermostated water. The sensitivity of the instrument is $\pm 0.05 \text{ mNm}^{-1}$. The critical micelle concentration (cmc) values were determined from surface tension-concentration (γ -Log C) isotherms through the least-squares regression analysis (Rosen, 1989; Barakat et al, 1989; El-Mergawy, 1988; Draper, 1968).

II.2- Clear Point of Witco TRS 10-80 :-

When this petroleum sulphonate is dissolved in brine, the resulting solution appears cloudy or turbid and at higher salinity precipitation observed. Salinity tends to increase clear point while cosolvent (alcohol) addition tends to decrease it. (Gale and Sandvick, 1973, Gendy et al., 1994). Solutions of Witco sulphonate in brine have clear point above 100°C (Ibrahim, 1998). The minimum amount of added alcohol required to obtain a clear sulphonate solution at room temperature (25°C), was determined. In all experiments, an aqueous phase containing 1 wt% petroleum sulphonate, a varying amount of NaCl, 3.5 wt % sec-butanol and 0.5 wt% iso-pentanol, was contacted with one of the liquid n-alkanes (n-pentane-n-hexadecane). Water : oil ratio (WOR) 4 was used.

II.3- Salinity Scan and Middle Phase Formation :-

The formation of the middle phase microemulsion was carried out by contacting 8 ml of an aqueous solution containing alcohol, sodium chloride and surfactant with 2 ml of an oil phase ($\text{C}_6\text{-C}_{18}$ n-alkanes), in pipettes (10 ml, 0.1 division, 4 mm i.d., and 300 mm long). Pipettes were sealed, labeled and gently shaken by inverting twice every hour for the first 3 days, then the system was left to equilibrate for 4 days in an incubator at 30°C . The range of salinity, where middle phase microemulsion appeared, was recorded at different oil phase alkane carbon numbers (ACN). (Cayias, 1976; Salager, 1977; Schechter and Wade, 1981; Ibrahim, 1998; mead, 2000). Figure 1 illustrates the formation of 3Φ region through salinity scan.

II.4- Width of Three-Phase Region and Optimum salinity :-

When a salinity scan was performed, and the range of salinity, which leads to the formation of three-phase (3Φ) microemulsion region, was determined, the center of this salinity range can be taken as the optimum salinity (S^*). For a system which exhibits three phases, S^* has been defined as the geometric average of the minimum and the maximum salinities. (Reed and Healy, 1967; Puerto and Gale, 1977; Salager, 1977; Ibrahim, 1998. Mead, 2000). Also, salinity range is known as the width of 3Φ region.

N.B. In a salinity scan when the middle phase microemulsion occurred at relatively low salinity range (0.5-1.0 wt% NaCl), it is better to make the scan varying the salinity by 0.05 wt% NaCl. When the salinity range occurred at higher than 1 wt% NaCl, it is varied by 0.1 wt% NaCl.

RESULTS AND DISCUSSION :

1- Characterization of the Employed Nonionics :

The employed nonionics include five members of polyoxyethylenated eugenol having 6.46, 8.88, 11.45, 14.85 and 17.87 oxyethylene (OE) units and an HLB range from 12.80 to 16.88. Some physical and surface properties of the prepared nonionics are listed in Tables 2-4. The CMC values of these nonionics decrease linearly with increasing the number (n) of oxyethylene units. However a non-linearity in CMC-HLB relationship which indicates that this nonionic group behaves in a different manner if compared with the reported polyoxyethylenated nonionics (Crook et al., 1963; Becher, 1966; El Kholy, 1993, Barakat, 1989). The unique behaviour of polyoxyethylenated eugenol is, most probably, due to the short unsaturated hydrophobic tail (Ibrahim, 1998; Mostafa, 1996). Also, a linear decrease in CMC with increasing temperature is the same trend for many nonionics (Mukerjee et al., 1971), and the increase in γ_{cmc} values with increasing polyoxyethylene chain, is a nonionic performance.

Effectiveness (π_{cmc}) and efficiency (pC_{20}) of the employed nonionics in surface tension reduction are calculated from the basic surface tension-concentration data (Ibrahim, 1998) following the definitions and formula of Rosen (1989):-

$$\text{Effectiveness } (\pi_{cmc}) = \gamma_0 - \gamma_{cmc}$$

where γ_0 = surface tension of pure solvent (distilled water)

γ_{cmc} = surface tension at cmc.

$$\text{Efficiency } (pC_{20}) = -\text{Log } C_{\pi=20}$$

where $C_{\pi=20}$ is the concentration of surfactant corresponding to 20 mN/m reduction in surface tension

From the calculated π_{cmc} and pC_{20} values, changing temperature from 28 to 58°C, has a rather minor effect on these quantities in presence or absence of electrolyte (Rosen et al., 1982; Dahanayake et al., 1986; El-Kholy, 1993). Efficiency, pC_{20} , in long-tailed surfactants, increases with increasing hydrophobic tail, but effectiveness, π_{cmc} usually decrease with this change (Lange, 1964; Rosen, 1972). The interpretation of these investigators was that surfactant having long hydrophobic tail tends to lower the surface tension of water with more efficiency, but much less effectively, than a shorter chain homologue. They have reached a general conclusion that increasing effectiveness tends to decrease efficiency and vice versa. The obtained results in Table 4 reveal that factors which cause a decrease in effectiveness do not cause an induced parallel increase in the corresponding efficiency. For example, increasing the polyoxyethylene chain length is usually followed by a decrease in efficiency in surface tension reduction which is a typical nonionic performance, whereas, effectiveness values (Table 4) give indication that polyoxyethylenated eugenol nonionics follow a pattern which is different from this class of nonionic surfactants.

In presence of added electrolyte, neither efficiency nor effectiveness results indicate a nonionic character. The discrepancy, in surface properties of polyoxyethylenated eugenol is mainly due to the less efficient short unsaturated hydrocarbon tail (Swarbrick et al., 1969).

2- Characterization of the Employed Sulphonate

Witco TRS 10-80 petroleum sulphonate is the anionic surfactant employed in this study, For economic considerations, this surfactant has been used in numerous studies (Cayias et al., 1977; Bennett et al., 1981; Bourrel and Chambu, 1983, Ibrahim, 1998). The specifications of Witco-petroleum sulphonate are given in Table 1 as received from the manufacturer.

CMC values of the employed petroleum sulphonate, were determined at different salinities and various alcohol concentration (Table 5). The presence of electrolyte in aqueous surfactant solutions, causes a decrease in the cmc value (Mysels and Mysels, 1965; Barakat et al., 1997). This decrease in cmc is more pronounced in anionic surfactants (e.g. sulphonates) than polyoxyethylenated nonionics (Rosen, 1989). The addition of alcohol increases the solubility of surfactant which subsequently decreases the cmc (Table 5).

3- petroleum Sulphonate-Brine – Oil System :-

Salinity scans were performed by contacting an aqueous solution, containing 1 wt % petroleum sulphonate, 3.5 wt % sec-butanol, 0.5 wt % iso-pentanol and a varying amount of NaCl, with one of the liquid n-alkanes (n-pentane-n-hexadecane). In all experiments, water : oil ratio (WOR) 4 was used. Three-phase (3 Φ) microemulsion regions were located by increasing the salinity of the aqueous phase and keeping concentrations of surfactant and alcohols constant. Figure 1 illustrates the formation of three phase (3 Φ) region through a salinity scan.

When a salinity scan was performed and the range of salinity, which leads to the formation of 3 Φ

microemulsion, was determined, the center of this salinity range can be taken as the optimum salinity (S^*). The optimum salinity of a system has been defined as the geometric average of the minimum and maximum salinities for a system which exhibits three phases (Reed and Healy, 1976; Puetro and Gale, 1977, Salager, 1977). In most practical cases, there is no significant difference between geometric average and the arithmetic one (Salager, 1977).

Table 6- lists the determined salinity ranges and optimum salinity (S^*) values of Witco-petroleum sulphonate at different oil phase alkane carbon numbers (ACN) and in presence of 3.5 wt% sec-butanol plus 0.5 wt % iso-pentanol at 30°C. For instance, the determined salinity range of sulphonate-n-hexane-brine system, is 0.625-0.775 wt % NaCl, and the optimum salinity, S^* , value is 0.70 wt% NaCl. This salinity range is often defined as the width of three-phase (3Φ) microemulsion region. From the determined salinity range data listed in Table 6, the width of 3Φ regions for petroleum sulphonate-n-hexane-brine and petroleum sulphonate-n-decane-brine systems, are 0.626-0.775 and 1.25-2.10 wt% NaCl, respectively. It can be concluded that the higher the alkane carbon number (ACN), the wider the salinity range required for the formation of 3Φ microemulsion. For surfactant flooding formulation systems, determination of salinity range in which 3Φ microemulsion exists, is highly important. It is well-known that the wider the 3Φ region, the less sensitive the system is to changes in reservoir conditions (Barakat et al., 1983_{a,b}; Haque and Scamehorn, 1986). Several investigators have shown that essentially all the petroleum sulphonate surfactant, which originally present in the aqueous phase, ends up in the 3Φ region or Type III microemulsion region, Figure 1. (Reed and Healy, 1976; Barakat et al., 1983; Haque and Scamehorn, 1986; Barakat and Ibrahim, 2011).

3.1- Salinity-ACN Phase Diagram of Sulphonate

Figure 2 shows the salinity-ACN phase diagram of Witco TRS 10-80 petroleum sulphonate in the presence of 3.5 wt% sec-butanol and 0.5 wt% iso pentanol. In this diagram, the formation of 3Φ region is shown by plotting the salinity range versus oil phase ACN. It can be seen that the width of 3Φ region increases by increasing the oil phase ACN. It is also obvious that increasing salinity produces a I→III→II transition, whereas increasing ACN produces a II→III→I transition as previously illustrated in Figure 1 (Winsor, 1948; 1952).

In Figure 3, by cutting the 3Φ region with iso-salinity lines at 1.0, 1.25, 1.50, 1.75, 2.0 and 2.5 wt% NaCl in the direction of increasing ACN and plotting the obtained ACN range versus the concentration of NaCl gives a better view in Figure 3. The three-phase region obtained at the preferred alkane carbon number range from hexane to nonane, ($3\Phi_{6-9}$), can be located. In surfactant flooding formulation system, it has been reported that the range of 6-9 on the alkane scale is important because these alkane carbon numbers are taken as equivalent models for crude oils (Barakat et al., 1983^a, 1983^b, 1982; Cayias et al., 1976, 1977; Cash et al., 1977, Doe et al., 1976^a, 1976^b).

It is clear from Figure 3 that the $3\Phi_{6-9}$ is achieved only at the vicinity of a salinity range of 1.0-1.25 wt% NaCl. At higher salinities, higher ACN ranges are observed in the 3Φ regions. A downward shift, in the higher ACN ranges, is required to make the investigated petroleum sulphonate suitable for recovering crude oils having equivalent alkane carbon number (EACN) of 6-9. Such a downward ACN shift could be achieved by increasing the temperature of the system and/or addition of polyoxyethylenated nonionic surfactant (Morgan et al., 1977; Schecter and wade, 1980). These investigators have reported that a downward shift of about one and half carbon atom per 10°C rise in temperature, has been achieved when they evaluated the phase behaviour of Matinez 420 (a commercial petroleum sulphonate) and C₁₅ O-xylene sulphonates over a range of temperature from 27 to 70°C.

Careful inspection of data in Figure 3 shows that a surfactant such as Witco-petroleum sulphonate which gave 3Φ region when contacted with 9-12 ACN range at 30°C in presence of 1.5 wt% NaCl, will also give 3Φ region when contacted with 6-9 ACN range at 50°C. This means that the investigated Witco-petroleum sulphonate formulation system is expected to be more suitable for crude oil recovery and oil field conditions when applied at temperature range in the vicinity of 50°C (Morgan et al., 1977).

Figure 4 shows that the logarithm of the optimum Salinity, S^* , is a linear function of the ACN. Thus, a correlation of the type :

$$\text{Log } S^* = K(\text{ACN}) + A(f)$$

is established, where k is the slope and A(f) represents a term which depends upon all other variables, particularly alcohol type and concentration. The value of k and A(f) are found to be 0.167859 and -1.24266, respectively. The coefficient of determination (R^2 value) equals 0.985658 which indicate the reliability of the fit.

3.2- Phase Behaviour of Petroleum Sulphonate – Eugenol Ethoxylate Mixtures:-

For phase behaviour study, four sulphonate/ ethoxylate mixtures, having the same composition (0.75 mole fraction of witco TRS 10-80 plus 0.25 mole fraction of any of the investigated eugenol ethoxylate) were employed in presence of 3.5% sec-butanol and 0.5 wt% iso-pentanol. All three-phase, 3Φ , regions are obtained by increasing the Salinity of the aqueous phase and keeping the total concentration of surfactant pair constant

(1.0 wt%).

Through salinity scans the width of the 3 Φ regions are determined for petroleum sulphonate/ eugenol- 6.6, petroleum sulphonate/ eugenol- 8.9, petroleum sulphonate/ eugenol- 11.5 and petroleum sulphonate/ eugenol- 14.5 mixtures. The obtained data are given in Table (7). From these data, salinity-ACN phase diagrams are plotted for each of the investigated mixtures and are shown in Figures 5-8.

Figure (5) shows the salinity-ACN phase diagram of witco TRS 10-80 petroleum Sulphonate/ eugenol- 6.6 mixture. When this nonionic is added a wider middle phase region is observed if compared with that of petroleum sulphonate alone Figure (2). Addition of eugenol-6.6 shifts the 3 Φ region to relatively higher concentration of NaCl for the hydrocarbon considered (hexane to hexadecane). Stated in another way, witco TRS petroleum sulphonate/ eugenol – 6.6 mixture is preferred, in recovering crude oils from high salinity reservoirs, than sulphonate alone.

In Figure (5) it is worth nothing that neither the I \rightarrow III \rightarrow II transition (which takes place by increasing salinity) nor the II \rightarrow III \rightarrow I transition one (which takes place by increasing the ACN) is affected by the addition of nonionic surfactant (eugenol 6.6). It can also be seen that increasing the ACN necessitates the presence of higher salinity ranges to form the 3 Φ microemulsion region, i.e the 3 Φ region is moved up to a higher salinity range. This higher salinity range permits partitioning of the employed surfactant mixture into the middle phase (Type III).

The phase behaviour diagram of sulphonate / eugenol- 8.9, sulphonate / eugenol- 11.5 and sulphonate / eugenol- 14.9 mixture are shown in Figure 6,7 and 8 respectively. It is obvious from these Figures that the 3 Φ regions are formed at higher salinity ranges than observed in Figure (2), for petroleum sulphonate alone. It can also be seen from Figure 5-8 that the measured 3 Φ microemulsion regions, bounded by the upper and lower phase boundaries (UPB and LPB), are relatively larger than that observed in Figure (2).

For the sake of fair comparison the total 3 Φ microemulsion regions, bounded between the UPB and LPB fitted curves for the whole ACN range (from hexane to hexadecane) and that which represents the EACN range of crude oils (from hexane to nonane), are determined by integrating the difference between the two fitted functions of the UPB and LPB curves in Figures 2,5,6,7,and 8. The measured areas designated 3 Φ_{6-16} and 3 Φ_{6-9} , are given in Table (8). The ratio between the 3 Φ_{6-9} of the employed surfactant mixtures to the 3 Φ_{6-16} of sulphonate alone is calculated to compare the performance between the different micellar flooding formulation systems.

The calculated ratios, shown in Table (8), reveal that sulphonate/eugenol 8.9 mixture gives the best performance with respect to microemulsion formation if compared with the other investigated micellar flooding systems. When sulphonate / eugenol - 6.6, sulphonate / eugenol – 8.9, sulphonate / eugenol – 11.5 and sulphonate / eugenol – 14.9 are employed, the measured 3 Φ_{6-9} regions increases approximately 13.36 , 13.53, 12.72 and 8.12 folds that of sulphonate alone, respectively.

The effect of salinity of the aqueous phase on the location of 3 Φ and the preferred 3 Φ_{6-9} regions is illustrated in Figure (9) is better visualized in Figure (10). It can be seen from this Figure that under a given set of conditions, the width of the 3 Φ_{6-9} region the same for sulphonate / eugenol – 6.6 and sulphonate / eugenol – 8.9 mixtures. However the 3 Φ_{6-9} regions of the former mixture are formed at relatively higher salinity ranges which are more preferable for application in high salinity ranges which are more preferable for application in high salinity reservoirs. It is also obvious from Figure (10) that sulphonate / eugenol mixtures give 3 Φ_{6-9} regions at relatively higher salinity ranges if compared with that of sulphonate alone.

Figure (10) reveals that when Witco TRS petroleum sulphonate is blended with eugenol ethoxylates having approximately 7-9 ethylene oxide (EO) units, wider 3 Φ_{6-9} regions are formed at relatively higher salinity ranges. Increasing the number of EO unit does not improve the performance of the employed sulphonate/ ethoxylate micellar flooding system.

The optimum Salinity S^* , values of petroleum sulphonate / eugenol ethoxylate mixtures, at different ACNs, are given in Table (9), S^* - ACN correlation for sulphonate / eugenol – 6.6 and sulphonate / eugenol – 8.9 mixtures are shown in Figure (11). It can be seen from this Figure that the logarithm of the optimum salinity S^* is a linear function of the ACN. Thus, equations (1) and (2) are developed for sulphonate / eugenol – 6.6 and sulphonate / eugenol – 8.9 mixtures, respectively.

$$\text{Log } S^* = 0.0905741 (\text{ACN}) - 1.7458 \dots\dots\dots(1)$$

$$\text{Log } S^* = 0.127204 (\text{ACN}) - 2.45202 \dots\dots\dots(2)$$

The coefficients of determination (R_2 values) for equations (1) and (2) are found to be 0.974957 and 0.994733 indicating the reliability of the fits.

S^* -ACN relationship sulphonate / eugenol – 11.5 and sulphonate / eugenol – 14.9 mixtures are shown in Figure 12 and 13, respectively. A polynomial equation (3) of the second degree is developed to describe the S^* -ACN relationship of the two mixtures.

$$S^* = \sum_i a_i (\text{ACN})^i \dots\dots\dots(3)$$

Where a_i represent the polynomial coefficients of the fits in Figure 12 and 13 (the polynomial

coefficients values are found to be $a_0 = -0.0793744$, $a_1 = 0.0198226$ and $a_2 = 0.00140627$ for sulphonate-eugenol – 11.5 with R_2 value of 0.997051, and $a_0 = -0.142029$, $a_1 = 0.0334144$ and $a_2 = 0.000992285$ for sulphonate / eugenol – 14.9 with R_2 value of 0.998411).

The developed equation (3) indicates that these mixtures have different performance if compared with sulphonate alone or sulphonate / eugenol – 6.6 and sulphonate / eugenol 8.9.

Conclusions :-

- * The width of the 3 Φ microemulsion region increases with increased oil phase molecular weight (ACN). The wider the 3 Φ region the less sensitive the system to changes in reservoir conditions.
- * For a system which exhibits three phases, a linear relationship exist between the logarithm of optimum salinity S^* , and oil ACN as follows:
 $\text{Log } S^* = 0.167859 (\text{ACN}) - 1.24266$
- * When Salinity – ACN phase behaviour diagrams are compared, the 3 Φ microemulsion regions are formed at wider salinity ranges in case of petroleum sulphonate / eugenol ethoxylate mixtures than that of sulphonate alone.

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Table 1- The Employed Petroleum Sulphonate (Witco TRS 10-80)

Manufacturer :	Witco Chemicals, Sonneborn Divison
Type :	Petroleum sulphonate sodium salt
Appearance :	Brown viscous liquid*
Structure :	Unknown, presumed to contain naphthalene and phenanthrene aryl groups, and more than one alkyl chain.
Mean Equivalent Weight :	425
Active Material :	80 wt %
Moisture :	9 wt %
Unsulphonated Oil :	10 wt %
Inorganic Salts :	1 wt %
Other :	When a solution is left to settle several days, a brown solid residue separates from the solution; it was identified as an iron compound by the characteristic reaction with KSCN.

Ibrahim, 1998, Cayias et al 1977

* After de-oiling, desalting and drying, the 100% active material is pale yellow hygroscopic powder. (Ibrahim, 1998)

Table 2- Some Physical Properties of Polyoxyethylenated Eugenol

Nonionic designation	n	%OE	HLB (%OE/5)	Mol.Wt*	Physical Form at 25°C	n_D^{30}	Specific gravity, 30/30°C	Cloud point °C @	pH of 1% aq. solution	Appearance of 1% aq. solution
Eugenol-2.7	2.70	41.98	8.40	294	liquid	1.5231	1.5231	28	4.9	clear
Eugenol-6.6	6.64	64.02	12.80	468	liquid	1.5112	1.5112	65	4.8	clear
Eugenol-8.9	8.88	70.41	14.08	565	liquid	1.5012	1.5012	80	4.8	clear
Eugenol-11.5	11.45	75.42	15.08	680	liquid	1.4894	1.4894	86	4.6	clear
Eugenol-14.9	14.85	79.92	15.98	802	Soft waxy	1.4882	1.4882	88	4.5	clear
Eugenol-17.9	17.87	82.73	16.55	925	Soft waxy	1.4841	1.4841	92	4.5	clear

* calculated from the mol.wt.of eugenol (164.2) plus the formula wt of n oxyethylene units as determined from ¹H NMR analysis.

@ for 1 % aqueous solution

Table 3- Critical Micelle Concentration (CMC) and Surface Tension at CMC (γ_{cmc}) of Polyoxyethylenated Eugenol at Different Temperatures and Salinities.

n	NaCl wt%	CMC $\times 10^6$ mol.dm ³				γ_{cmc} , mNm ⁻¹			
		28 °C	38 °C	48 °C	58 °C	28 °C	38 °C	48 °C	58 °C
6.64	-	3296.4	1400.4	1372.8	1049.4	38.9	35.3	35.1	33.7
8.88	-	4604.6	2724.6	1928.3	1510.3	40.1	37.9	35.1	34.3
11.45	-	4882.2	4807.9	3409.7	2050.0	41.1	45.1	35.8	35.7
14.85	-	8210.0	5053.9	4199.1	3520.0	45.9	48.1	42.1	42.0
17.87	-	8805.0	6200.0	5200.0	4180.0	48.7	47.6	44.0	43.0
6.64	1.0	716.6	482.8	413.8	385.9	41.4	38.1	35.1	34.1
6.64	2.0	514.7	472.6	379.4	283.0	34.1	32.3	31.8	31.3
6.64	3.0	493.6	426.4	388.3	273.2	33.6	31.8	31.3	31.1
6.64	4.0	453.5	397.0	399.6	278.6	35.1	32.8	32.1	31.8
6.64	5.0	472.3	362.1	359.8	263.3	35.6	33.8	32.8	32.3

Table 4- Effectiveness (π_{cmc}) and Efficiency (pC_{20}) of the Prepared Polyoxyethylenated Eugenol in Surface Tension Reduction at Different Temperatures and Salinities.

n	NaCl wt%	π_{cmc}				pC_{20}			
		28 °C	38 °C	48 °C	58 °C	28 °C	38 °C	48 °C	58 °C
6.64	-	32.81	34.69	30.86	30.24	5.437	5.266	4.863	4.552
8.88	-	31.62	32.03	30.86	29.65	4.484	4.233	4.207	4.152
11.45	-	30.62	31.87	30.12	28.23	4.227	4.081	3.563	3.329
14.85	-	25.82	24.87	23.86	21.97	3.519	3.303	3.196	3.155
17.87	-	22.99	22.35	21.95	21.03	3.269	3.157	3.095	3.049
6.64	1.0	30.32	31.87	30.86	29.85	5.134	4.944	5.226	4.877
6.64	2.0	38.12	38.17	34.66	32.85	9.230	-	-	-
6.64	3.0	37.62	37.67	34.16	32.65	6.080	6.808	6.583	6.626
6.64	4.0	36.62	37.17	33.86	32.15	5.277	6.389	5.763	5.797
6.64	5.0	36.32	36.17	33.16	31.65	5.062	5.739	5.244	5.269

Table 5- CMC* values of Witco TRS 10-80 at Different Salinities and added sec-Butanol concentration

Additives	CMC μ mol/litre
0.0 wt % NaCl	170
0.2wt % NaCl	105
0.5 wt % NaCl	38
1.0 wt % NaCl	34
1.5 wt % NaCl	25
2.0 wt % NaCl	20
1.0 wt % NaCl + 1.0 wt % sec-Butanol	25
1.0 wt % NaCl + 2.0 wt % sec-Butanol	20
1.0 wt % NaCl + 3.0 wt % sec-Butanol	17
1.0 wt % NaCl + 4.0 wt % sec-Butanol	15
1.0 wt % NaCl + 5.0 wt % sec-Butanol	13
1.0 wt % NaCl + 6.0 wt % sec-Butanol	11

* Determined at 25°C using de-oiled purified sample.

Table 6- Salinity Range and Optimum Salinity (S^*) at Sulphonate-Brine-Oil System at 30°C@.

Oil Phase	ACN	Salinity range (WT % NaCl)	S^* (WT % NaCl)
n-Hexane	6	0.625-0.775	0.70
n-Heptane	7	0.85-1.05	0.95
n-Octane	8	0.95-1.25	1.10
n-Nonane	9	1.15-1.50	1.35
n-Decane	10	1.25-2.10	1.67
n-Undecane	11	1.45-2.35	1.90
n-Dodecane	12	1.6-3.00	2.30
n-Tetradecane	14	1.90-4.10	3.00
n-Hexadecane	16	2.25-5.50	3.87

@ aqueous phase : 1 wt % Witco sulphonate + 3.5 wt % sec-butanol + 0.5 wt % iso-pentanol + wt % NaCl, WOR = 4.

Table 7- Width of 3 Φ Regions of Petroleum Sulphonate-Eugenol Ethoxylate Mixtures at Different ACNs

Oil ACN	Width of 3 Φ Regions (Salinity, wt % NaCl)			
	Witco TRS 10-80 + Eugenol-6.6	Witco TRS 10-80 + Eugenol-8.9	Witco TRS 10-80 + Eugenol-11.5	Witco TRS 10-80 + Eugenol-14.9
6	1.25-2.50	1.00-2.10	0.75-1.75	0.90-1.55
7	1.50-2.75	1.00-2.25	0.75-1.90	1.00-1.75
8	1.75-3.00	1.00-2.35	0.80-2.10	1.15-2.00
9	1.90-3.25	1.10-2.60	0.90-2.40	1.25-2.25
10	2.00-3.50	1.20-2.90	1.00-2.60	1.50-2.50
11	2.25-4.00	1.30-3.25	1.10-3.00	1.60-2.75
12	2.50-4.25	1.50-3.60	1.25-3.50	1.75-3.25
14	2.85-5.25	1.75-4.50	1.50-4.25	2.25-4.25
16	3.50-6.75	2.75-6.50	2.00-6.00	3.00-6.00

3 Φ = three-phase microemulsion

Table 8- Salinity Ranges and The Measured 3 $\Phi_{6,9}$ and 3 $\Phi_{6,16}$ Regions

Surfactant	Salinity Ranges, of 3 $\Phi_{6,9}$ Regions (wt% NaCl)	Measured 3 $\Phi_{6,9}$ Region	Salinity Ranges, of 3 $\Phi_{6,16}$ Region (wt% NaCl)	Measured 3 $\Phi_{6,16}$ Region	3 $\Phi_{6,9}$ /3 $\Phi_{6,16}$ Ratio*
Sulphonate	0.625-1.50	0.061	0.625-5.50	0.285	0.21
Sulphonate ⁺ Eugenol 6.6	1.25-3.25	3.807	1.25-6.75	18.402	13.36
Sulphonate ⁺ Eugenol 8.9	1.00-2.60	3.857	1.00-6.5	20.724	13.53
Sulphonate ⁺ Eugenol 11.5	0.75-2.35	3.626	0.75-6.00	20.88	12.72
Sulphonate ⁺ Eugenol 14.9	1.00-2.25	2.314	1.00-6.00	14.285	8.12

* The 3 $\Phi_{6,9}$ for the investigated sulphonate / eugenol mixture
 The 3 $\Phi_{6,16}$ for sulphonate only.

Table 9- S^* Values of Petroleum Sulphonate-Eugenol Ethoxylate Mixtures at Different ACN

ACN	S^* Values, wt % NaCl			
	Sulphonate + Eugenol-6.6	Sulphonate + Eugenol-8.9	Sulphonate + Eugenol-11.5	Sulphonate + Eugenol-14.9
6	1.875	1.550	1.250	1.225
7	2.125	1.625	1.325	1.375
8	2.375	1.675	1.450	1.575
9	2.575	1.850	1.650	1.750
10	2.750	2.050	1.800	2.000
11	3.125	2.275	2.050	2.175
12	3.375	2.550	2.375	2.500
14	4.050	3.125	2.875	3.250
16	5.125	4.625	4.000	4.500

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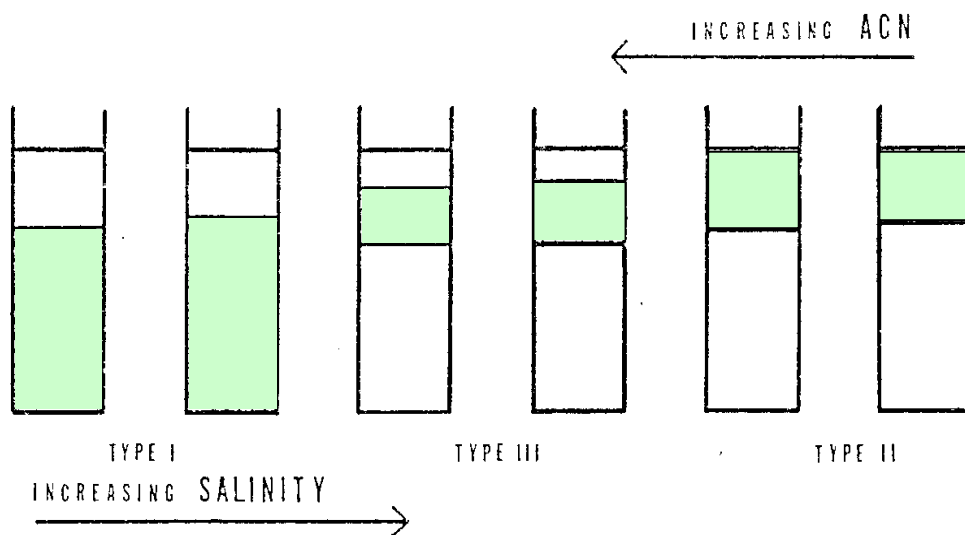


Figure (1)
Illustrates The Formation of Three-Phase (3Φ)
Region Through a Salinity Scan.

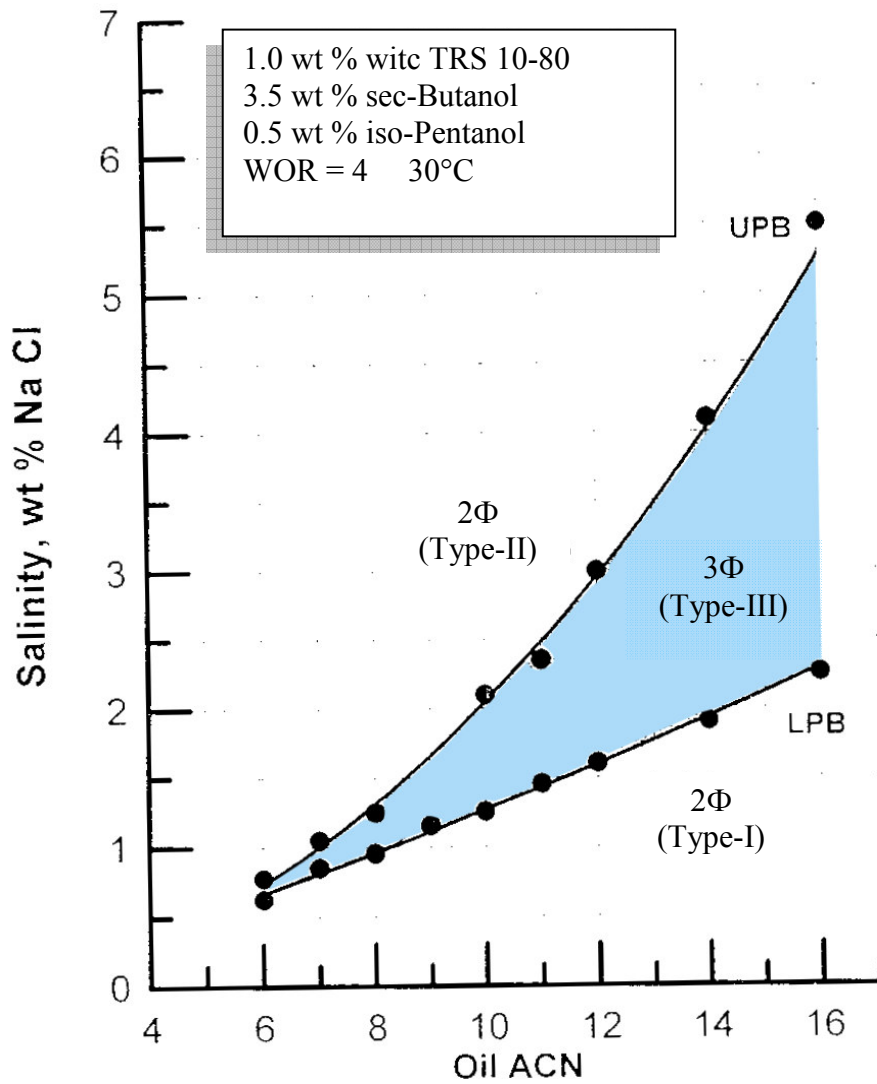


Figure (2)
Salinity-ACN Phase Diagram Using
Petroleum Sulphonate (Witco TRS 10-80)

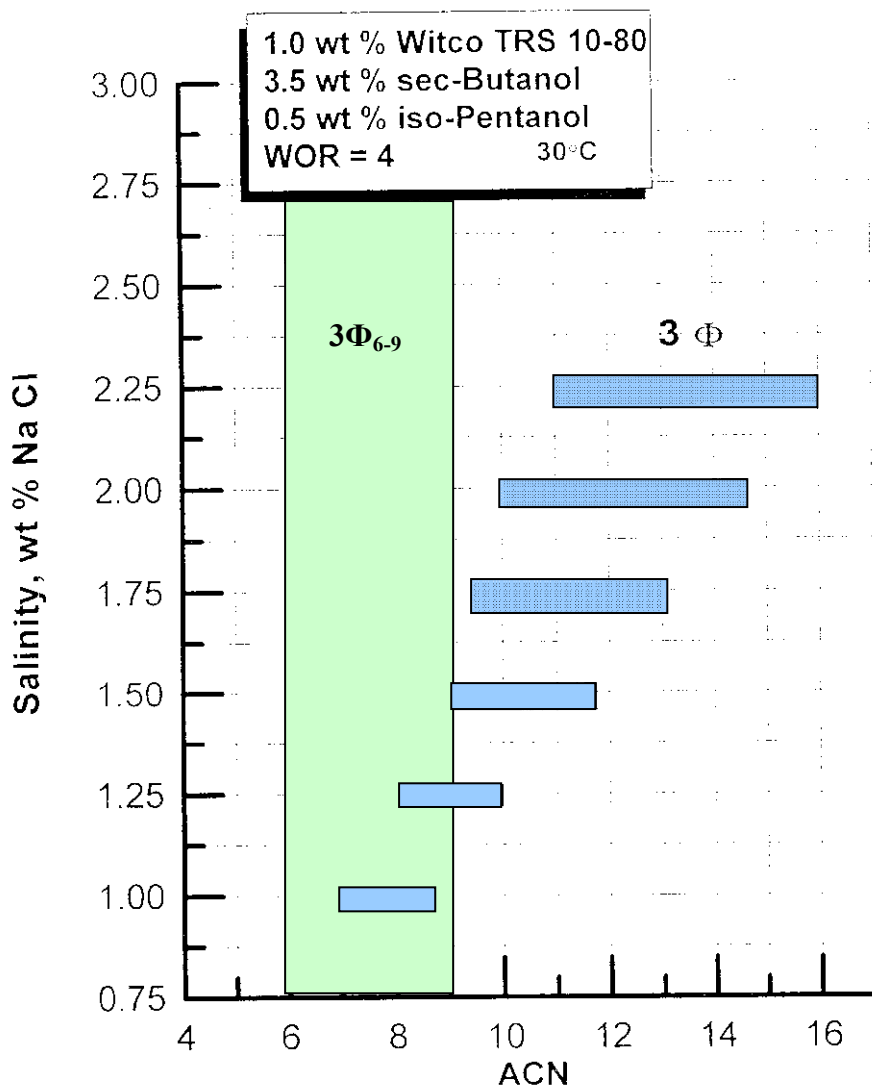


Figure (3)
Effect of Salinity on The Three-Phase
Region and Location of The 3Φ₆₋₉ Region

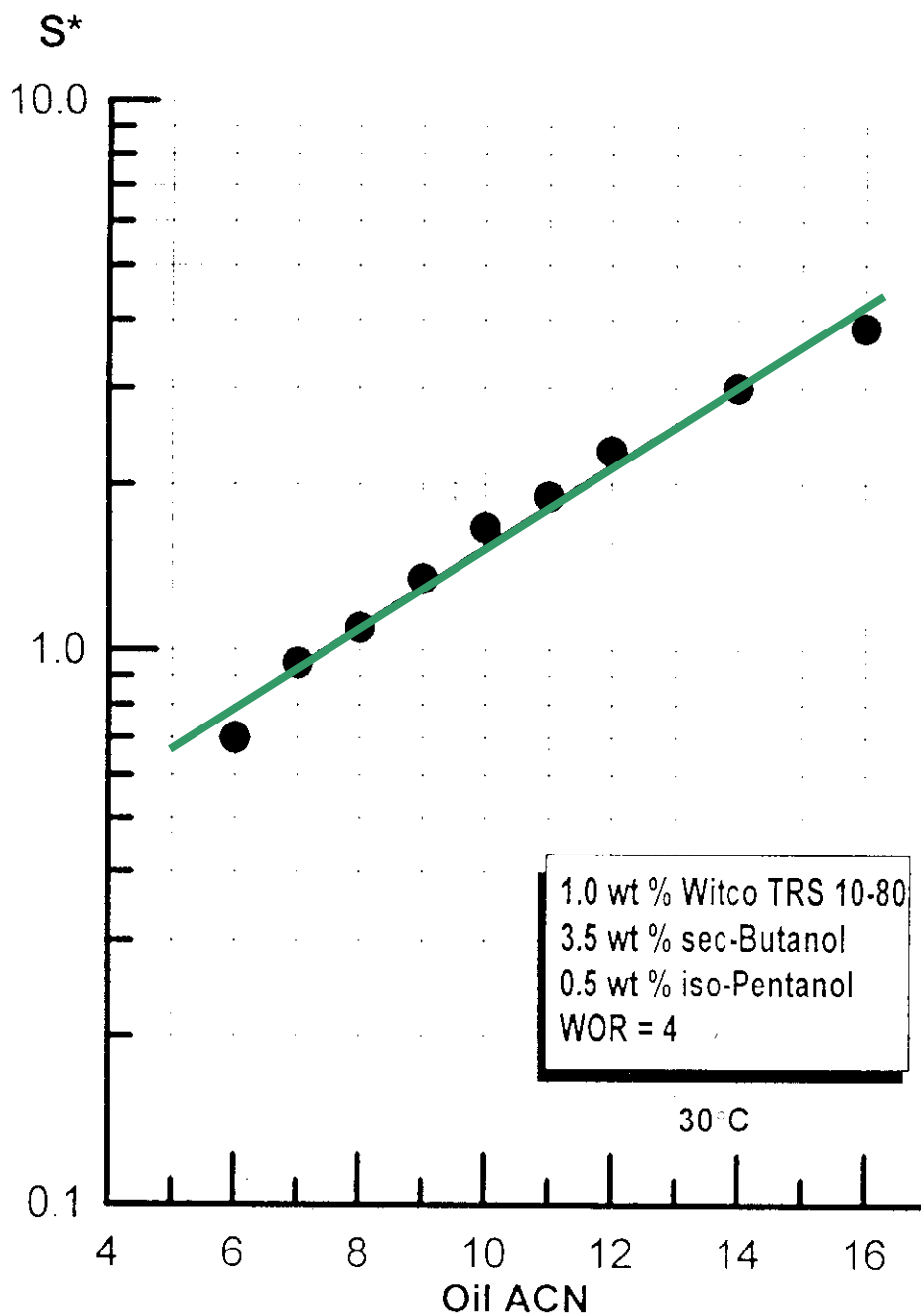


Figure (4)
Relation Between The Optimum
Salinity (S^*) and Oil ACN for
Witco TRS 10-80

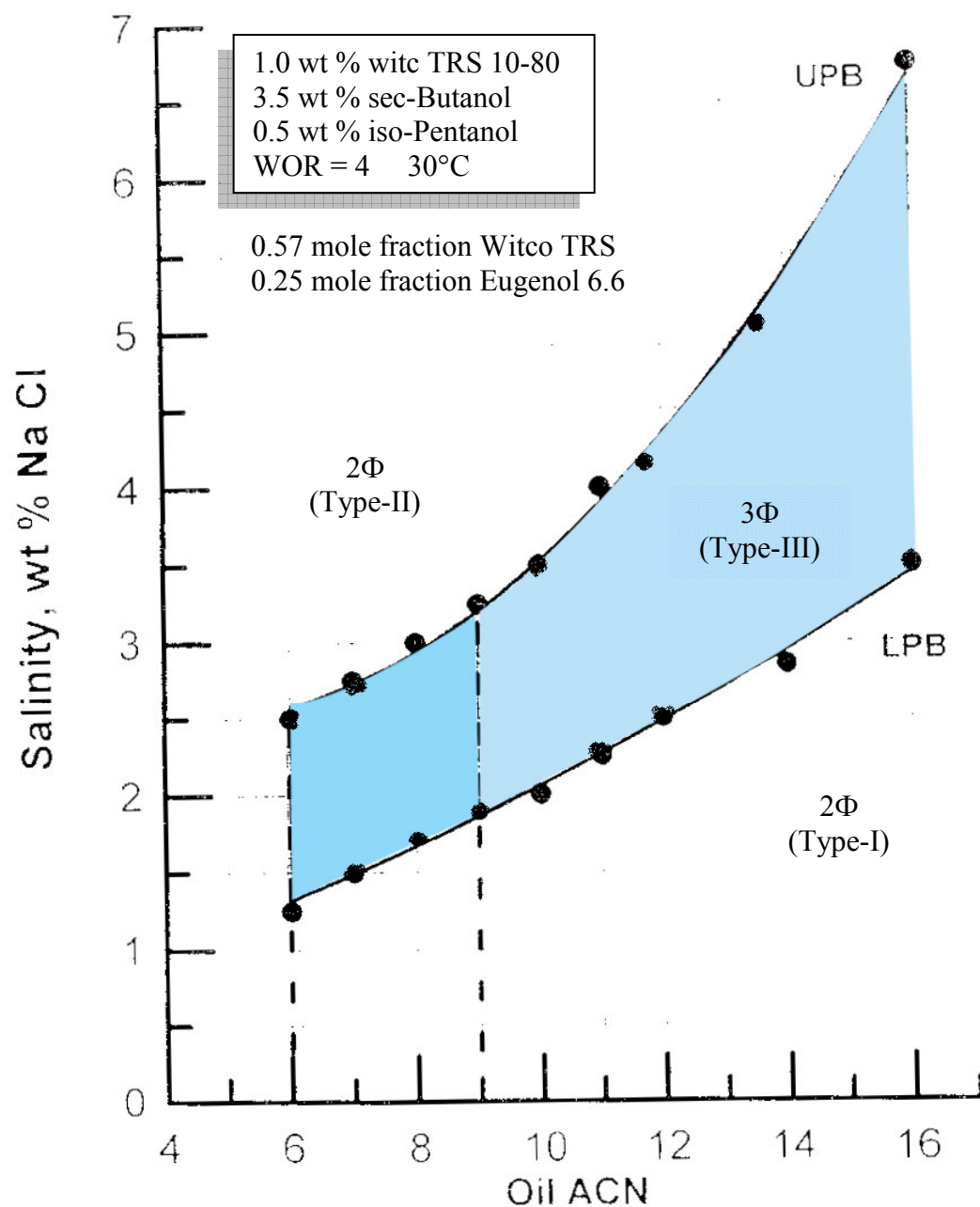


Figure (5)
Salinity-ACN Phase Diagram Using
Petroleum Sulphonate / Eugenol-6.6 Mixture

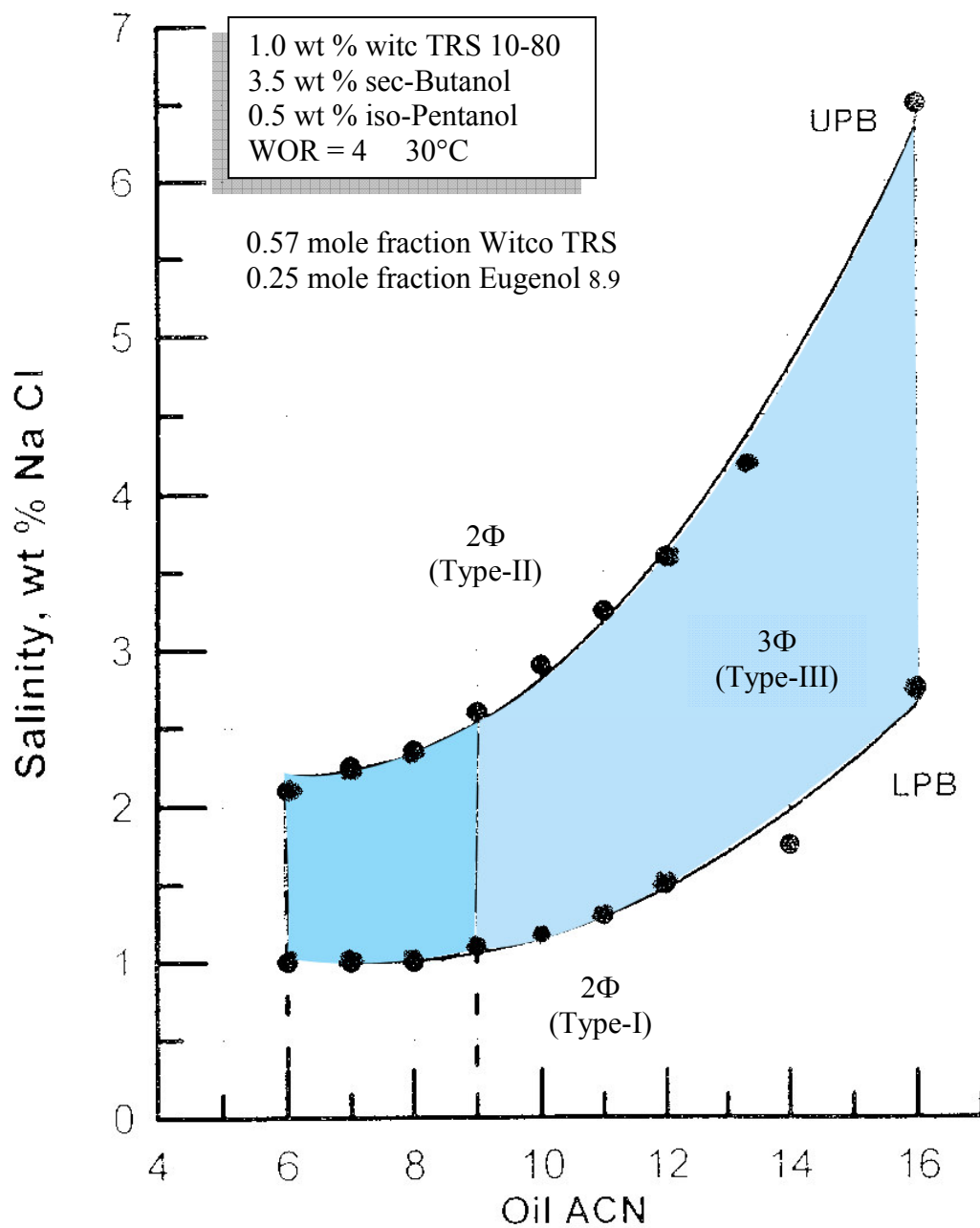


Figure (6)
Salinity-ACN Phase Diagram Using
Petroleum Sulphonate / Eugenol-8.9 Mixture

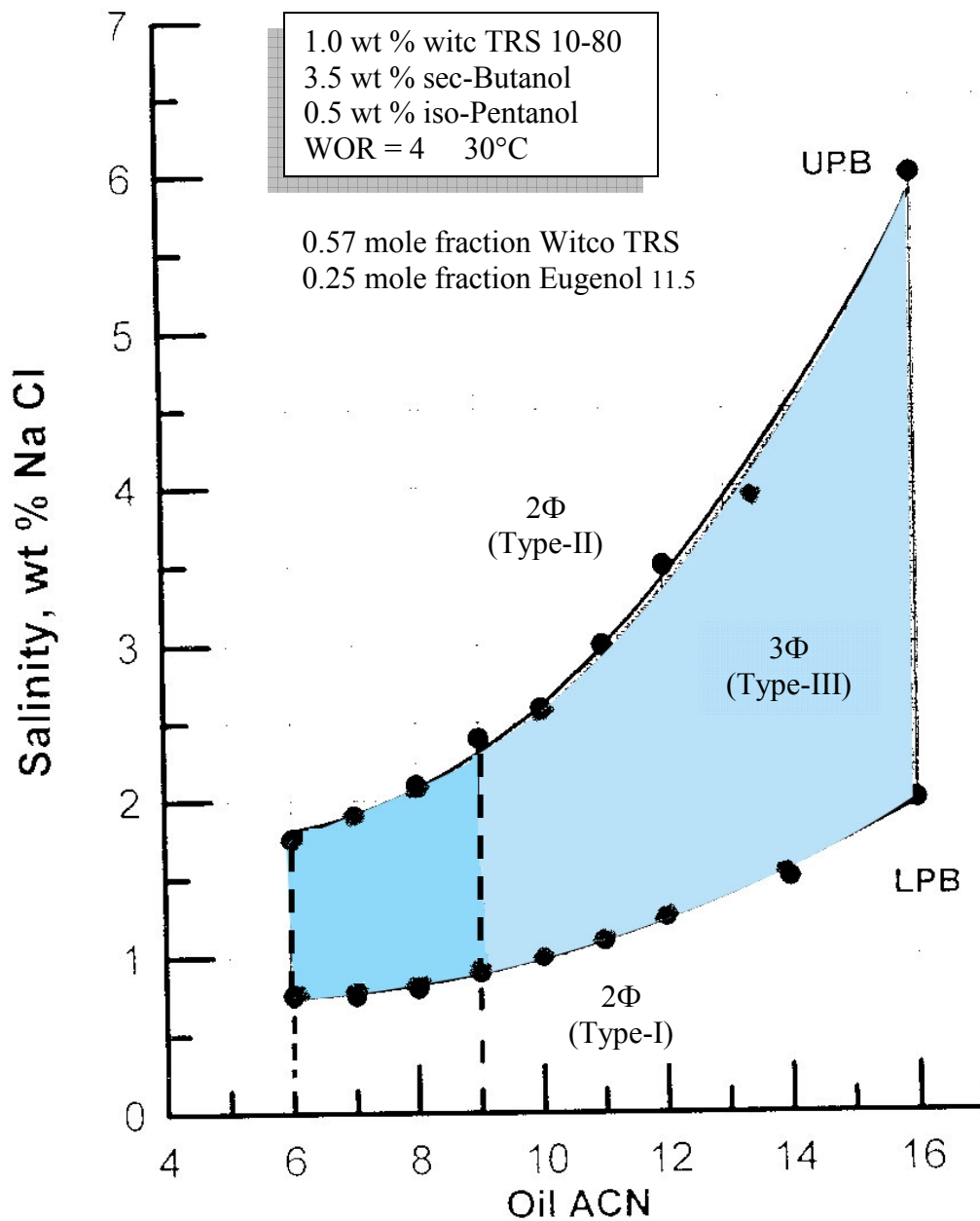


Figure (7)
Salinity-ACN Phase Diagram Using
Petroleum Sulphonate / Eugenol-11.5 Mixture

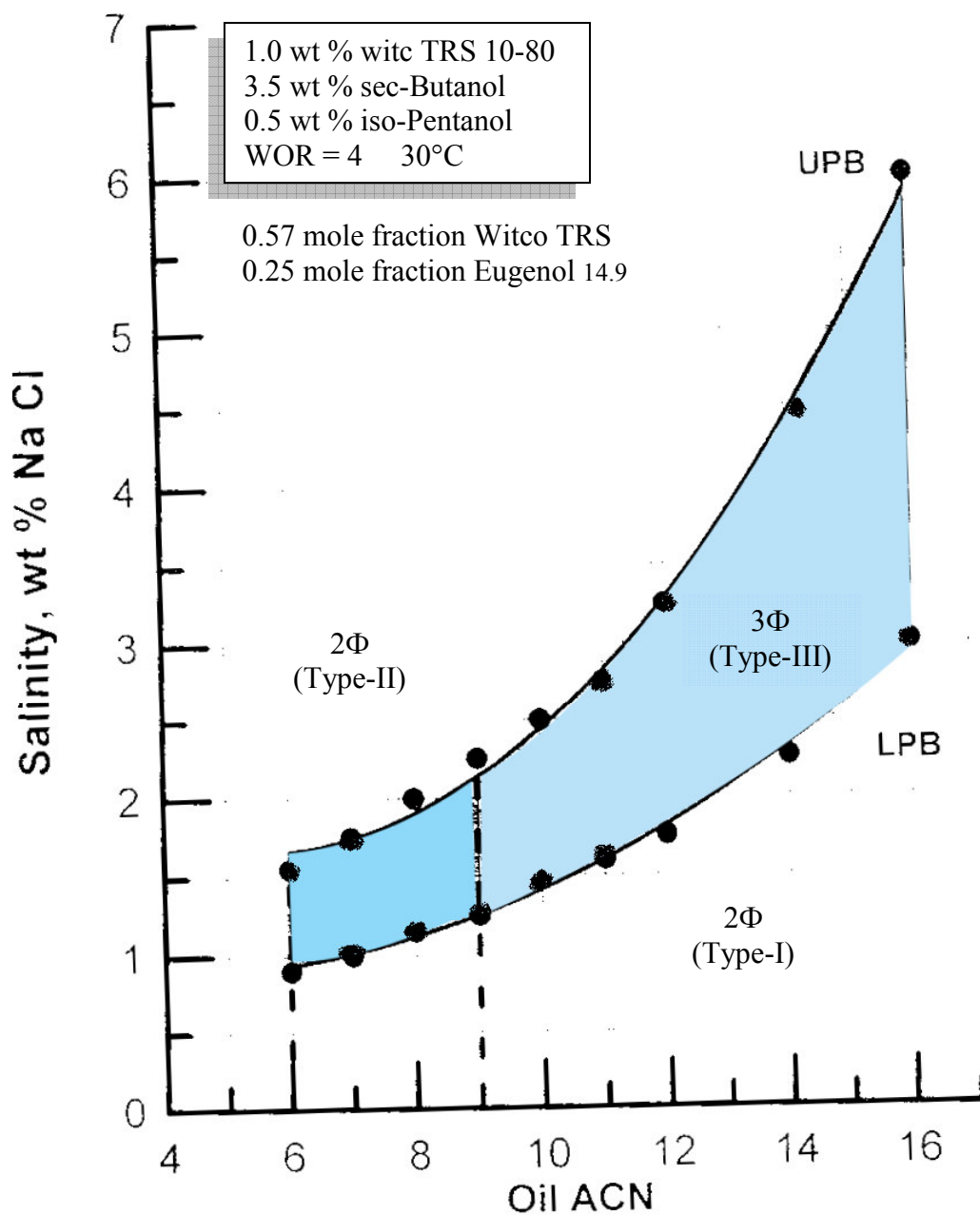


Figure (8)
Salinity-ACN Phase Diagram Using
Petroleum Sulphonate / Eugenol-14.9 Mixture

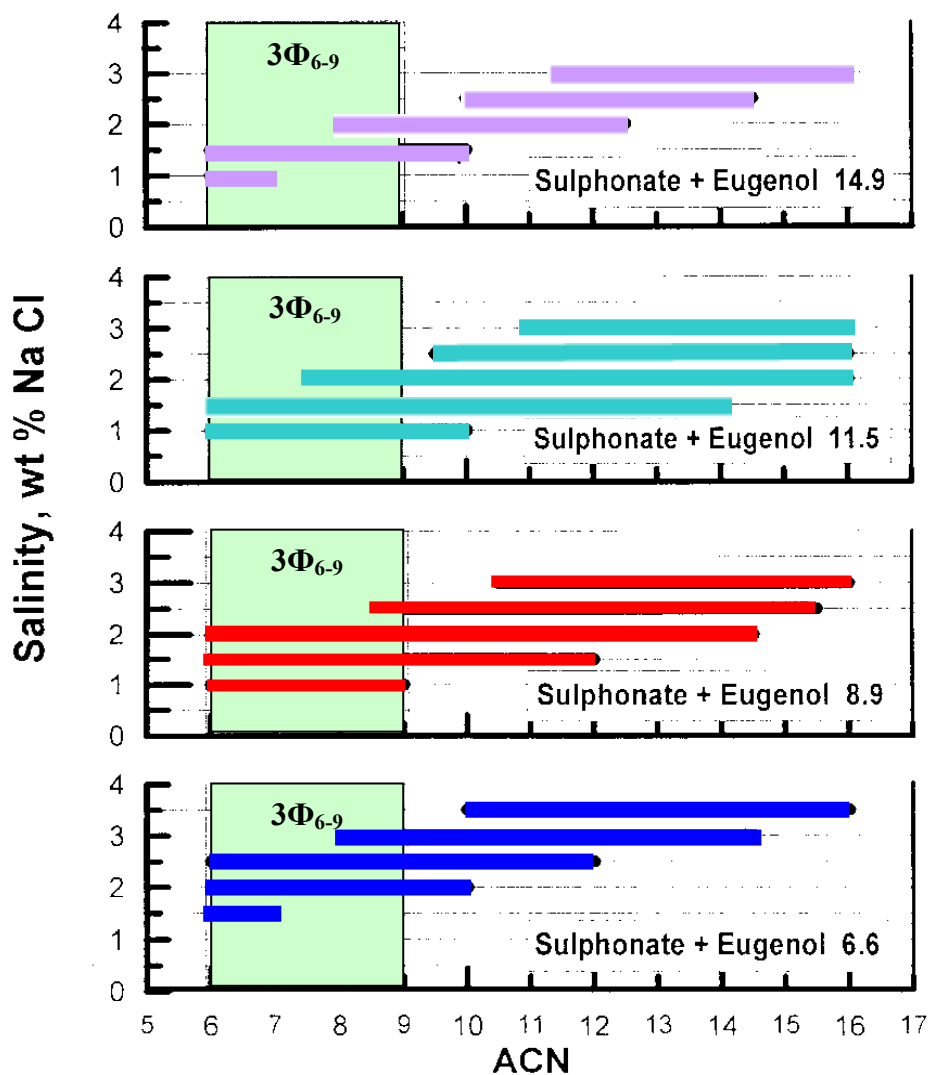


Figure (9)
Illustrates The Location of 3Φ₆₋₉
Regions of Sulphonate / Ethoxylate Mixtures

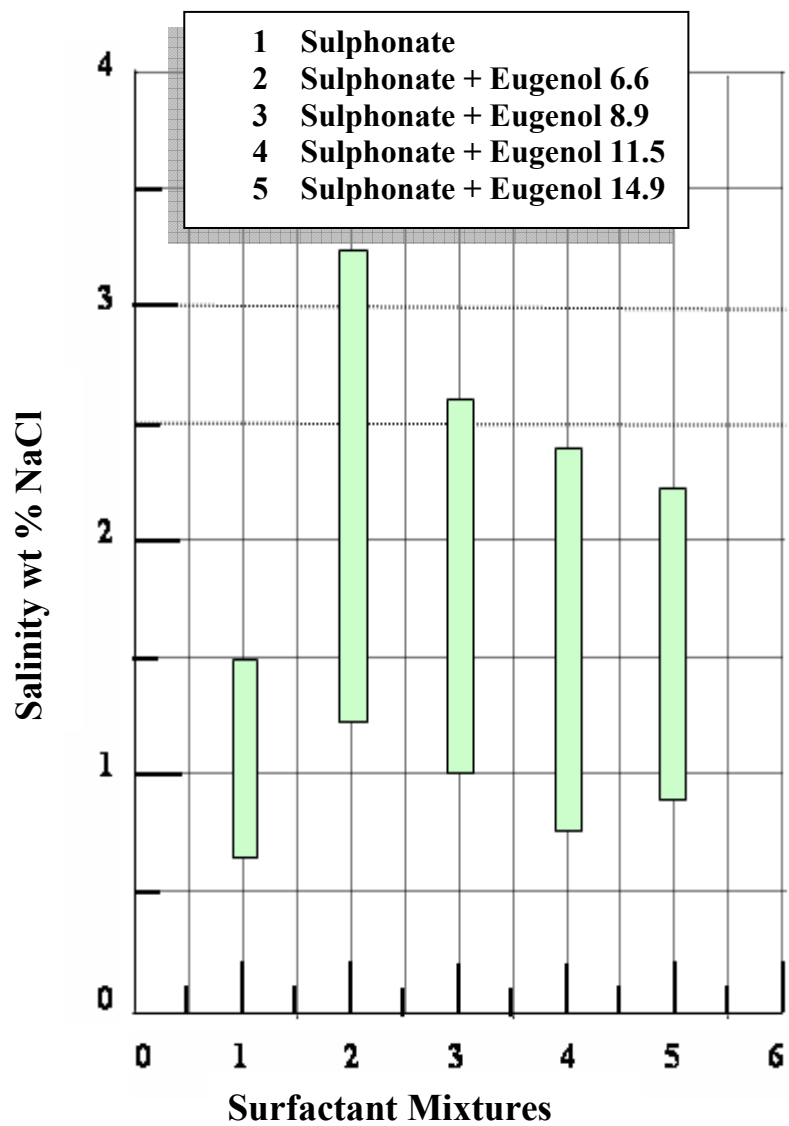


Figure (10)

Illustrates The Width of $3 \Phi_{6,9}$ Regions for Sulphonate and Sulphonate / Ethoxylated Eugenol mixtures

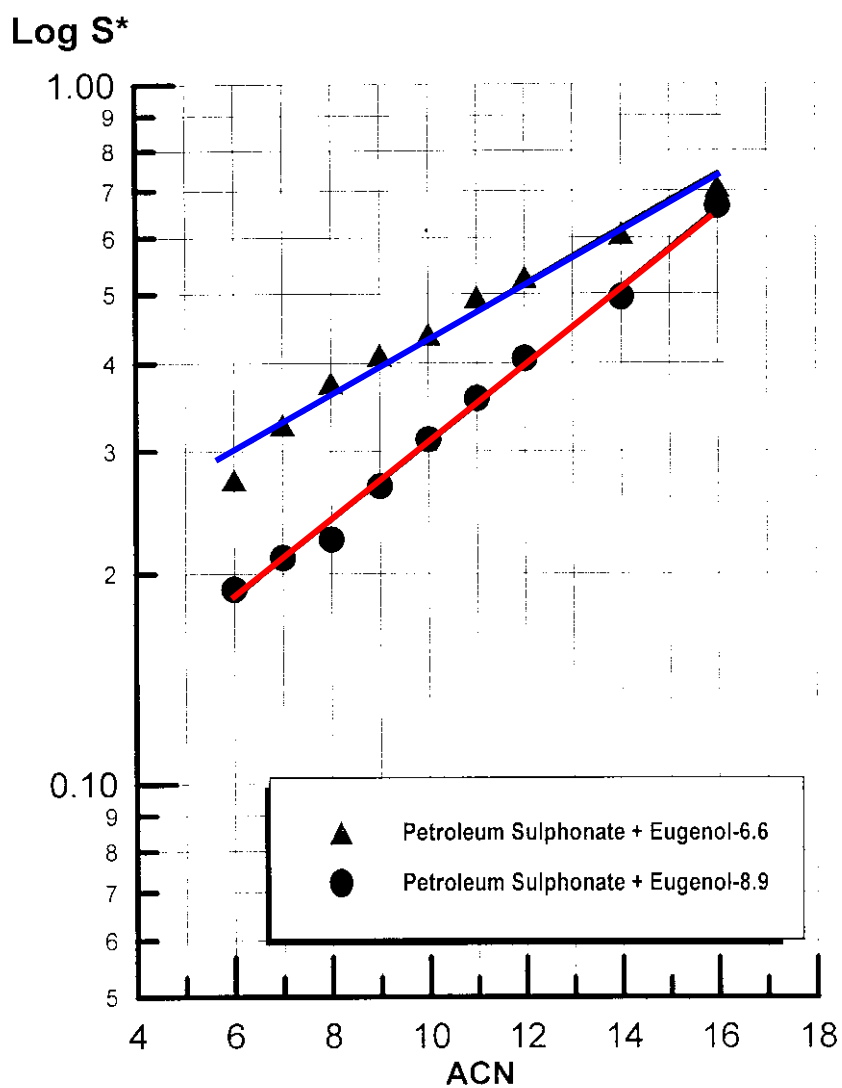


Figure (11)
S*- ACN Correlation for Sulphonate / Eugenol-6.6
and Sulphonate / Eugenol-8.9 Mixtures.

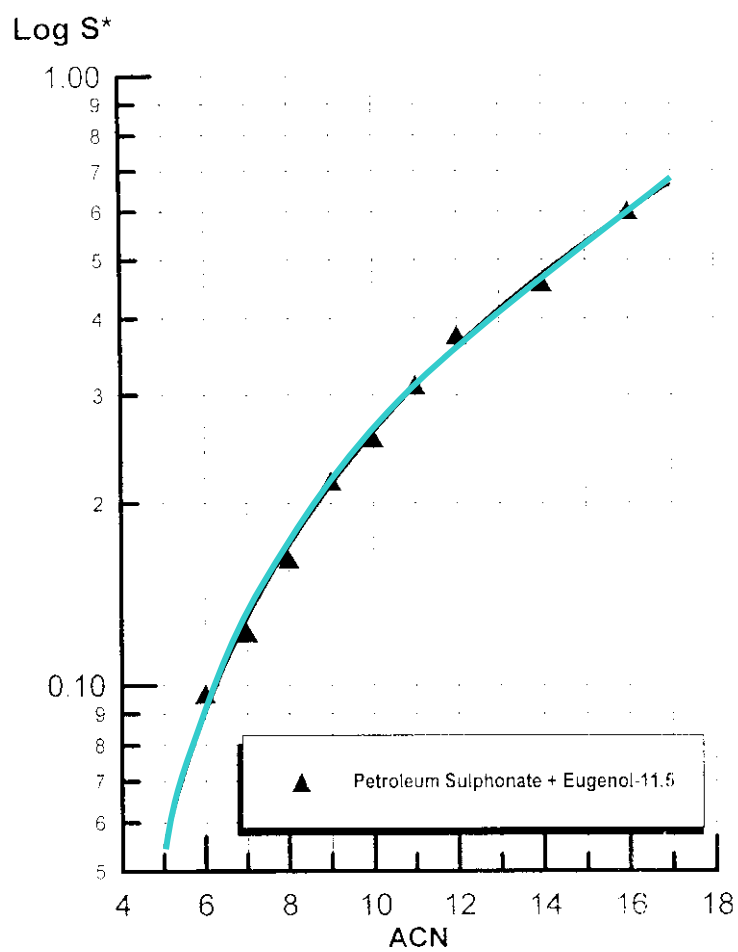


Figure (12)
S*- ACN Relationship for Sulphonate / Eugenol-11.5

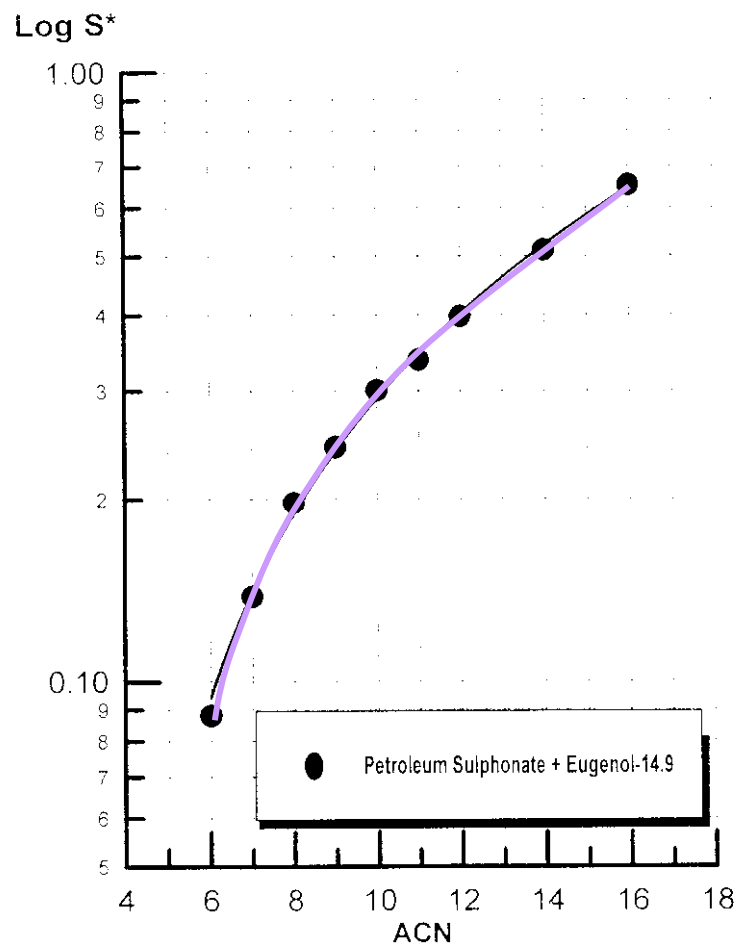


Figure (13)
S*- ACN Relationship for Sulphonate / Eugenol-14.9

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