Mojdeh Delshad

A STUDY OF POLYMER/SURFACTANT INTERACTIONS FOR

MICELLAR/POLYMER FLOODING APPLICATIONS

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A STUDY OF POLYMER/SURFACTANT INTERACTIONS FOR

MICELLAR/POLYMER FLOODING APPLICATIONS

By

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THESIS

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ABSTRACT

Static measurements of the phase volumes of mixtures of surfactant, polymer, alcohol, water, n-octane, sodium chloride, and in some cases polymer additives were made. A limited number of viscosity, phase concentration, and IFT measurements were also made. The purpose was to systematically determine the affect of various polymers on the phase behavior of various surfactant formulations. Measurements with and without oil (n-octane) were made across a range of salinity appropriate to the particular surfactant at temperatures between 24 and 75° C. The polymers used were xanthan gum, hydrolyzed polyacrylamide, polyacrylamide, hydroxyethylcellulose, and polyethyleneoxide of three different molecular weights. The surfactants used were Exxon's C_{12} MEAOXS, Witco's TRS 10-80, Stepan's Petrostep 465, Alcolac's Siponate DS-10, GAF's Igepal CO-530 and CO-610, and Witco's ethoxylated alcohol TDA-100. The alcohols were isobutyl, secondary butyl, isopentanol, and isopropanol.

The oil free (i.e. no added oil) solutions showed a characteristic phase seperation into an aqueous surfactant rich phase and an aqueous polymer rich phase, at some sufficiently high salinity (NaCl concentration), which we call the CEC. The CEC was found to be a characteristic of a given surfactant/alcohol combination, which shifts with the solubility of the surfactant, qualitatively the same way as the optimal salinity does. But the CEC was found to be independent of the polymer type, polymer concentration (between the 100 and 1000 ppm limits investigated), and surfactant concentration. The CEC increases with temperature for the anionic surfactants and decreases with temperature for the nonionic surfactants.

When oil was added to the above mixtures an entirely different pattern

of phase behavior was observed. The particular formulations form the typical sequence of lower phase microemulsion and excess oil; middle phase microemulsion, excess oil, and excess brine; and upper phase microemulsions and excess brine; as salinity increases. The sequence with polymer was precisely the same over most of the salinity range but deviated over a limited range of salinity: the three phase region simply shifts a small distance to the left on the salinity scale. Also, and probably more significantly, some of the "aqueous" phases in the critical region of the shift (which is also just above oil-free CEC salinity) were found to be gel-like in nature. These apparently occur under conditions such that the polymer concentration in the excess brine of the three phase systems becomes very high, due to the fact that almost all the polymer is always in the brine phase, even when the brine phase is very small. Thus an overall 1000 ppm of polymer can easily be concentrated to 10000 ppm or more. One of the most remarkable aspects of the phase behavior of the surfactant/polymer systems is that the same patterns are observed for all combinations of anionic and nonionic surfactants and polymers. Also, little difference was observed in the IFT values with and without polymer. The three phase systems still exhibited ultra-low IFT values. Obviously, significant differences did occur in the brine viscosities when polymer was added. The polymer free mixtures were themselves quite viscous, however; and the viscosity of the oil free surfactant rich phases (above the CEC) were significantly higher when in equilibrium with a polymer rich aqueous phase, even though apparently containing almost no polymer. The polymer rich phases had normal viscosities as judged by the same polymer in the same brine at the expected concentration assuming all of the polymer was in the polymer rich phase. The affect of polymer on the systems with oil was to increase the viscosity of the

water rich phase only, with little effect on the microemulsion phase unless it was

the water rich phase.

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CHAPTER I

INTRODUCTION

In one variation of micellar/polymer flooding, polymer is used both in the micellar slug and in the mobility buffer bank. This necessitates surfactant/polymer compatibility. In another vaiation of micellar/polymer flooding, oil is used in the slug, but compatibility is still necessary, because polymer is used in the drive and mixing occurs between the two due to dispersion and other mixing mechanisms [1-4].

However, compatibility is meaningful only with respect to the corresponding surface activity region and shifts with the same variables. For example, lowering the salinity may increase the compatibility [2, 5, 6], but it will also increase the interfacial tension [7-13], and the extent of the two phase region [14-21].

The objective of this study is to determine the phase behavior of various mixtures of surfactant, alcohol, oil, polymer, and brine. Specifically, this includes determining when the polymer induces a separate, additional phase. Also, what chemicals are most compatible and why and what are the optimal concentrations.

Surfactant and polymer play equally important roles in micellar/polymer flooding. The surfactant is necessary to lower the interfacial tension and/or to stabilize oil/water emulsions. The polymer is necessary to control the mobility of the injected fluids. The total cost of each of these chemicals is roughly the same since the polymers are used over a greater time (or pore volumes injected) and cost more per pound. The complexity of the various

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phenomena due to each is also about the same. Other important but less essential chemicals include hydrocarbons, electrolytes, alcohols, co-surfactants, biocides, and oxygen scavengers. Still others may be added in special cases or for special purposes, for example, tracers of various sorts.

The phase behavior, and to a limited degree the phase properties, especially viscosity, of various mixtures of these chemicals were studied. Specifically, we studied the effect of various water-soluble polymers on the phase behavior of surfactant/alcohol combinations in brine and hydrocarbon. Both anionic and nonionic surfactants and polymers were used. The phase behavior of the surfactant systems without polymer is relatively well known. Also, it is known that the polymers can cause marked changes in the phase behavior of these systems. Trushenski [1,2] and Szabo [6] reported this and referred to it as surfactant/polymer interaction (SPI). This past work is reviewed below. We have systemically investigated the complex behavior of these systems as a function of surfactant type, polymer type, alcohol type, temperature, and the concentrations of surfactant, polymer, alcohol, sodium chloride, and oil (usually n-octane). Such behavior is important and must be considered due to the inevitable mixing of the chemicals in the reservoir being flooding. As noted above, this is true even if the microemulsion approach to micellar/polymer flooding is used, due to dispersion and inaccessible pore volume of the polymer, not to mention crossflow and other reservoir mixing mechanisms. In the aqueous approach, polymer is added directly to the surfactant slug for mobility control [13, 22, 23, 24].

Review of Literature on Surfactant-Polymer Interaction

The earliest and most complete investigation of SPI reported is that of Trushenski and coworkers [1,2] at Amoco. Although others have briefly noted the

problem, the only other papers dealing with SPI as such are the one by Szabo [6] and the one by Noronha, Bansal, and Shah [7].

The phase behavior of surfactant-polymer systems is the basic information provided by all of these studies. In every case the systems were aqueous only (no added hydrocarbon). Additionally, Trushenski and coworkers and Szabo evaluated the effect of SPI on oil recovery by doing core floods. Szabo and Noronha et al., measured the rheological and interfacial properties of some of their mixtures.

Briefly, what Trushenski found was that some of the brine mixtures containing both surfactant and polymer separated into two phases, a surfactant rich phase and a polymer rich phase. This was called surfactant-polymer incompatibility, and attributed to surfactant-polymer interaction (SPI). He used a mahogany sulfonate with isopropyl alcohol (IPA) cosolvent and two polymers: hydrolyzed polyacrylamide (Dow's Pusher 700) and xanthan gum (Kelco's Kelzan, now sold under the tradename xanflood). These chemicals in sodium chloride brine formed one or two phases depending upon (1) the concentration of IPA (2) the concentration of NaCl and (3) the temperature. Higher concentration of IPA, lower concentration of NaCl or higher temperature increased the region of single phase behavior. There was little difference between the two polymers or between polymer concentrations of 500 and 1500 ppm.

A complete summary of what Trushenski et al. found from their core tests will not be attempted here since this study does not involve such tests and there are many complex interactions to consider. Very briefly, they found that a sulfonate containing phase could be trapped (or bypassed) in the rock when compositions corresponding to the two phase region of their aqueous samples were

formed in the rock being flooded. This caused an increase in total sulfonate retention. Polymer inaccessible pore volume increased the mixing in the rock and thus the SPI. By changing one of the above three items in a favorable direction, the SPI was eliminated or at least minimized. Of course, even when this is possible, both technical and economic tradeoffs or costs must be made.

Szabo reported data on several additional polymers and sulfonates. The polymer types were xanthan gum, polyacrylamide, hydrolyzed polyacrylamide, 2-acrylamido-2-methyl-propane sulfonate (AMPS), a copolymer of AMPS and acrylamide (Calgon's 340), hydrolyzed 340, carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC), and an experimental polymer called 106, of unspecified structure. All of Szabo's mixtures were two or three phase. This contrasts sharply with Trushenski's results and our own. Part of the reason for this was because of the relatively high salinities Szabo used in most of his samples, but it is not clear that this was the only reason.

Szabo's most important contribution was his concentration data. He found that in every case the polymer rich phase contained almost all the polymer, typically 97% or so. On the other hand, both aqueous phases contained appreciable concentrations of sulfonate, although the sulfonate rich phase contained four to nine times higher concentration than the polymer rich phase.

Szabo established that both anionic and nonionic polymers mixed with sulfonates behave in a very similar way. Our work shows that this is also true for a variety of both anionic and nonionic surfactants.

Szabo also reported a variety of core flood, viscosity, and interfacial tension data. Although no clear, apparent trend is evident from these data, worthwhile observations can be made: (1) lowering the salinity of the polymer

drive improved the oil recovery efficiency of his core floods, just as reported by Trushenski, and presumably for the same reasons (2) the viscosity of the sulfonate rich phase (the bottom phase in his samples) can be quite viscous, in fact in his tests was frequently more viscous than the polymer rich phase and (3) the IFT between his separated aqueous phases was often very low, sometimes as low as 10^{-4} or 10^{-5} dyne/cm. The second point is significant with respect to which phase will tend to propagate faster in a porous medium. The third point is significant with respect to the question of phase trapping and increased sulfonate retention, suggesting that this will not always be a problem, even with phase separation, or so called SPI.

The third study, by Noronha et al., was very limited in scope, but new types of data, surface viscosity, screen factor, light scattering, and surface yield value, were reported. However, it is not at all clear what the significance of these data were with respect to SPI. Also, these authors included calcium salts as well as sodium salts in their study. They concluded that Na^+ has a shielding effect upon the polymer molecules, while Ca^{++} enhances association of surfactant and polymer molecules.

Perhaps it should be pointed out that none of these studies answered the question of what interaction is actually occurring between surfactant and polymer molecules and why. All of the results are limited to indirect indications, principally phase behavior data. Furthermore, even here, excepting the very complicated and indirect information from core floods, all of the phase data were without added oil. The inclusion of hydrocarbons, which sometimes completely changes the observed behavior of these systems, was one of the objectives of this research. We have also measured various phase properties, but the basic question

of exactly what the molecular interactions are remains unanswered. Our data do suggest that whatever the interactions are, they are exceedingly nonspecific. Thus, the thermodynamics of mixing large molecules may in fact be all that is necessary to explain the SPI phenomenon.

CHAPTER II

MICELLAR SOLUTIONS

It is well-known that oil and water do not mix. Although this is true, it is possible to have a homogeneous mixture of oil and water if a third substance is added. This third substance is recognized by a number of different names: soap, emulsion-former, detergent, surface-active agent, surfactant, etc.. The role of the surfactant molecule is to bind oil and water, i.e., to act as a bridging agent between the two immiscible liquids.

A surfactant molecule typically is composed of two portions: an ionic portion which, because of its electrostatic charge, is water-soluble; and a nonionic hydrocarbon portion which chemically resembles oil and is soluble in oil. In the early 1900's it was recognized that, when soap is dissolved in water at sufficient concentrations, the soap molecule form aggregates, which are termed "micelles" [25], [26, 27]. The formation of micelles in hydrocarbon solvents using oil-soluble soap was later verified [28, 29, 30]. These micellar aggregates have the capacity of solubilizing oil or water within their centers, depending upon the type of micelle [31, 32], viz., whether the micelle is formed by a water-soluble surfactant in water or oil-soluble in oil. Micellar sizes are in the range of 10^{-6} to 10^{-4}mm [33, 34].

Micellar solutions are composed of three basic components: hydrocarbon, surfactant, and water. Almost any hydrocarbon, pure or unrefined, can be used. For example, liquified petroleum gas (LPG), pentane, or crude can be utilized. A wide variety of cationic, anionic, and nonionic surfactants are effective [35 - 42]. Water can be distilled, fresh, or briny. Actually, the use of brine constitutes a fourth component in the fluids-electrolytes of all kinds allow

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additional freedom in slug composition so that certain desirable properties can be obtained. A fifth component often used in micellar solutions is cosurfactant such as an alcohol, aldehyde, ketone, or other semipolar organic substance [43]. They can be either oil- or water-soluble.

Microemulsions are isotropic, clear, or translucent, thermodynamically stable oil/water/surfactant dispersions. Microemulsions can be considered as swollen micelles. However, all micellar solutions cannot be swollen to the extent of microemulsions unless the specific structural requirements and conditions are satisfied. Shah et al. classified various dispersed systems as shown in figure 1 [44]. Solutions of inorganic salts such as sodium chloride or compounds such as sugar form true molecular solutions in which the dispersed phase (solute) has dimensions up to 10 $\overset{o}{A}$. The dimensions of the dispersed phase in micellar solutions may range from 20 to 100 $\overset{o}{A}$ depending upon the length of the surfactant molecule and the aggregation number in micelles. The dispersed phase in microemulsions may have a diameter in the range of 100-1000 $\overset{o}{A}$. In colloidal dispersions of polymers, polysaccharides, or polymer latex, the dimensions of dispersed phase can be in the range of 0.1 to 1 micron. In macroemulsions, the dimension of the dispersed phase may be in the range of 1 to 10 microns.

Ternary Phase Diagram

The phase behavior of a microemulsion containing ternary system was characterized by Winsor [14] who defined three types of ternary diagrams as shown in Figure 2. The Type I diagram has a two-phase region with tie line slopes such that any system, the composition of which lays in the two-phase region, will separate into an aqueous phase rich in amphiphilic compound and containing some solubilized oil, and a hydrocarbon phase consisting of almost pure oil. In this case,

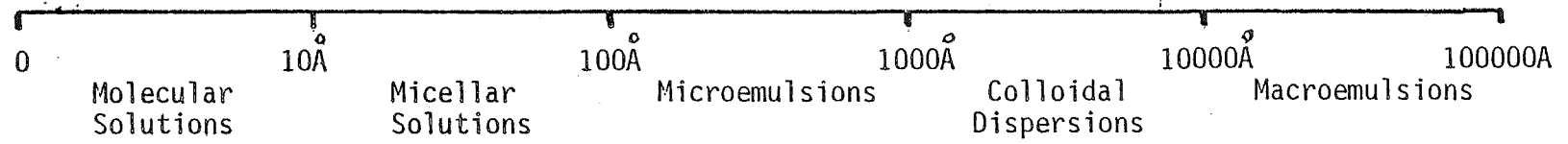| 0	10Å	100Å	1000Å	10000Å	100000A
Molecular Solutions	Micellar Solutions	Microemulsions	Colloidal Dispersions	Macroemulsions	

FIGURE 1. A SCHEMATIC PRESENTATION OF DIMENSIONS OF DISPERSED PHASE IN VARIOUS SYSTEMS

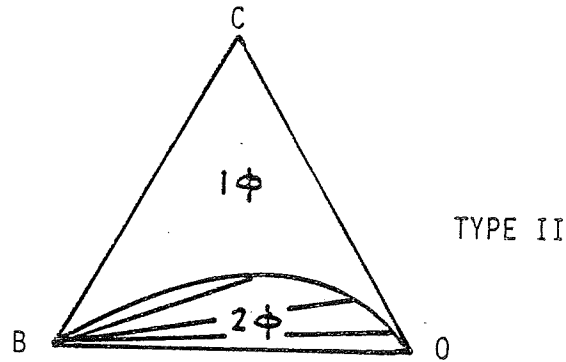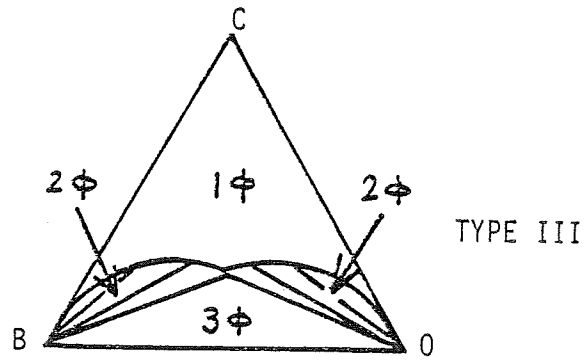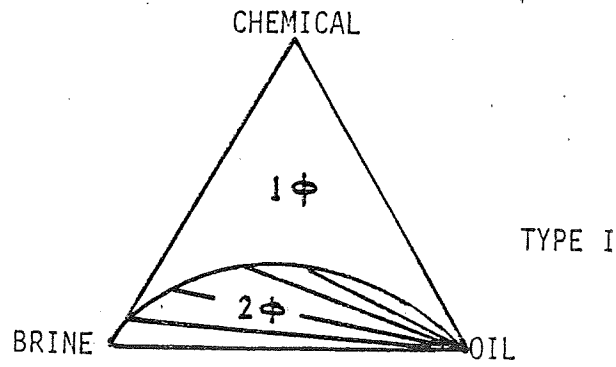FIGURE 2. WINSOR TERNARY DIAGRAM TYPES

microemulsion is in the equilibrium with excess oil. Type I was called Type II (-) by Nelson and Pope [15].

The Type II diagram has a two-phase region like Type I, but this time the slope of the tie lines is such that any system, the composition of which lays in the two-phase region, will separate into an oil phase rich in amphiphilic compound and containing some solubilized water, and an aqueous phase consisting of almost pure water. In this case, microemulsion is in equilibrium with excess water. Type II has also been termed Type II (+) [15].

Type III diagram contains a single phase region, two two-phase regions and a three-phase region. In the two-phase node on the left of the Type III diagram, like Winsor's Type II, the microemulsion is in equilibrium with excess water. But, the microemulsions usually are more highly swollen with brine in a Type III phase environment than in a Winsor's Type II phase environment. In the other two-phase node on the right of the Type III diagram, like Winsor's Type I, the microemulsion is in equilibrium with excess oil. The microemulsions usually are more highly swollen with oil in a Type III phase environment than in a Winsor's Type I phase environment [15]. In the three-phase region, microemulsion is in equilibrium with oil and water.

Healy et al. [16-20] and others [11, 12, 15] have shown that any change in a surfactant-brine-oil system which favors the solubility of the surfactant in the oil relative to the brine causes the phase environment type to shift in the II(-) to III to II(+) direction. The path a-d-e-f-c in Figure 3 illustrates this change in phase environment type. No a-b-c path was observed. As salinity increased, phase type goes from II (-), through III, to II(+). Temperature and water-oil ratio also affect the change of phase type.
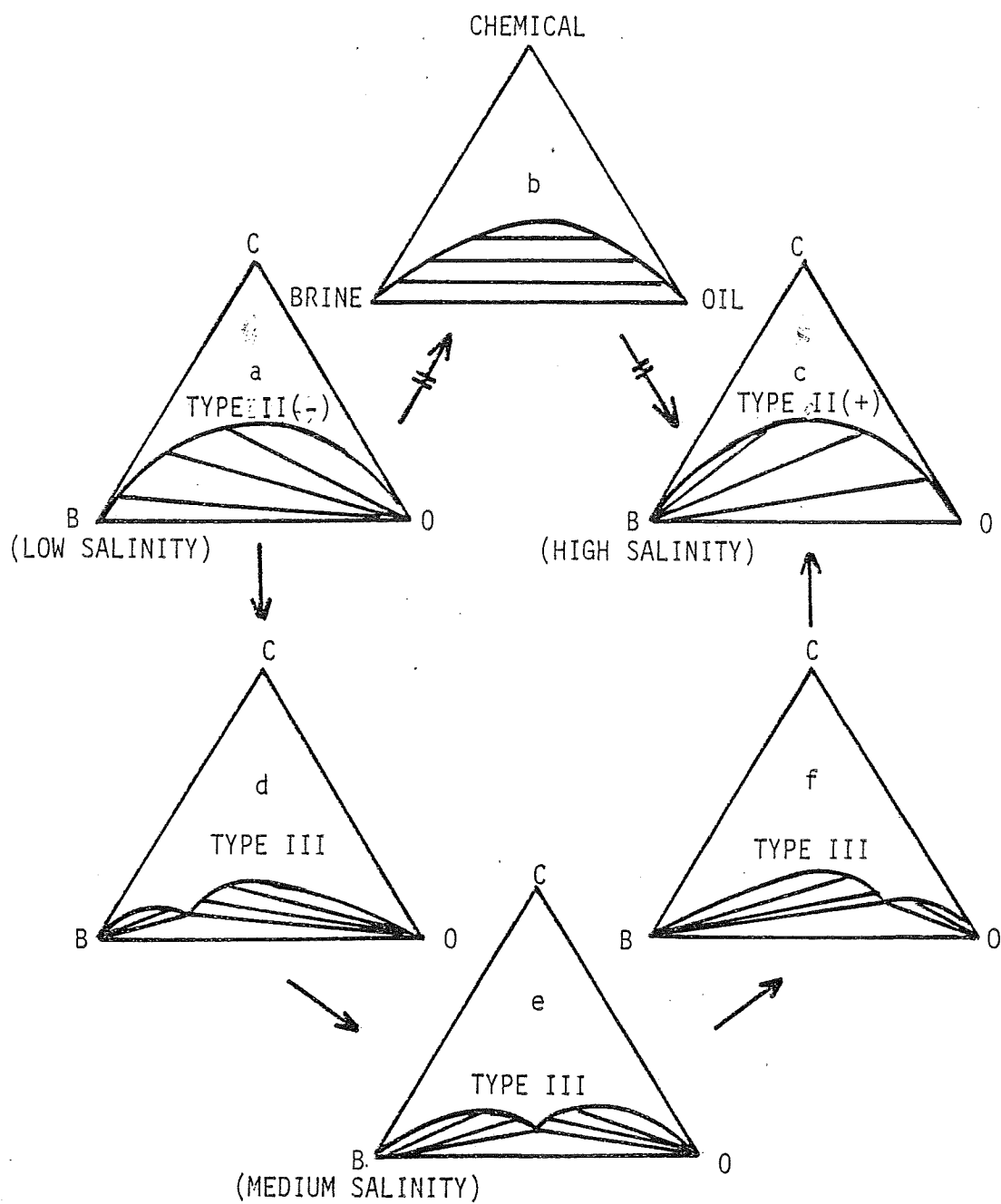
FIGURE 3. GENERALIZED PHASE DIAGRAMS ILLUSTRATING EFFECT OF CHANGING BRINE SALINITY

Factors Affecting the Phase Behavior

The phase behavior of amphiphilic compounds is affected by the types and concentrations of surfactant, alcohol, oil, electrolyte, and by temperature.

Nonionic surfactants and ionic surfactants are used in phase behavior studies. They play different roles.

The nonionic surfactants are not so sensitive to salt as ionic surfactants. Hydrogen bonding makes nonionic surfactants water-soluble. Increasing temperature will drop the hydrogen bonding strength and decrease the water solubility of the nonionic surfactant. Type II(-) can be changed to II(+), through Type III, if temperature or salinity is increased [21].

The anionic surfactants used in micellar solutions usually are petroleum sulfonates manufactured from hydrocarbons ranging from liquid petroleum gas to crude oil. Different from the nonionic surfactants, anionic surfactants are dissolved in water by electrostatic strength. Therefore, salinity is an important factor to affect the anionic surfactant's water solubility. Increasing the salinity will decrease the water solubility of surfactant. The optimum salinity can be defined as the geometric average of the range of salinity for which the system exhibits three phases [11]. An analytical expression for this optimum salinity for anionic surfactants was established by Salager [11, 12]:

$$\ln S^* = K(ACN) + f(A) - \sigma + a_T(T-25) + \frac{0.05}{WOR} - \frac{0.05}{4} \quad \text{EQ(1)}$$

where:

S^* = optimum salinity in gram of NaCl per deciliter aqueous phase

K = 0.16 for alkyl aryl sulfonates/alkanes/NaCl

ACN = oil alkane carbon number

f(A) = alcohol effect

σ = surfactant characteristic parameter

= EPACNUS x K

a_T = temperature coefficiency

= 10^{-2}

T = temperature $^\circ$C (5-50°C)

WOR = water-oil ratio (9 > WOR > 0.5)

CHAPTER III

POLYMER SOLUTIONS

Certain high molecular weight polymers exhibit large increases in solution viscosity at concentrations as low as a few hundred parts per million. This property has led to extensive use of polymers to control the movement of fluids in porous media. Oil displacement resulting from the addition of such water-soluble polymers to flood water has been investigated for about 20 years. Laboratory studies easily show that, under proper conditions, polymer flooding, or the injection of a polymer solution behind a chemical slug (which may also contain polymer), will significantly increase oil recovery. This polymer can provide mobility control and reduce channeling [45 - 61]. In order to obtain mobility control in a flood, it is necessary for the displacing fluid to have a mobility less than or equal to the mobility of the displaced fluid. This mobility relationship can be expressed as following for the case of water and oil

$$M = \frac{\lambda_\omega}{\lambda_o} = \frac{K_\omega / \mu_\omega}{K_o / \mu_o}$$

where:

M = mobility ratio of displacing fluid to oil

λ_ω = mobility of water phase

λ_o = mobility of oil phase

K_ω = permeability of water phase

K_o = permeability of oil phase

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$$\mu_\omega \quad = \quad \text{viscosity of water phase}$$

$$\mu_o \quad = \quad \text{viscosity of oil phase}$$

The addition of the selected polymers to water increases the viscosity. In some cases the polymers reduce the permeability of reservoir rock to the water phase.

Ionic and Nonionic Polymers

Several kinds of water-soluble polymers are used in polymer flooding, including polyacrylamide (PAM), hydrolyzed polyacrylamide (HPAM), xanthan gum, polyethylene oxide (PEO), hydroxyethylcellulose (HEC), and various copolymers of acrylamide.

Xanflood, a commercial xanthan gum product of Kelco Co., is a high molecular weight polysaccharide produced in a pure culture fermentation process by the microorganism xanthomonas campestris [62-72]. The molecular weight of the polymer is probably on the order of 2 million but has been reported to as high as 13-50 million [73]. These differences are probably due to association phenomena between polymer chains. Three different monosaccharides are found in xanflood: mannose, glucose, and glucuronic acid (as a mixed potassium, sodium, and calcium salt).

Calgon 800 is a high molecular weight polyacrylamide. Pushjer 700, a commercial product of Dow Chemical Co., is a hydrolyzed polyacrylamide with molecular weight of one to ten million [45, 50, 60].

Polyox water-soluble resins are nonionic polymers of ethylene oxide, manufactured by Union Carbide Corp.. The chemical structure is:

$$-CH_2-CH_2-O-CH_2-CH_2-O-$$
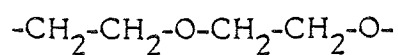
The molecular weight ranges from several hundred thousand to 5 million and

above. For example, Coagulant, WSR-301, and WSR N-3000 have molecular weights of approximately 5 million, 4 million, and 400,000, respectively [53, 74, 75]. Unlike the ionic polymers, Polyox resins are not only soluble in water, but also soluble in a wide variety of organic solvents at various temperatures. Typical organic solvents include most halogenated hydrocarbons as well as various ketones, alcohols, aromatic hydrocarbons, and esters. Polyox resins are generally not soluble in aliphatic hydrocarbon solvents, glycols, diols, and aliphatic ethers.

Natrosol 250 HHR is one of a series of commercial polymers sold by Hercules of the HEC type (a hydroxyethyl ether of cellulose). Each anhydroglucose unit in the cellulose molecule has three reactive hydroxyl groups. By treating cellulose with sodium hydroxide and reacting with ethylene oxide, hydroxyethyl groups are introduced to yield a hydroxyethyl ether. The number that is substituted in any reaction is known as the "degree of substitution". In reacting ethylene oxide with cellulose to form the hydroxyethyl ether of cellulose, solubility in water is achieved as the degree of substitution is increased. Natrosol 250, which has optimum solubility in water, has degree of substitution of 2.5. The viscosity of a Natrosol solution is affected by Natrosol concentration, shear rate, temperature, and pH value. Natrosol is somewhat more resistant to biological attack than are some other water-soluble gums and polymeric materials [76, 77].

A comparision in viscosity of 1000 ppm of xanflood, Pusher 700, and Natrosol 250 HHR is shown in Figure 4. Electrolyte concentration is 1% NaCl, and temperature is 24°C.

Rheology of Polymer Solutions

At very low shear rate, polymer solutions behave like Newtonian fluids. As the shear rate increases, the viscosity of the polymer solutions
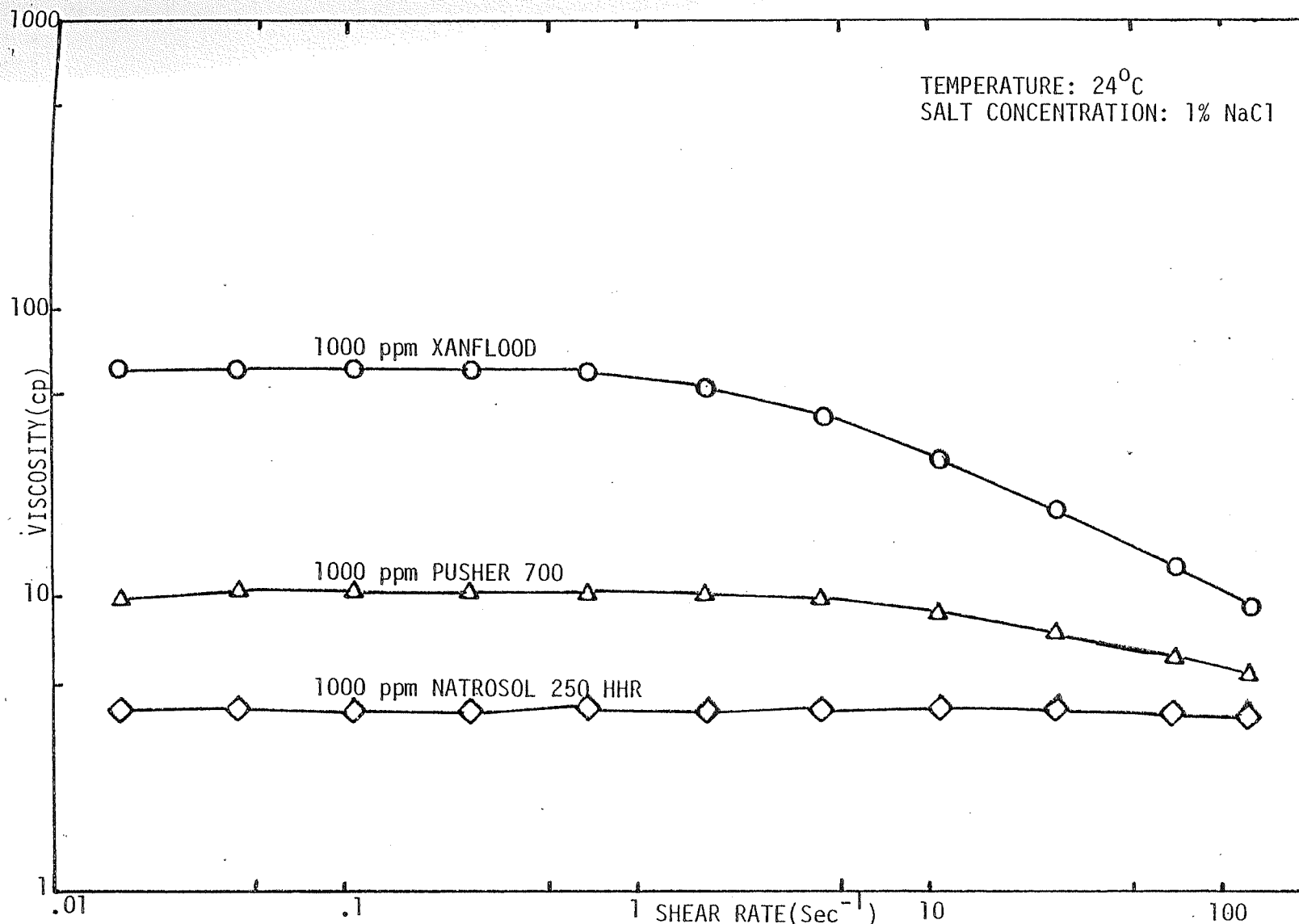
FIGURE 4. VISCOSITY COMPARISION OF XANFLOOD, PUSHER 700, AND NATROSOL 250 HHR

decreases. A higher concentration of polymer gives a higher viscosity. The stability of the polymer solution is of major importance since the polymers must function for long periods of time, frequently at elevated temperatures. Mechanical (shear), chemical, and thermal stability should be considred. Xanflood solution is highly tolerant to electrolyte [41, 64], and does not shear degrade under reservoir conditions [64]. When HPAM is dissolved in a brine water, repulsion between the carboxyl groups is reduced by the attraction of the cations present in the brine to the anionic charge on the carboxyl group. This causes the molecule to be compressed from its enlarged state and results in low viscosity. A highly viscous, highly pseudoplastic solution in deionized water becomes a relatively low viscosity, almost Newtonian solution in brine. The higher the molecular weight of the Polyox resins, the higher the viscosity. Increasing temperature will decrease the viscosity.

CHAPTER IV

MICELLAR/POLYMER SOLUTIONS

Micellar/polymer flooding is an improved oil recovery method employing multiple banks. Typically, a brine preflush conditions the reservoir, micellar fluid displaces the formation oil and water, a polymer-thickened mobility buffer bank displaces the micellar fluid, and finally, drive water follows the mobility buffer bank. Complex interactions occur between the injected fluid banks; between the crude oil, formation water, and injected fluids; and between the injected fluids and the rock surface. The micellar bank, which is of primary importance, must have: low interfacial tension with oil and water, low sulfonate loss, adequate viscosity, and compatibility with all contacted fluids.

Sulfonate loss is the major factor which determines the optimum volume of the expensive micellar fluid needed to displace the tertiary oil. Sulfonate adsorption by the rock surface usually is assumed to be the only source of loss. Extensive oil displacement tests in consolidated cores show that many micellar fluids are not compatible with the polymer from the mobility buffer bank[2]. When polymer invades or dilutes the micellar fluid, multiple phases often develop (sulfonate-polymer incompatibility). If the interfacial tension between these sulfonate-containing phases is high, phase trapping may occur in the porous medium. This sulfonate loss causes reduced oil displacement effectiveness and increased chemical requirements.

CHAPTER V

EXPERIMENTAL PROCEDURES

Oil Free Systems

Surfactant, polymers, alcohols, and brine are used in this study. Surfactants (basis "as is" unless otherwise stated) are dissolved in distilled water with alcohol and polymer. For example, to make a solution containing 2% wt of TRS 10-80, 2000 ppm of Pusher 700, and 8% wt of iso-butanol in distilled water, 2 grams of TRS 10-80, 50 grams of concentrated (4000 ppm) Pusher 700 solution, and 8 grams of iso-butanol are mixed with 40 grams of distilled water. The surfactant is dissolved in the distilled water first, then alcohol added, and finally the concentrated polymer solution. This solution is then used to mix with brine. The salinity of the brine is varied within a certain range depending on the optimum salinity of that system. This can be estimated by using Eq(1).

Polymer solutions are made in different ways depending upon the polymers. HPAM solutions are made by adding a certain amount (by weight) of polymer to a certain amount (by weight) of distilled water with magnetic stirring. The rate of addition should be slow enough for the particles to separate in water without lump formation, but not so slow that the solution thickens appreciably before all the solid is added. From eight to twenty four hours are required for complete hydration.

A general mixing procedure for xanthan gum is as following:

1. Add distilled water to a Waring blender. Determine amount such that total weight of final solution is 500 grams.

2. Blend in electrolyte by weight.

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3. Blend in enzyme by weight.

4. If oxygen scavengers and anti-oxidants are to be used, add them at this point. Filter through 0.45 Millipore if final solution is to be used in filtration study.

5. Add gum, at low speed blender setting. Then increase blender speed and mix for 10 minutes. Dry gum in dessicator at low temperature (25°-35°C) before using.

6. Transfer to flask and heat in water bath for 30 minutes after reaching 50°C. Swirl occasionally.

7. Add biocide.

8. Dilute desired amount to desired final gum concentration. Save balance in closed container for any additional experiments. Dilute by stirring for a few minutes with magnetic stirrer on "high" speed, or 1 or 2 minutes with blender on "low" speed (to avoid air entrainment).

9. Filter, if necessary.

Enzyme is used [55] to metabolize the shell of xanthomonas campestris. Heating increases the metabolization rate. Since xanthan gum is a biodegradable, biocide is needed to preserve the polymer solution.

An example of making a solution of 10,000 ppm of xanflood is shown in the following:

1. Put 494.28 grams of distilled water in blender.

2. Add 0.5 grams of sodium bicarbonate in the distilled water.

3. Mix 0.02 grams of alcalase P1.5 in the water with low stirring speed.

4. Add 5 grams of dry xanflood slowly to the solution with stirring.

5. Switch to high speed of blending for 10 minutes.

6. Transfer this polymer solution to a volumetric flask, and leave it in 50°C water bath for 30 minutes with occasional stirring.

7. Add 0.6 grams of Dowicide B in the polymer solution and stir by magnetic stirrer.

This xanflood solution, thus, contains following:

Xanflood	=	10,000 ppm
NaHCO$_3$	=	1,000 ppm
Dowicide B	=	1,200 ppm
Alcalase	=	40 ppm

Brine solutions containing surfactant and alcohol were prepared at various NaCl concentrations. One set of solutions contained polymer and the other did not. The samples were observed until they appeared to equilibrate at room temperature (about 24°C). Typically, the polymer-free samples were all single phase, but in some cases a solid phase or a second liquid phase formed. The objective was to see when the polymer caused the formation of an additional phase. Thus, again typically, both the samples with and without polymer were single phase at low salinity, and the polymer-free samples remained single phase at the higher salinities, while the ones containing polymer turned two phase at some critical salinity. Low and high salinity are strictly relative terms. The more water soluble the surfactant, the higher the salinity before the solution becomes turbid. The turbid samples are the ones which typically turn two phase in the presence of polymer. Of course, for any given ACN, higher salinity is also required to produce low interfacial tension as the water solubility of the

surfactant increases.

The phases volumes were then read for those samples which were not single phase. The volume fraction of the surfactant rich phase was then plotted versus salinity. When surfactant, polymer, or alcohol concentration, or temperature, were varied, a family of such curves were plotted. Also, various crossplots were made in such cases.

An example system was 1% TRS 10-80, 4% sec-butanol, and 1000 ppm xanflood in brines of 0 to 2% NaCl, at intervals 0.2% NaCl. Observations were made at both 24°C and 75°C.

Systems with Oil

Two methods were used in this study. One was to fix the oil, alcohol, and surfactant concentrations and vary salinity. The other was to fix the salinity and vary the total amount of surfactant and alcohol at a fixed ratio and also vary the oil concentration. These data were then represented on a ternary diagram. The pseudo-components chosen were brine, surfactant plus alcohol, and oil. Sets with and without polymer in the brine were made. These two sets, with and without polymer in brine, are then compared in order to find how polymer affected the phase behavior. The procedure for preparing the ternary diagram is as following:

1. Determine the optimum salinity (S*) by using Eq(1) for a fixed system (i.e. ACN, temperature, surfactant, and alcohol).

2. Make a brine and a brine/polymer solution with salinity S*. Other systems are prepared at values centered around salinity S*.

3. Select a pure hydrocarbon, or prepare a hydrocarbon mixture.

4. Make a surfactant/alcohol solution.

5. Mix the solutions prepared in steps #2, #3, and #4 by volume for selected data points.

6. After two days, read the phase volumes for each mixture. Volume fractions of the phases are related to distance ratio on the phase diagrams as shown in Figure 5. At lower salinity, Type II(-) diagram is obtained as shown on the top of Figure 5. The tie line is the line through the overall composition point, with one end at the corner of oil, the other end, designated as ⊢, at the microemulsion composition. The ratio of a/b is the ratio of the volumes of oil and microemulsion for the experimental sample. All of the ⊢ points can be connected to form a smooth curve called the binodal curve. For the Type II(+) diagram, the tie line has one end at the brine corner instead at the oil corner, because d/c is the volume ratio of brine to microemulsion, not oil to microemulsion, when salinity is high enough and II(+) is formed. In the Type III case, the same treatment is done in both of the two phase nodes. The one on the right side is like II(-), and the one on the left side is like II(+). For the three phase region, the composition of the invarient point, marked as ◇ , can be calculated by the following equations, assuming no surfactant in oil and brine phases:

$$C_{33} = C_3 \left(V/V_{me} \right)$$
$$C_{23} = \left(C_2 V - V_o \right)/ V_{me}$$
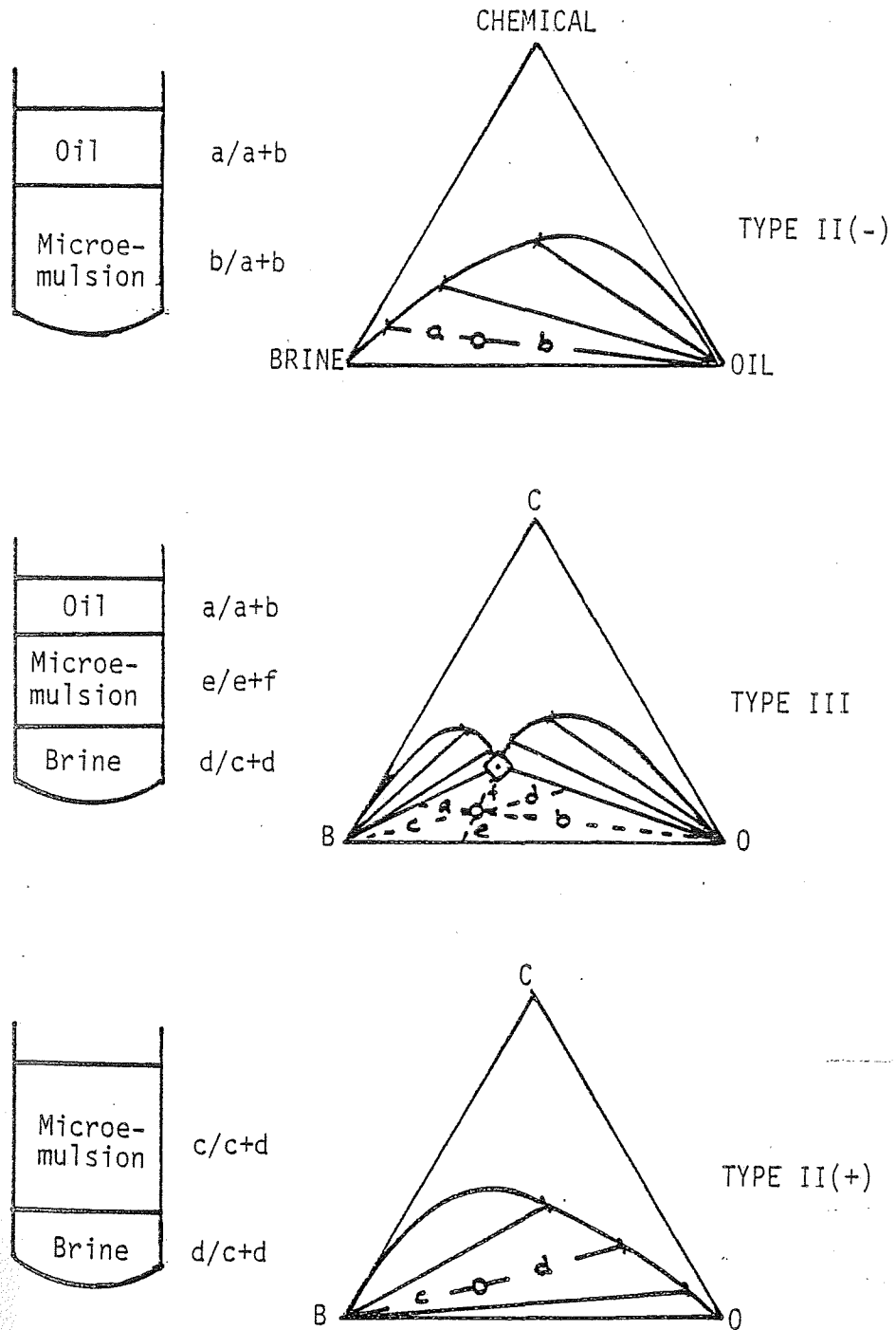$$C_{13} = 1 - C_{23} - C_{33}$$

FIGURE 5. TERNARY REPRESENTATION OF PHASE RELATIONSHIPS

where, C_{13}, C_{23}, C_{33} is the invarient compostion, C_1, C_2, C_3 is the overall composition, and V, V_o, V_{me} are the volumes of the total sample, the oil phase, and microemulsion phase.

Example: Ternary Diagrams of TRS 10-80/Sec-butanol/N-octane at 75°C

1. Determine the salinity of the brine which makes II(-), III, or II(+) type, when the oil is n-octane (ACN=8).

   Using Eq(1), with WOR=4, TRS 10-80= 1% wt, sec-butanol=3%,

   $$K= 0.16, a_T = 0.01, T= 75^oC, \sigma = 0.96, f(A) = -0.16,$$

   In $S* = 0.16(8) + (-0.16) -0.96 + 0.01(75-25) = 0.66$

   $$S* = 1.93$$

   The optimum salinity is 1.93% NaCl. If the salinity fo the brine is low enough, #3 will be two phases, oil on the top, and microemulsion on the bottom as in Figure 6. All the surfactant is assumed in the microemulsion phase, not in the oil phase. Trial tests showed that salinities which make Type II(-), III, and II(+) are 1.125%, 1.69%, and 2.25%, respectively. Therefore, the salinity of the brine was set at 1.125%, 1.69%, and 2.25% NaCl.

2. Mix 63 grams of TRS 10-80 with 37 ml of sec-butanol to make the surfactant/alcohol solution used as the chemical component.

3. A number of samples were made. For example, #3 of Figure 6 was made of 4.5 ml of 1.125% NaCl brine, 5.0 ml of n-octane, and 0.5 ml of TRS 10-80/sec-butanol solution in a total volume of 10.0 ml. All fo these samples were mixed well and saved in the oven at 75°C.

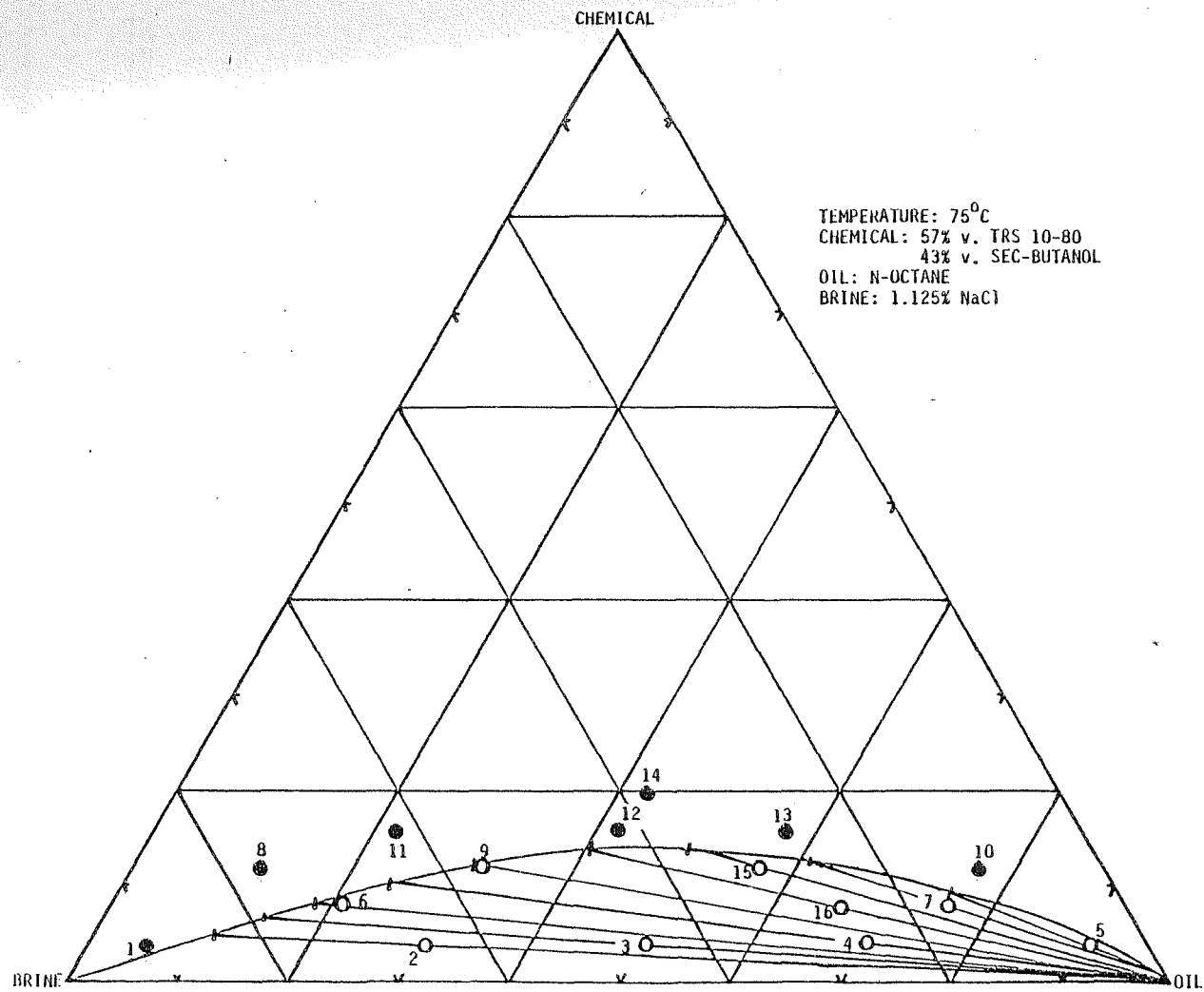4. Volume fraction of these samples are used to determine the

FIGURE 6. TERNARY DIAGRAM OF TRS 10-80

binodal curve. For example, the volume fraction of #3 in Figure 6 is 0.42/0.58 of oil/microemulsion, or volume of top phase to bottom phase. Thus, the distance ratio of a/b in the tie line across the point #3 is 0.42/0.58. The composition of the microemulsion is, then, expressed as $\leftarrow$.

5. When 1.69% NaCl was used a Type III diagram was obtained. The composition of the invarient point can be calculated by the equations shown before. Each three phase sample gives one invarient point. The invarient points do not match together. They spread out because of the non-ideal pseudo-components. Two two-phase nodes also appeared in the Type III diagram. But in this TRS 10-80 system, no samples with oil on the top and microemulsion on the bottom were found. All the two phases samples were microemulsion on the top and brine on the bottom. A dotted curve was drawn to bound the two phase region of the right node (see Figure 7).

6. In the Type II(+) case, 2.25% NaCl was used. The binodal curve was plotted by the same way as in the Type II(-) diagram (see Figure 8).

Ultraviolet Spectroscopy

In order to determine which phase contains a higher surfactant concentration in an oil-free surfactant-polymer system, Ultraviolet Spectroscopy can be used.

UV absorbance spectroscopy provides a simple and quick technique to measure or estimate the concentration of alkyl aryl sulfonates. All aromatic
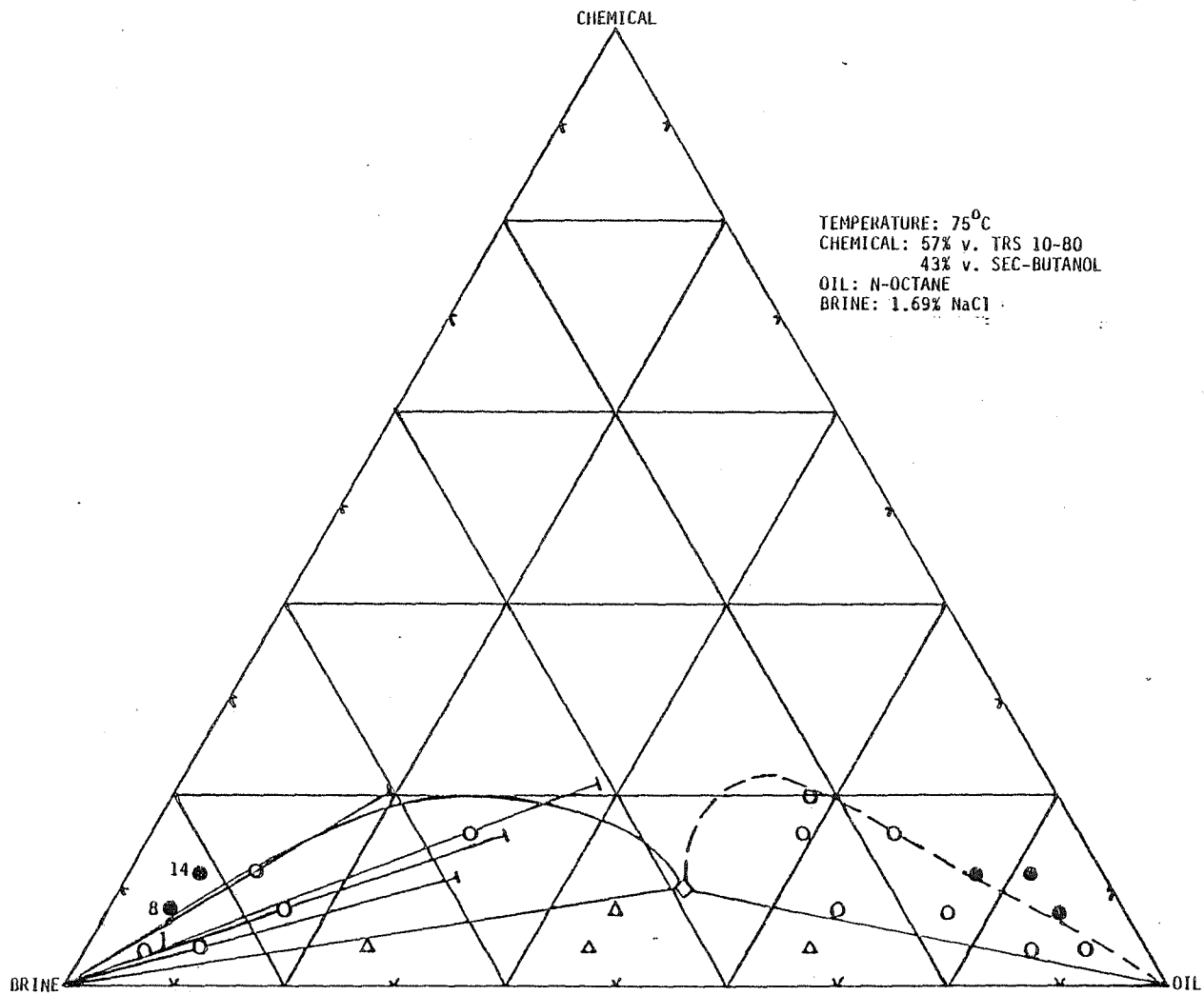
CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 57% v. TRS 10-80
43% v. SEC-BUTANOL
OIL: N-OCTANE
BRINE: 1.69% NaCl

BRINE

OIL

FIGURE 7. TERNARY DIAGRAM OF TRS 10-80

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 57% v. TRS 10-80
43% v. SEC-BUTANOL
OIL: N-OCTANE
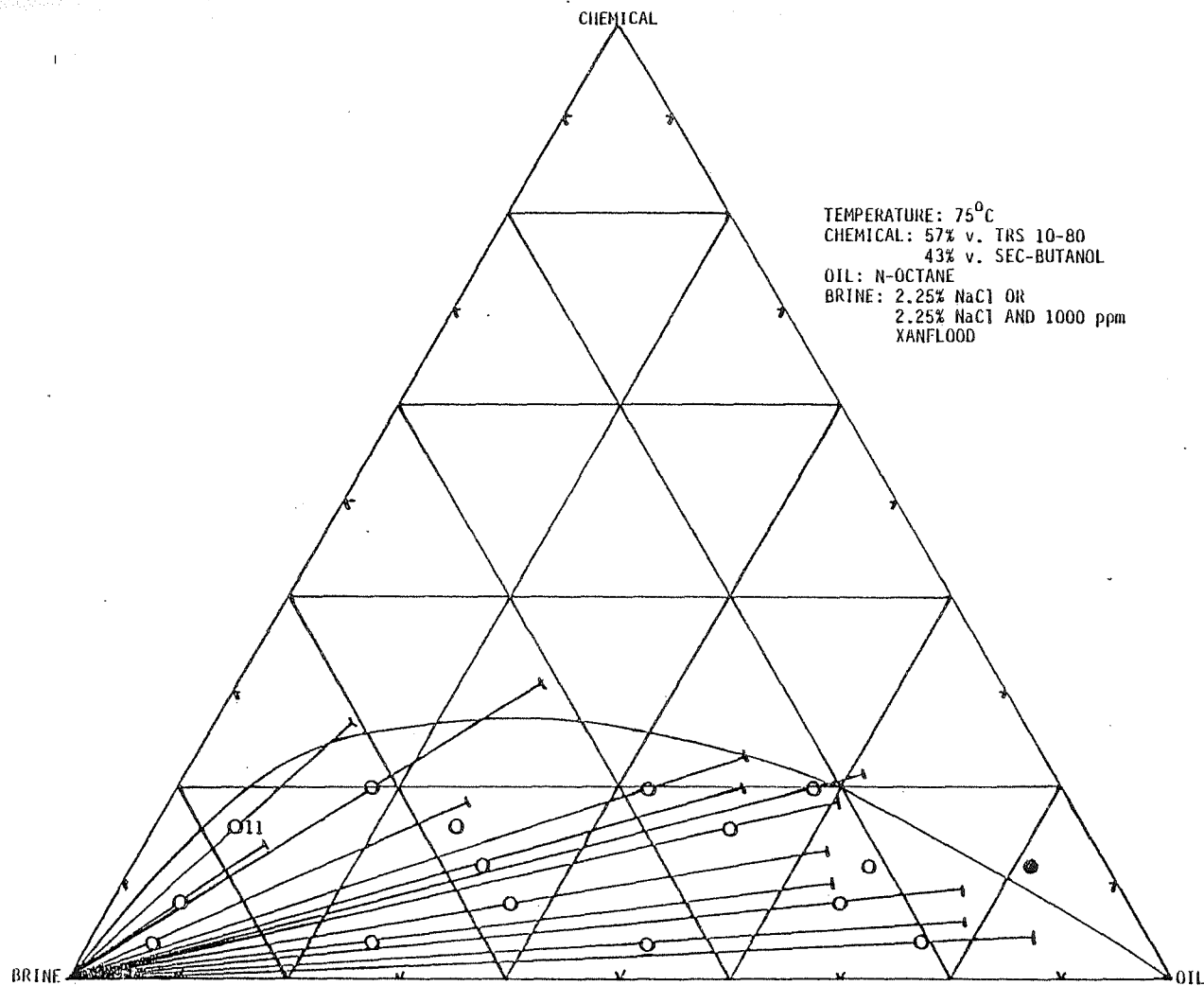BRINE: 2.25% NaCl OR
2.25% NaCl AND 1000 ppm
XANFLOOD

BRINE

OIL

FIGURE 8. TERNARY DIAGRAM OF TRS 10-80

compounds exhibit a strong absorbance peak near 220 nm and secondary peaks in the 260-280 nm range. By comparing the height of the peaks on two sulfonate-contained samples, a surfactant-rich phase can be identified. Figure 9 shows the UV spectra of 50 ppm TRS 10-80, 100 ppm xanflood, 0.15% wt sec-butanol, and 1% wt NaCl brine solutions.

Viscosity Measurement

The viscosity of polymer solutions or microemulsions were measured by both a Brookfield viscometer and a Contraves Low-shear viscometer, LS-30. Only a very small amount of sample (1 ml) is necessary for the LS-30.

The operating procedure used with the Brookfield viscometer was as follows:

1. Attach the U.L. Adapter with 20 ml of sample to the viscometer, and level the whole set.

2. Depress the clutch and turn on the viscometer's motor. Release the clutch and allow the dial to rotate until the pointer stabilizes at a fixed position on the dial. The time required for stabilization will depend on the speed at which the spindle rotates: at speed above 4 rpm this will be generally about 20-30 seconds, while at lower speeds it may take the time required for one revolution of the dial. It is possible to observe the pointer's position and stability at low speeds while the dial rotates but at higher speeds it will be necessary to depress the clutch and snap the motor switch to stop the instrument with the pointer in view.

3. Take the readings and convert to viscosity by multipling by the conversion factor. The product of the conversion factor and the
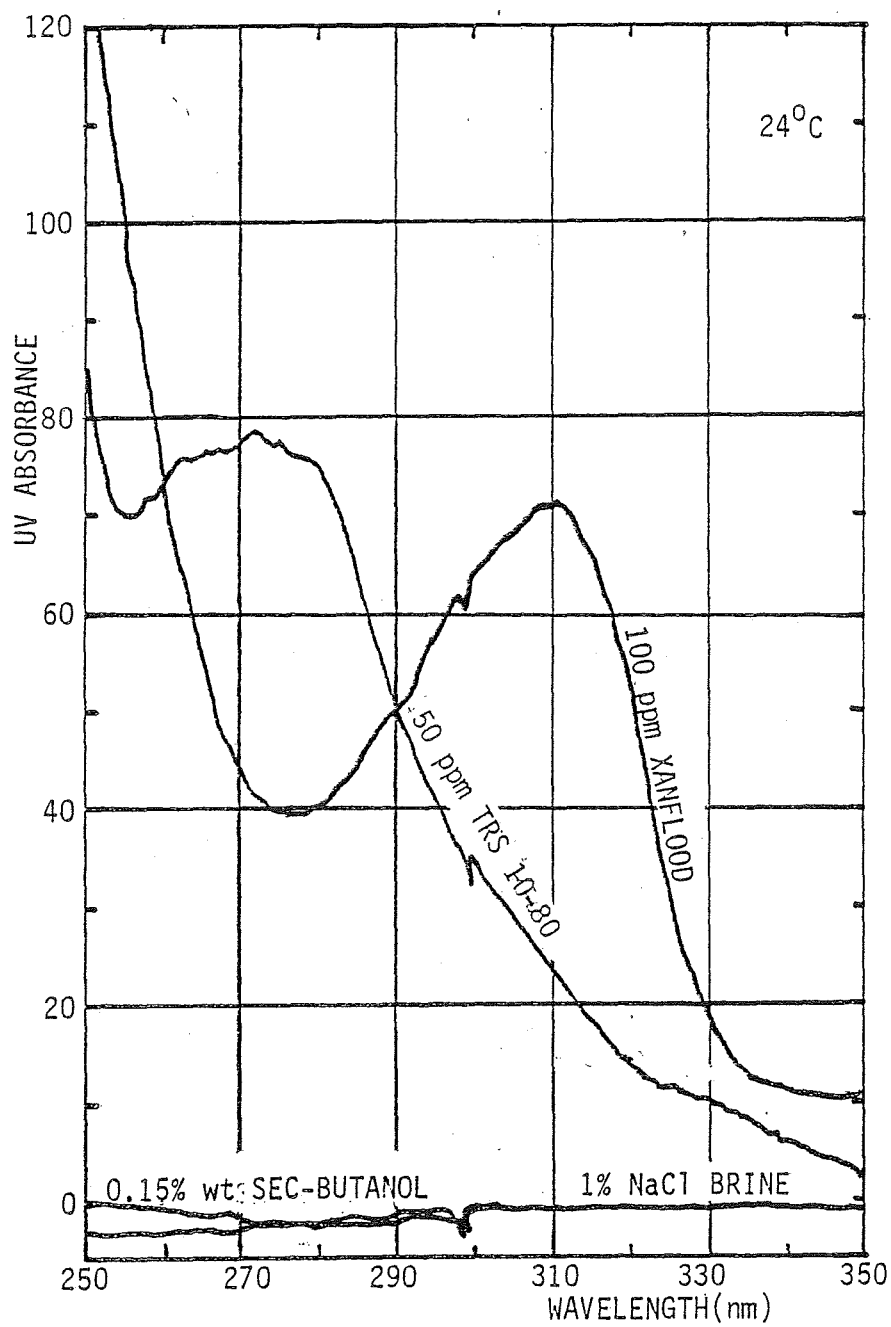
FIGURE 9. UV SPECTRA OF XANFLOOD, TRS 10-80, SEC-BUTANOL, AND 1% NaCl SOLUTIONS

rpm is 6. If a rpm of 60 is used, the conversion factor is 0.1.

The Low-shear viscometer, LS-30, has a broader range of shear rate ($0.01747-128.5$ sec^{-1}) than the Brookfield ($0.37-73.5$ sec^{-1}) and is about 1000 times more sensitive, so very low shear stresses can be measured. The operating procedure used was as follows:

1. Put 1 ml of the sample in the bowl. Insert the spindle into the sample avoiding any formation of bubbles. Make sure the spindle is in the middle of the bowl. To keep away the wind, a shielding is installed around the sample.

2. Turn on the main power and the motor.

3. Adjust the zero point by the zero adjustment screw, while the speed stays at zero, range stays from 5 to 1, and dampling sets at 1.

4. Take readings for each speed starting from lower to higher. The maximum number of the digital reading is 199. As soon as the reading becomes over scale, a higher range should be used.

5. Using the factor in the manual, the viscosity is the product of the reading and the conversion factor.

Experimental results for 1000 ppm of xanflood solution in 1% NaCl at $24^{\circ}C$ are shown in Figure 10. The solid curve was measured by the LS-30 and the dotted line by the Brookfield. The agreement is good because the shear stress for the Brookfield samples was relatively high even at low shear rate due to the high viscosity of the sample.
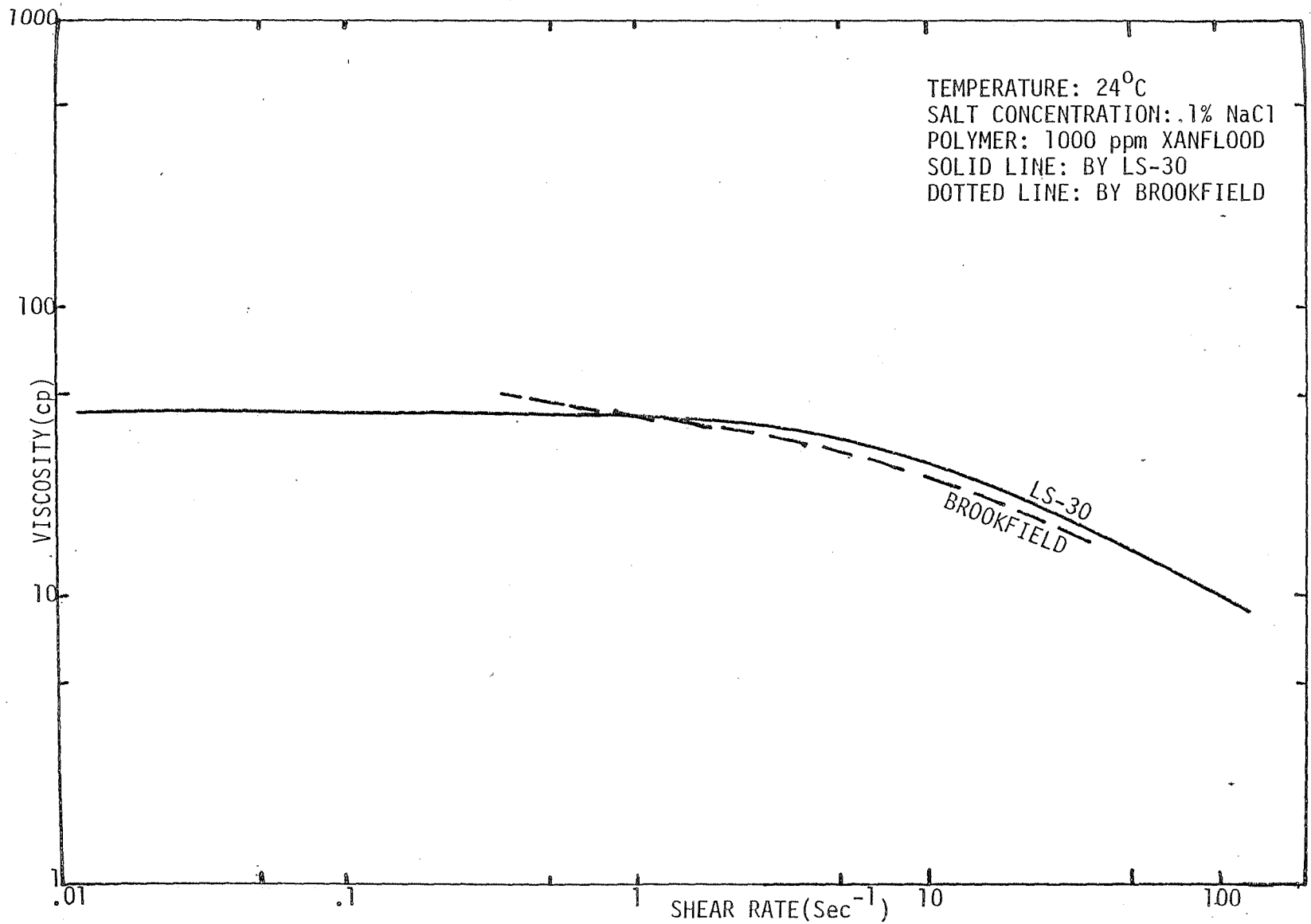
TEMPERATURE: 24°C
SALT CONCENTRATION: .1% NaCl
POLYMER: 1000 ppm XANFLOOD
SOLID LINE: BY LS-30
DOTTED LINE: BY BROOKFIELD

FIGURE 10. VISCOSITY COMPARISION MEASURED BY LS-30 AND BROOKFIELD VISCOMETERS

CHAPTER VI

EXPERIMENTAL RESULTS

Table 1 and Table 2 list the surfactants and polymers used in the study. Table 3 shows the combinations of surfactants and polymers studied. Experimental results are expressed two ways: the ternary diagram system and the phase volume fraction system. Some viscosity data of polymer solutions and microemulsions are also included.

In the ternary diagram, three pseudo components, surfactant/alcohol, oil, and brine, are set on three corners. Chemical is on the top, which consists of surfactant (100% active basis) and alcohol. The right bottom corner is the oil component, a pure n-octane, or a mixture of n-octane and benzene. Brine is set on the left bottom corner. It may be a distilled water or NaCl brine. Polymer is also included in the brine component, if used. For convenience, some symbols which were used in the ternary diagrams should be mentioned here. A single phase point is express as ⦁ . A double phase point is expressed as ⊙ . A triple phase point is expressed as △ , and a four phase point is ⊡ . ⊢ represents the calculated phase composition. A calculated invarient point is expressed as ◈ .

All results are organized and discussed below corresponding to the surfactant used.

Witco TRS 10-80

The chemical component is a mixture of TRS 10-80 and sec-butanol with an active volume ratio of 57/43. N-octane is used as the oil component. Phase type changes from Type II (-) to Type II (+),through Type III, as salinity increases from 1.125% NaCl to 2.25% NaCl in a polymer-free system. TRS 10-80

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TABLE 1

NAMES OF SURFACTANTS AND SURFACTANT COMPANIES

Company Name and Address	Chemical	Trade Name or Abbreviation
Witco Chemical Corporation 3230 Brookfield Houston, Texas 77045	Petroleum Sulfonate	TRS 10-80
Stepan Chemical Company Northfield, Illinois 60093	Petroleum Sulfonate	Petrostep 465
Alcolac Inc. 3440 Fairfield Rd. Baltimore, MD 21226	Dodecyl Benzene Sulfonate	Siponate DS-10
Exxon Chemical Company 8230 Stedman Street Houston, Texas 77029	Orthoxylene Sulfonate	$MEAC_{12}OXS$
Witco Chemical Corporation 3230 Brookfield Houston, Texas 77045	Ethoxylated Alcohol	TDA-100
GAF Corporation 140 West 51 Street New York, N.Y. 10020	Ethoxylated Phenol	Igepal CO-530 Igepal CO-610

TABLE 2

NAMES OF POLYMERS AND POLYMER COMPANIES

Company Name and Address	Chemical	Trade Name or Abbreviation
Kelco, Division of Merck & Co., Inc. 8355 Aero Drive San Diego, CA 92123	Xanthan Gum	Xanflood
Dowell, Division of Dow Chemical Co. 3634 Richmond Avenue Houston, Texas 77048	Hydrolyzed Polyacrylamide	Pusher 700
Calgon, Division of Merck & Co., Inc. P. O. Box 1346 Pittsburgh, PA 15230	Polyacrylamid	Calgon 800
Hercules Incorporated Redman Plaza-Suite 260 2540 Walnut Hill Lane Dallas, Texas 75229	Hydroxyethyl Cellulose (HEC)	Natrosol 250 HHR
Union Carbide Chemical Co. 2710 Stemmons Freeway Dallas, TX 75207	Polyethylene Oxide (PEO)	Polyox WSR N-3000 Polyox WSR 301 Polyox Coagulant

TABLE 3

COMBINATIONS OF POLYMERS AND SURFACTANTS STUDIED

	Kelco Xanflood	Dow Pusher 700	Union Carbide Polyox	Calgon PAM	Hercules Natrosol
Witco TRS 10-80	X	X	X	X	X
Alcolac Siponate DS-10	X				X
Exxon MEAC12OXS	X				
Stepan Petrostep 465	X				
Witco Ethoxylated Alcohols	X		X		
GAF Ethoxylated Phenols	X		X		

does not show a very ideal Type III plot or Type II(+) plot. But the Type II(-) diagram, shows a very nice binodal curve. In the Type II(-) case, many of the points changed to three phases when 1000 ppm of xanflood was included (see Figures 6 and 11). One oil phase and two aqueous phases were formed. Gel was observed as shown in Figure 11. All of these data were observed at higher temperature, 75°C. Working at a higher temperature increases the equilibrium rate. When 1000 ppm of xanflood is included in the brine component, phase diagrams of Type III and Type II(+) show relatively little change compared with those without polymer. In Figure 7, datum point #1 was changed from two phases to three phases when polymer was included. Also, point #8 became three phases and point #14 became four phases (see Figure 12). Gel was formed on #14. Other points were as the same as without polymer. In Figure 8, datum point #11 became three phases when 1000 ppm of xanflood was added.

Another TRS 10-80/sec-butanol test with a different type of oil was done. The oil component is a mixture of 90% vol. of n-octane and 10% vol. of benzene (see Figures 13 and 14).

Exxon MEAC12OXS

MEAC12OXS, monoethanolamine dodecyl orthoxylene sulfonate, was supplied by Exxon Company. 57% vol. of 100% active basis of MEAC12OXS and 43% vol. of sec-butanol were used as the chemical component in the test. The oil was n-octane. The ternary diagram shifts from II(-), to III, to II(+), as the salinity changes from 1.125%, to 2%, to 2.8% NaCl. Polymer did not affect Type III and Type II(+) phase diagrams (see Figure 17, 18). An additional phase was formed in some data points of the Type II(-) diagram (see Figure 15, 16). Gel formed in those points with low brine content or brine saturation at 75°C. Figure 19 shows
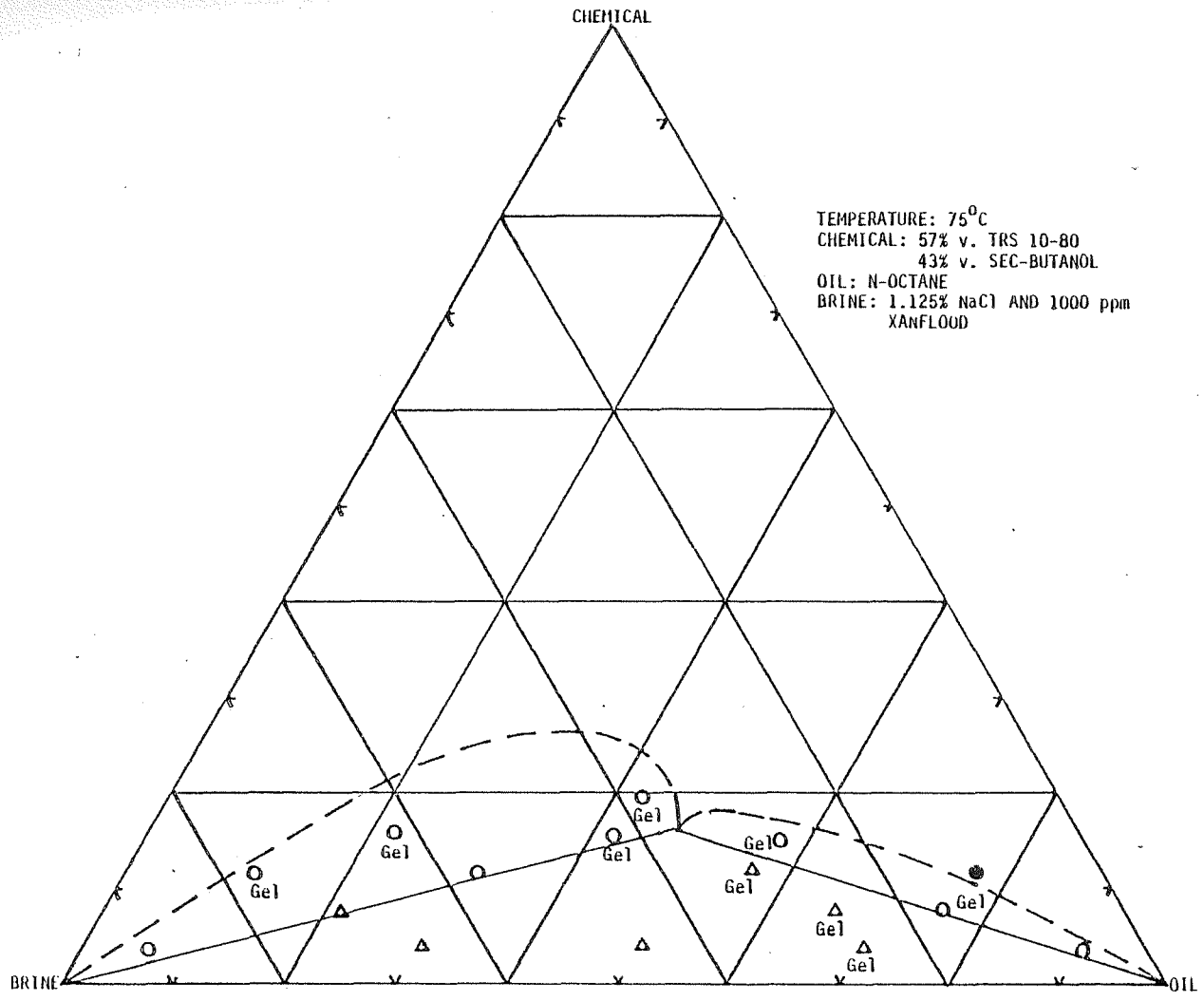
CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 57% v. TRS 10-80
         43% v. SEC-BUTANOL
OIL: N-OCTANE
BRINE: 1.125% NaCl AND 1000 ppm
       XANFLOOD

BRINE   OIL

FIGURE 11. TERNARY DIAGRAM OF TRS 10-80

41
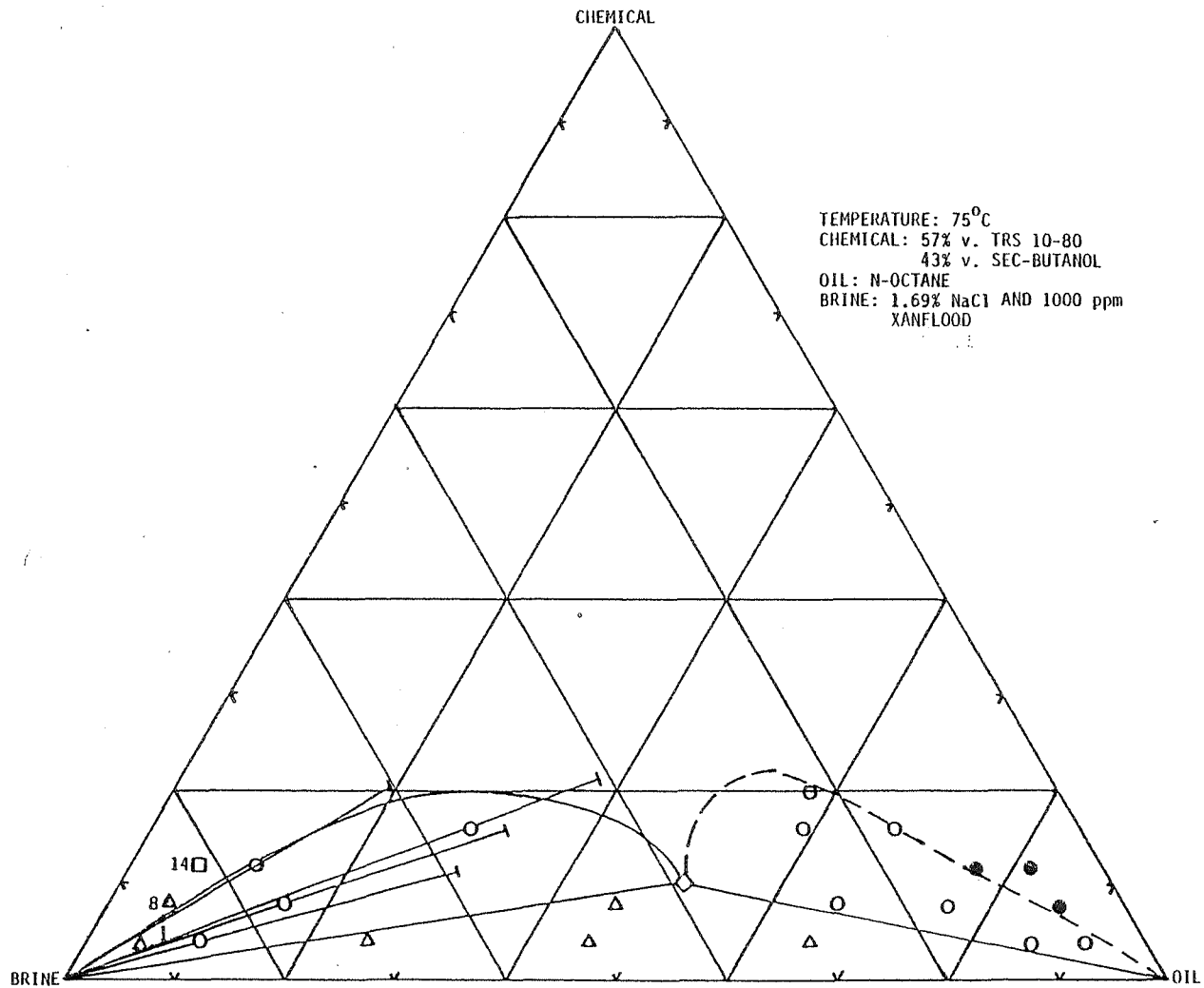
FIGURE 12. TERNARY DIAGRAM OF TRS 10-80 WITH XANFLOOD

TEMPERATURE: 75°C
CHEMICAL: 57% v. TRS 10-80
43% v. SEC-BUTANOL
OIL: N-OCTANE
BRINE: 1.69% NaCl AND 1000 ppm
XANFLOOD

CHEMICAL

BRINE

OIL

42

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 57% v. TRS 10-80
        43% v. SEC-BUTANOL
OIL: 90% N-OCTANE
     10% BENZENE
BRINE: 0.75% NaCl

BRINE

OIL
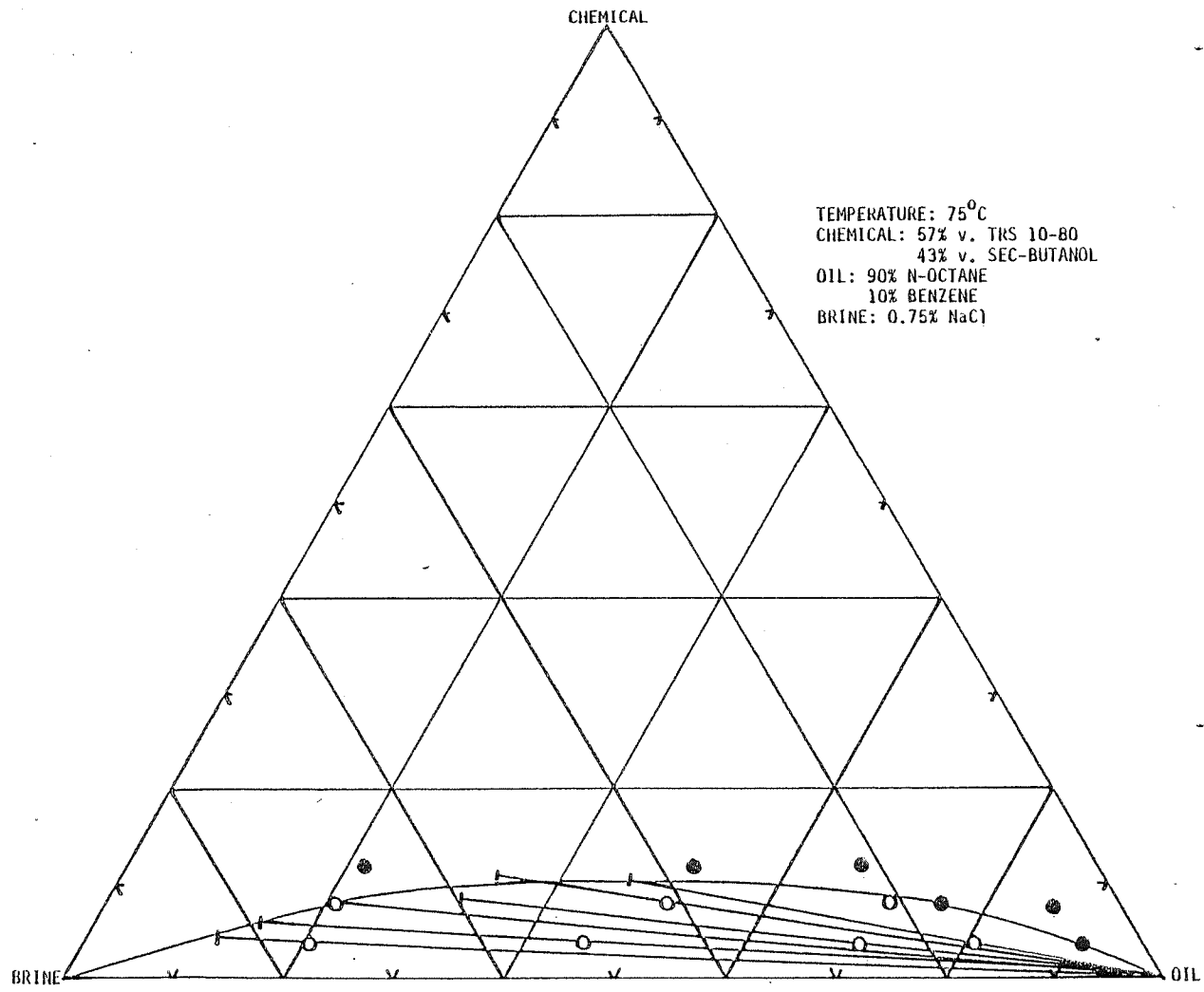
FIGURE 13. TERNARY DIAGRAM OF TRS 10-80

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 57% v. TRS 10-80
43% v. SEC-BUTANOL
OIL: 90% v. N-OCTANE
10% v. BENZENE
BRINE: 1.5% NaCl

$C_3/C_1=0.28(C_3/C_2)^{-0.78}$

BRINE

OIL
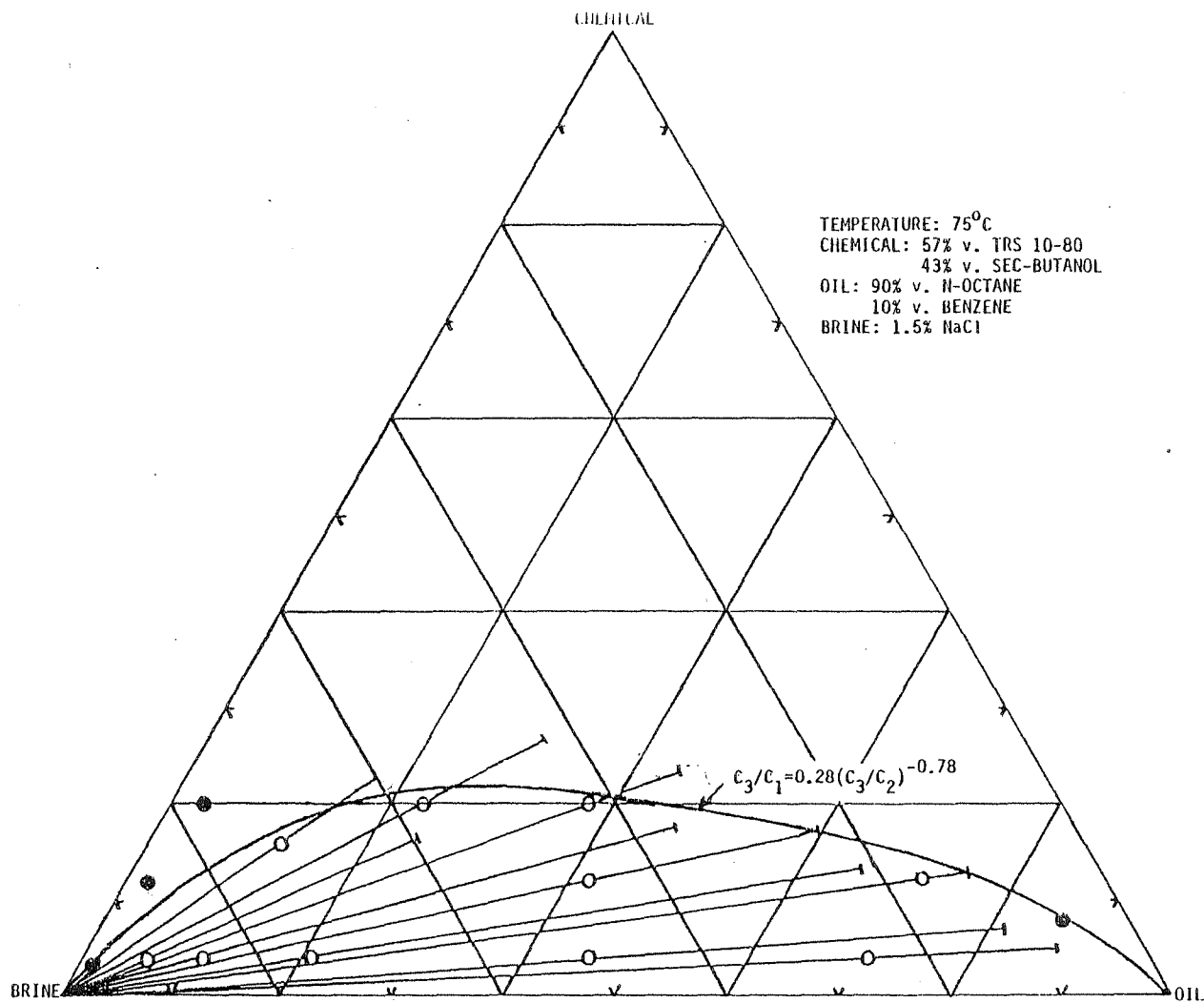
FIGURE 14. TERNARY DIAGRAM OF TRS 10-80

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 57% v. MEAC120XS
43% v. SEC-BUTANOL
OIL: N-OCTANE
BRINE: 1.125% NaCl

BRINE

OIL
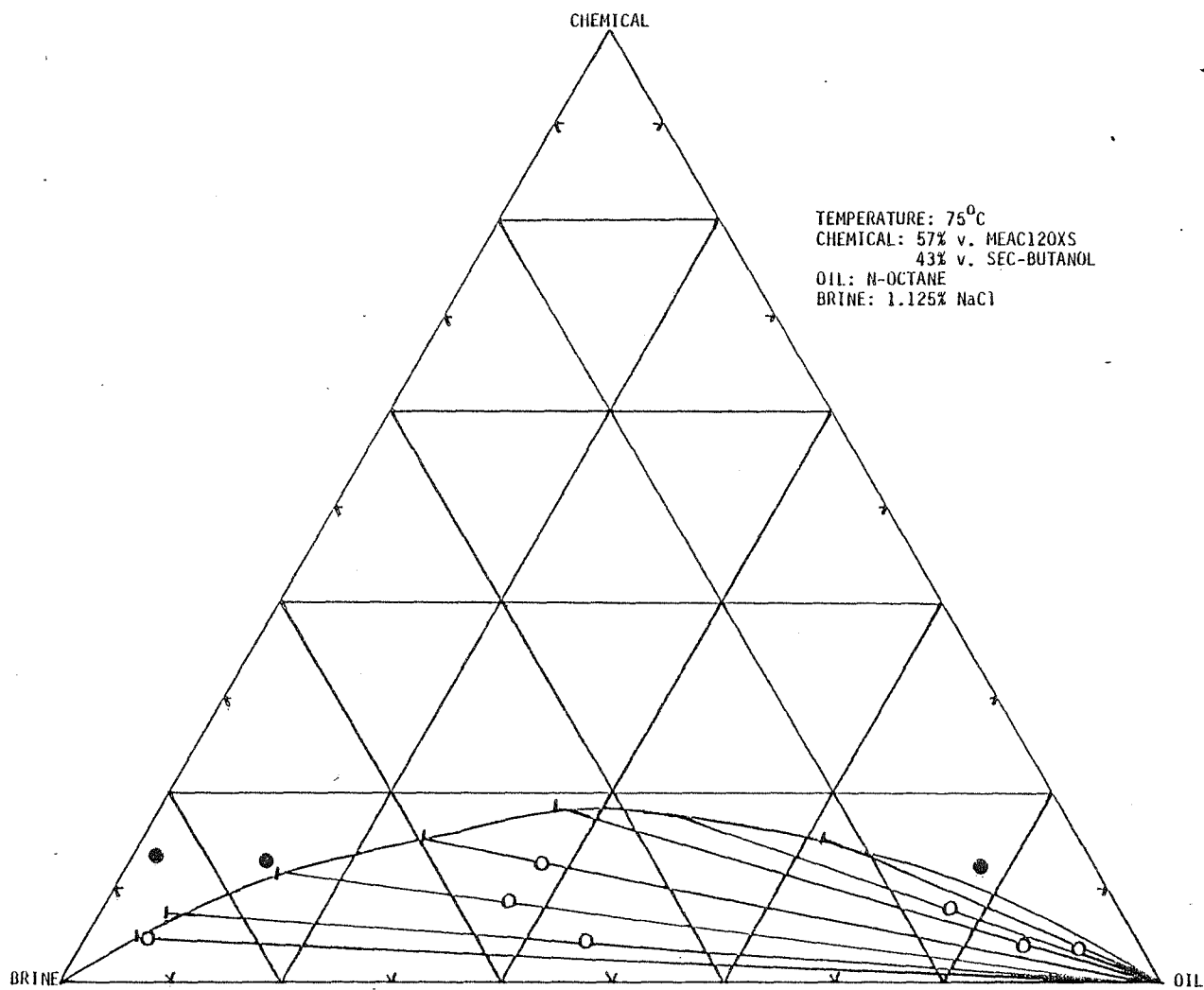
FIGURE 15. TERNARY DIAGRAM OF ORTHOXYLENE SULFONATE
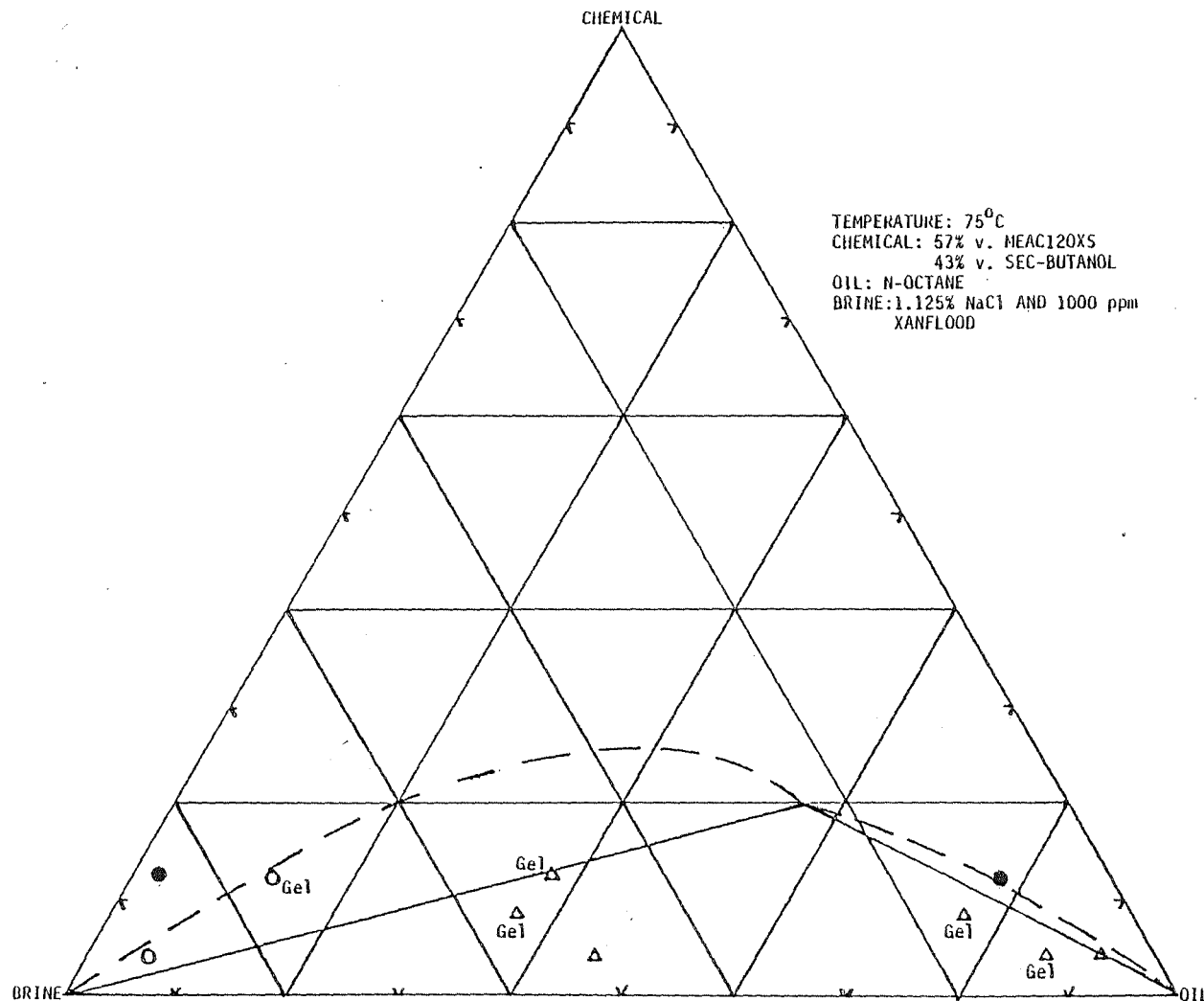
FIGURE 16. TERNARY DIAGRAM OF ORTHOXYLENE SULFONATE

CHEMICAL (top vertex)

TEMPERATURE: 75°C
CHEMICAL: 57% v. MEAC120XS
         43% v. SEC-BUTANOL
OIL: N-OCTANE
BRINE:1.125% NaCl AND 1000 ppm
         XANFLOOD

BRINE (bottom left vertex)
OIL (bottom right vertex)
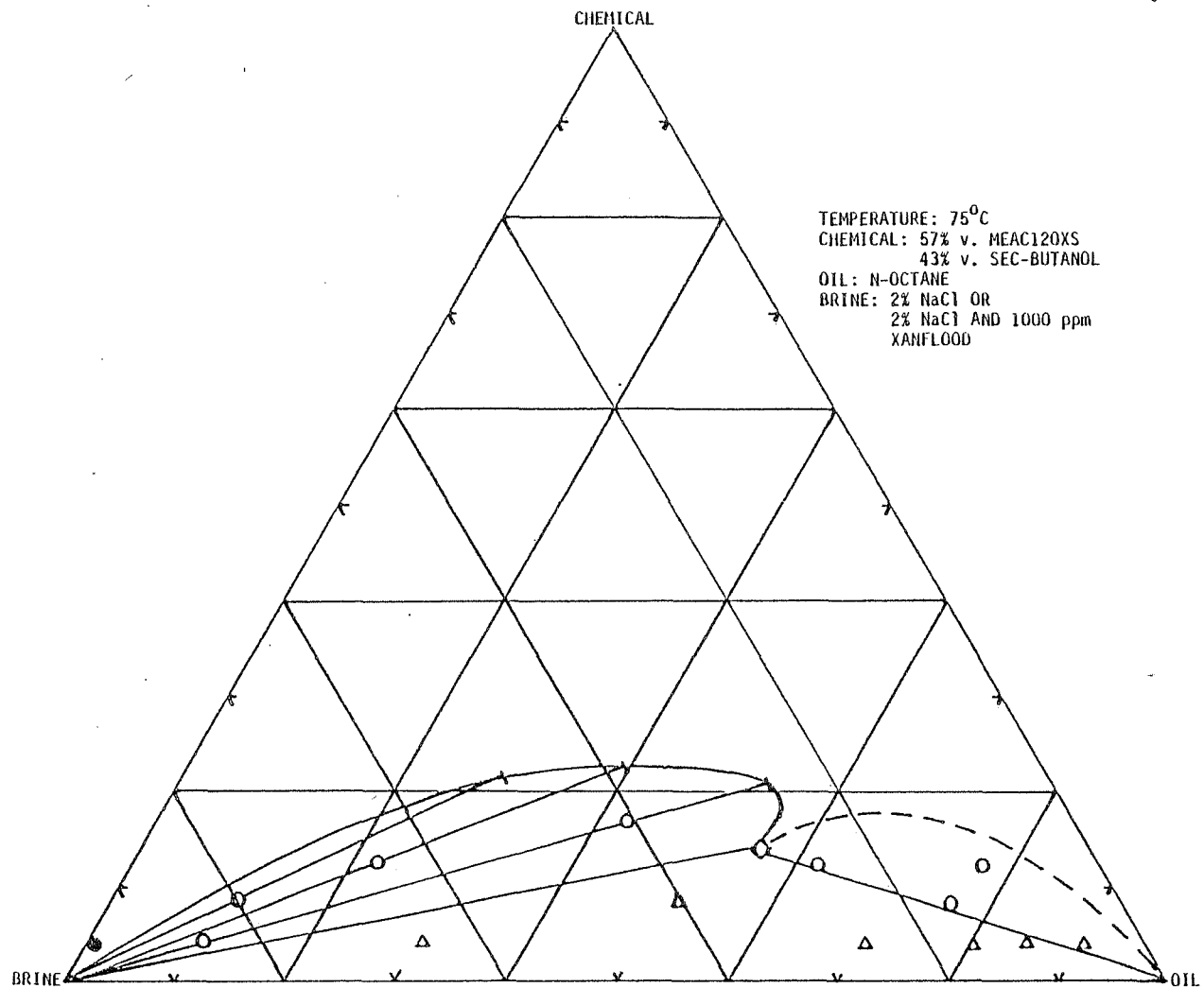
FIGURE 17. TERNARY DIAGRAM OF ORTHOXYLENE SULFONATE
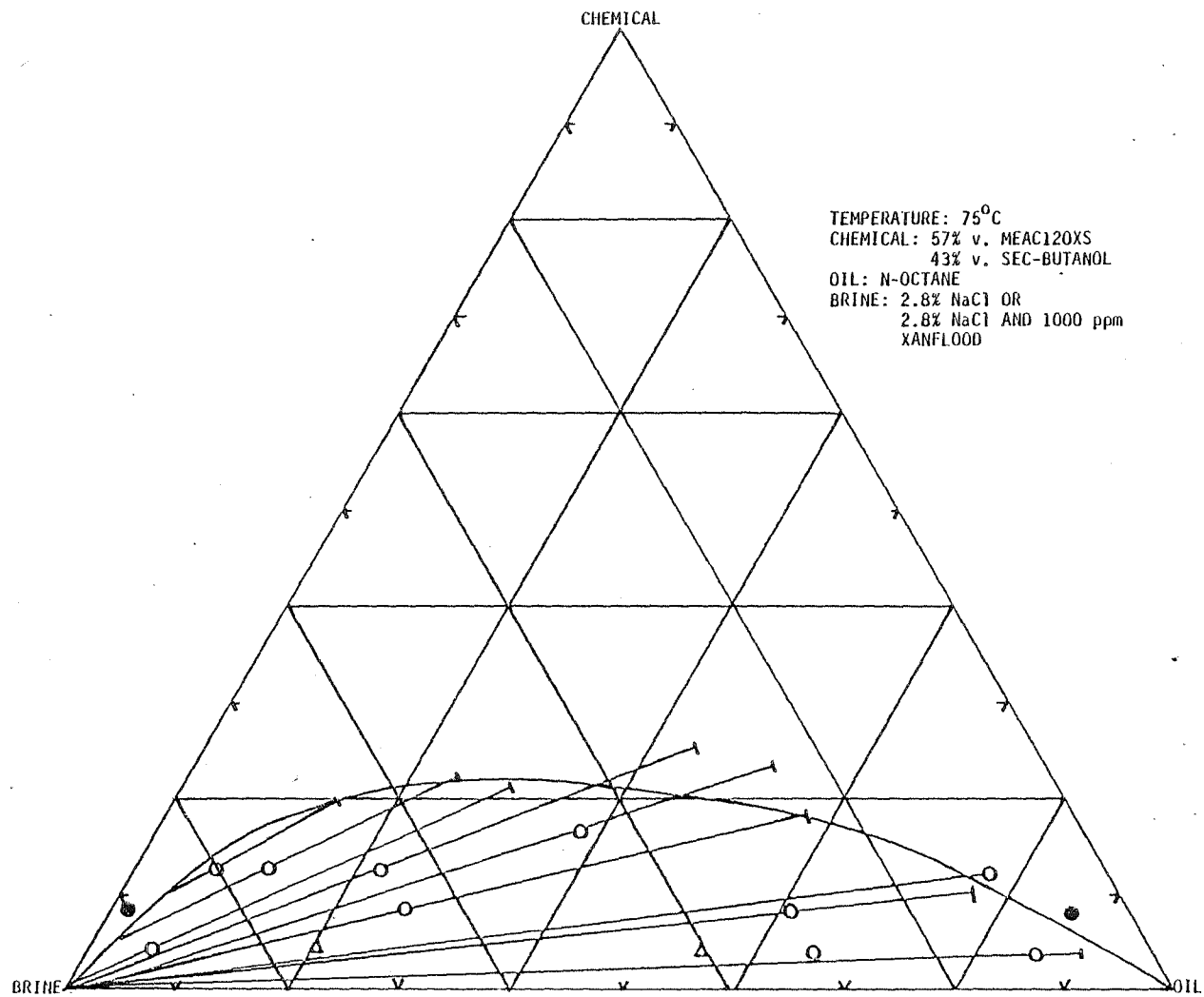
FIGURE 18. TERNARY DIAGRAM OF ORTHOXYLENE SULFONATE

CHEMICAL

TEMPERATURE: 75^{0}C
CHEMICAL: 57% v. MEAC120XS
            43% v. SEC-BUTANOL
OIL: N-OCTANE
BRINE: 1% NaCl

BRINE

OIL
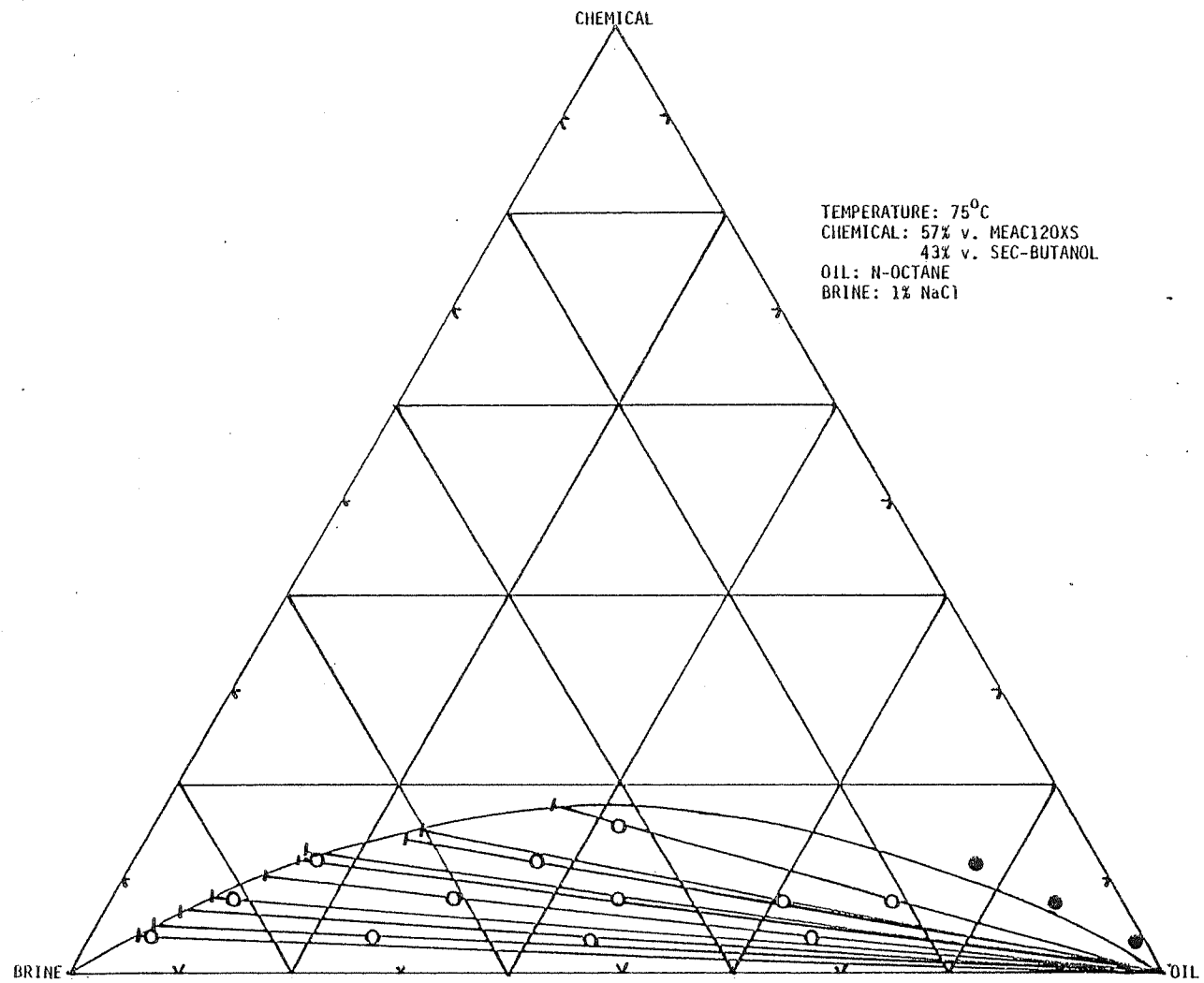
FIGURE 19. TERNARY DIAGRAM OF ORTHOXYLENE SULFONATE

that a Type II(-) was obtained at the salinity at 1% NaCl. Those compositions, with the symbols of ⊢ , along the binodal curve, were tested for viscosity. The viscosities of these microemulsions were plotted versus the volume fraction of oil shown in Figure 20. The volume fraction of oil was read from the composition point, ⊢ , along the binodal curve of Figure 19.

Comparing the Type II(-) diagrams of TRS 10-80 and MEAC12OXS at the same condition, Figures 6 and 15, the TRS 10-80 gives a lower height of the binodal curve. Also, the invarient point in the TRS 10-80 system is lower than that in the MEAC12OXS system (see Figures 8 and 17).

Stepan Petrostep 465

50% vol. fo 100% active Petrostep 465 and 50% vol. of sec-butanol were used in the chemical component. Oil is a mixture of 90% vol. of n-octane and 10% vol. of benzene. Salt concentration was set as 0.3%, 0.75%, 2.8%, and 9% of NaCl. The first two sets gave Type II(-) diagrams. Type III diagram was obtained at 2.8% NaCl. No Type II(+) diagram formed until salt concentration reaches about 9% NaCl.

As before, polymer induces an additional phase in the Type II(-) case at 0.75% NaCl. The Type III and Type II(+) cases were unchanged for Petrostep 465 (see Figures 21-24), except the point #8 of Figure 23 became four phases when xanflood was included. However, when the salinity was lowered from 0.75% to 0.3% NaCl, the polymer did not affect the Type II(-) phase diagram. Figure 25 shows that same Type II(-) diagram was obtained even when 1000 ppm of xanflood was added at 0.3% NaCl brine.

Figure 26 shows a Hand-plot curve of Figure 25. All the circle points in Figure 26 were derived from the ⊢ points in Figure 25. For example, sample
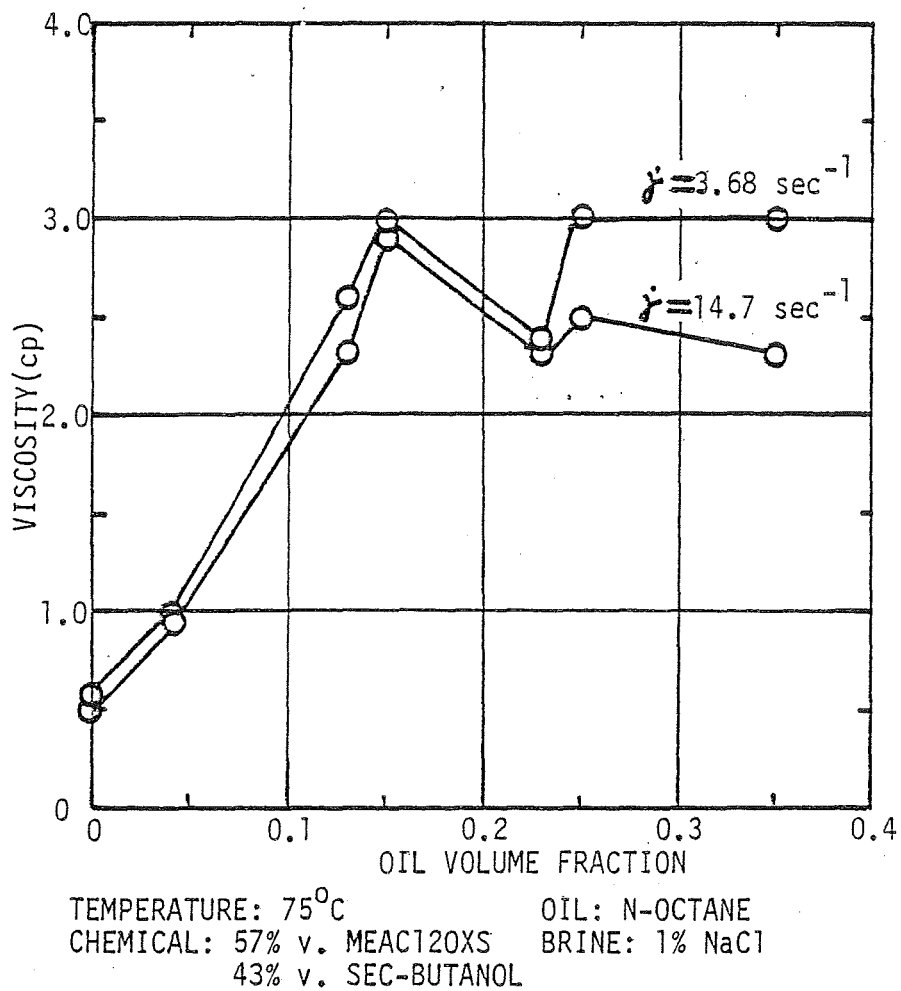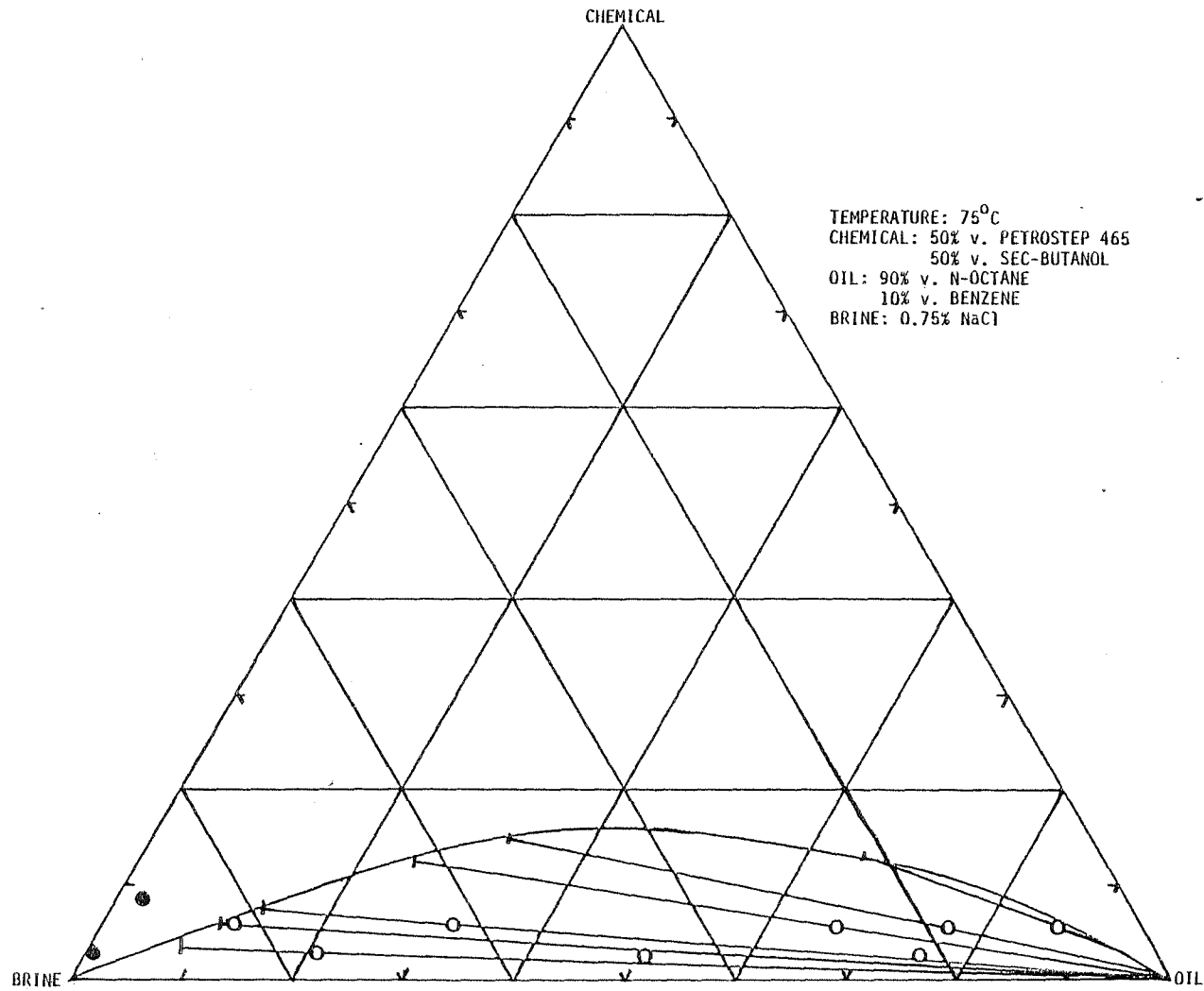
FIGURE 20. VISCOSITY OF MEAC12OXS MICROEMULSION

TEMPERATURE: 75°C
CHEMICAL: 50% v. PETROSTEP 465
         50% v. SEC-BUTANOL
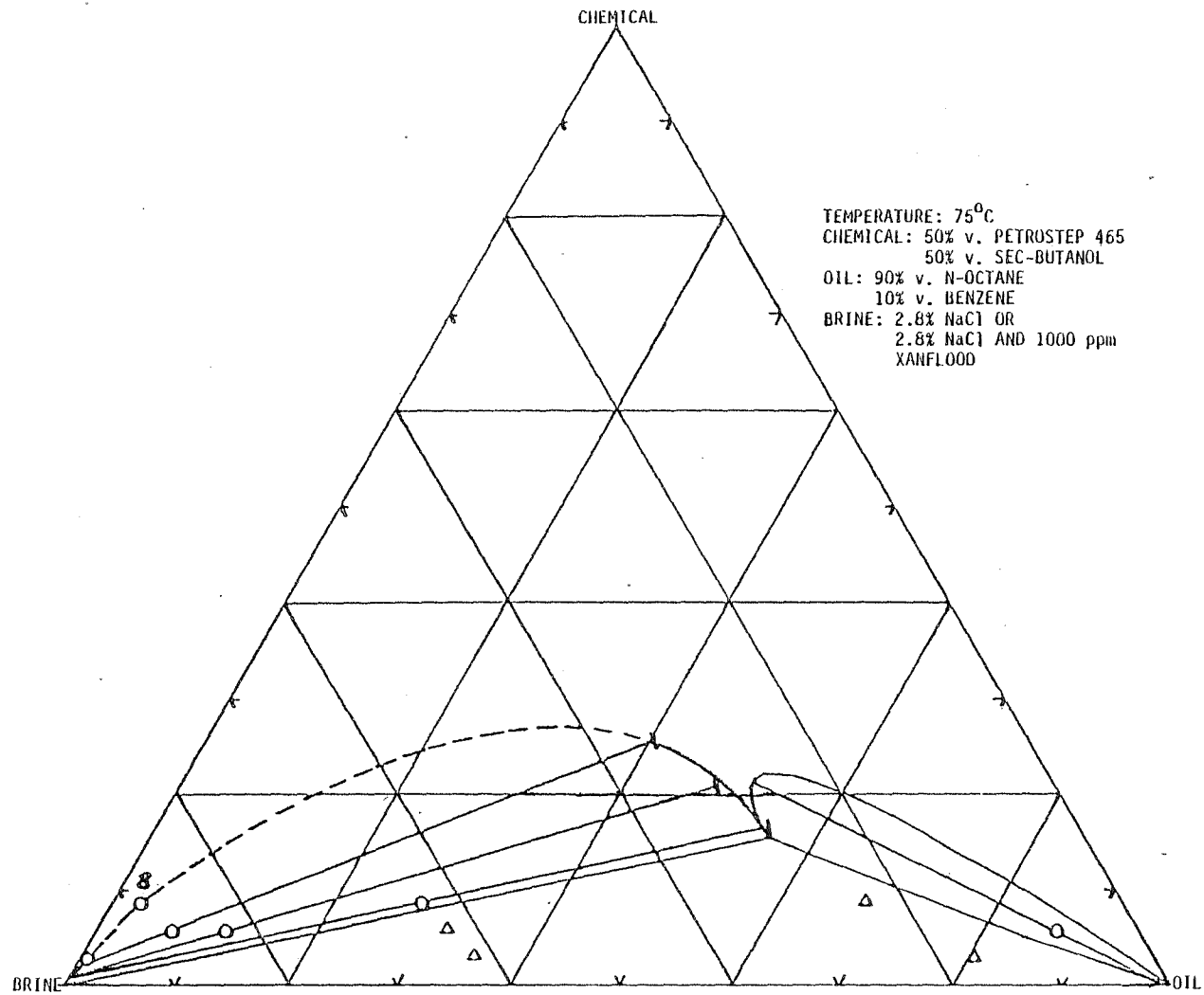OIL: 90% v. N-OCTANE
     10% v. BENZENE
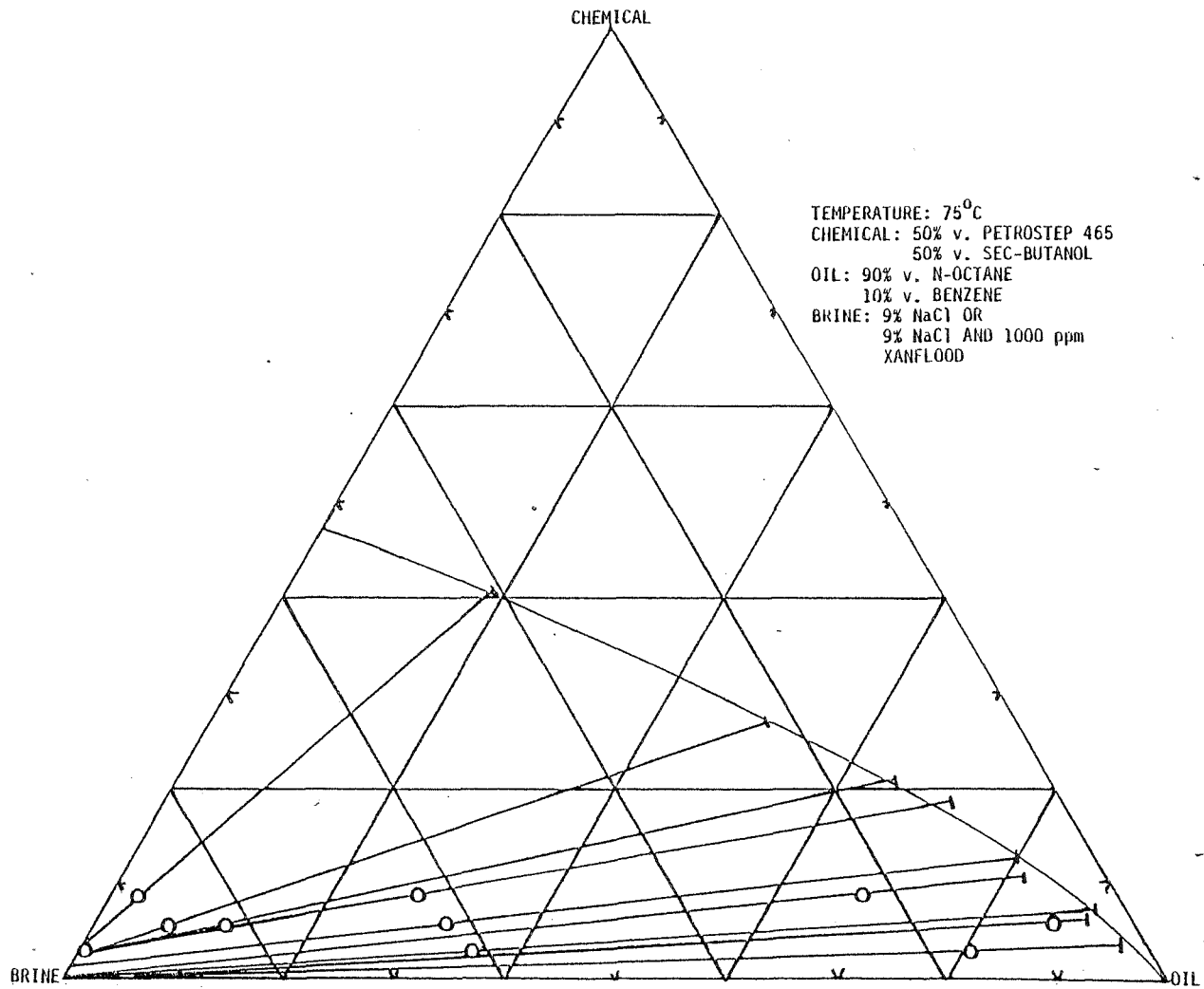BRINE: 0.75% NaCl

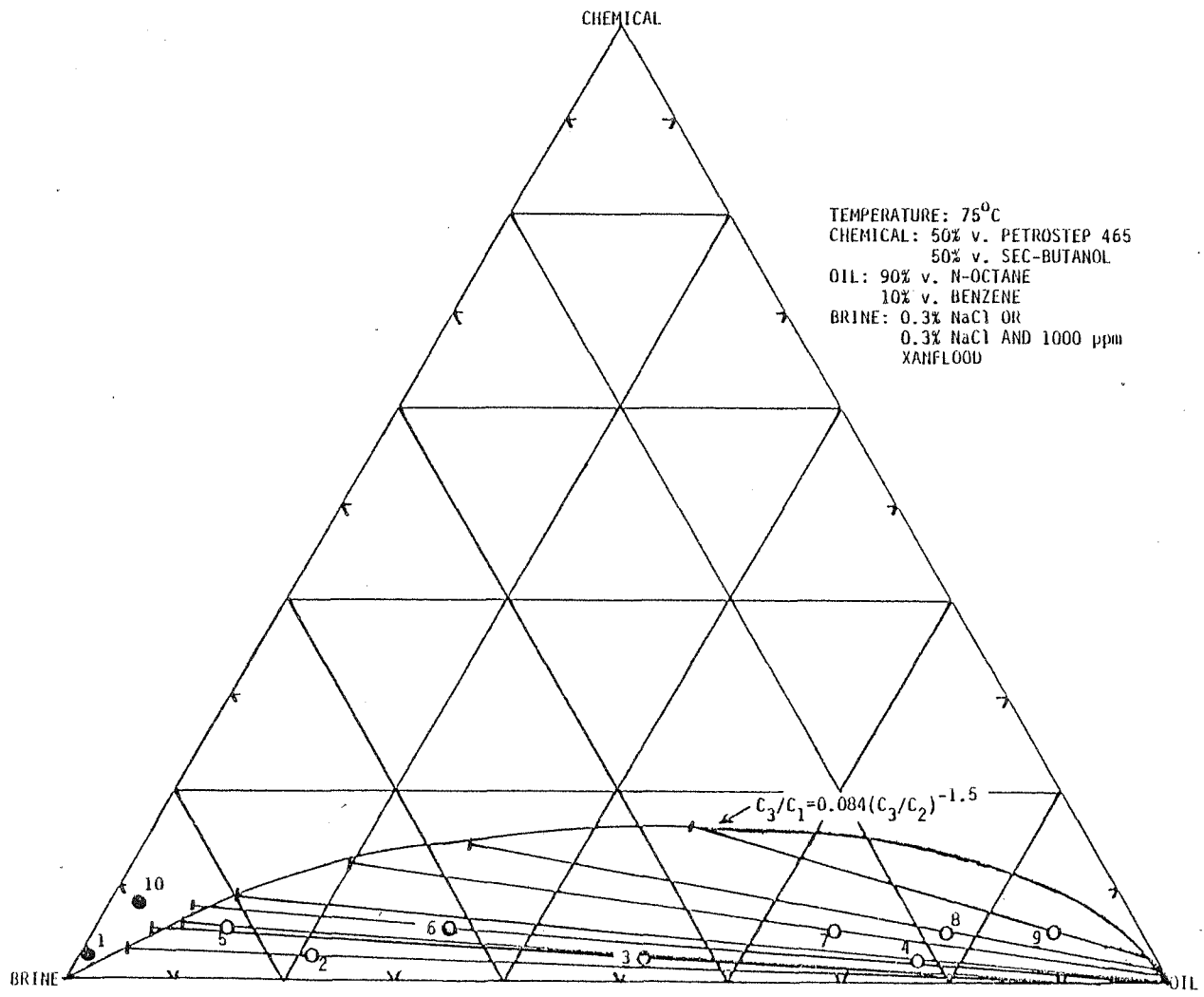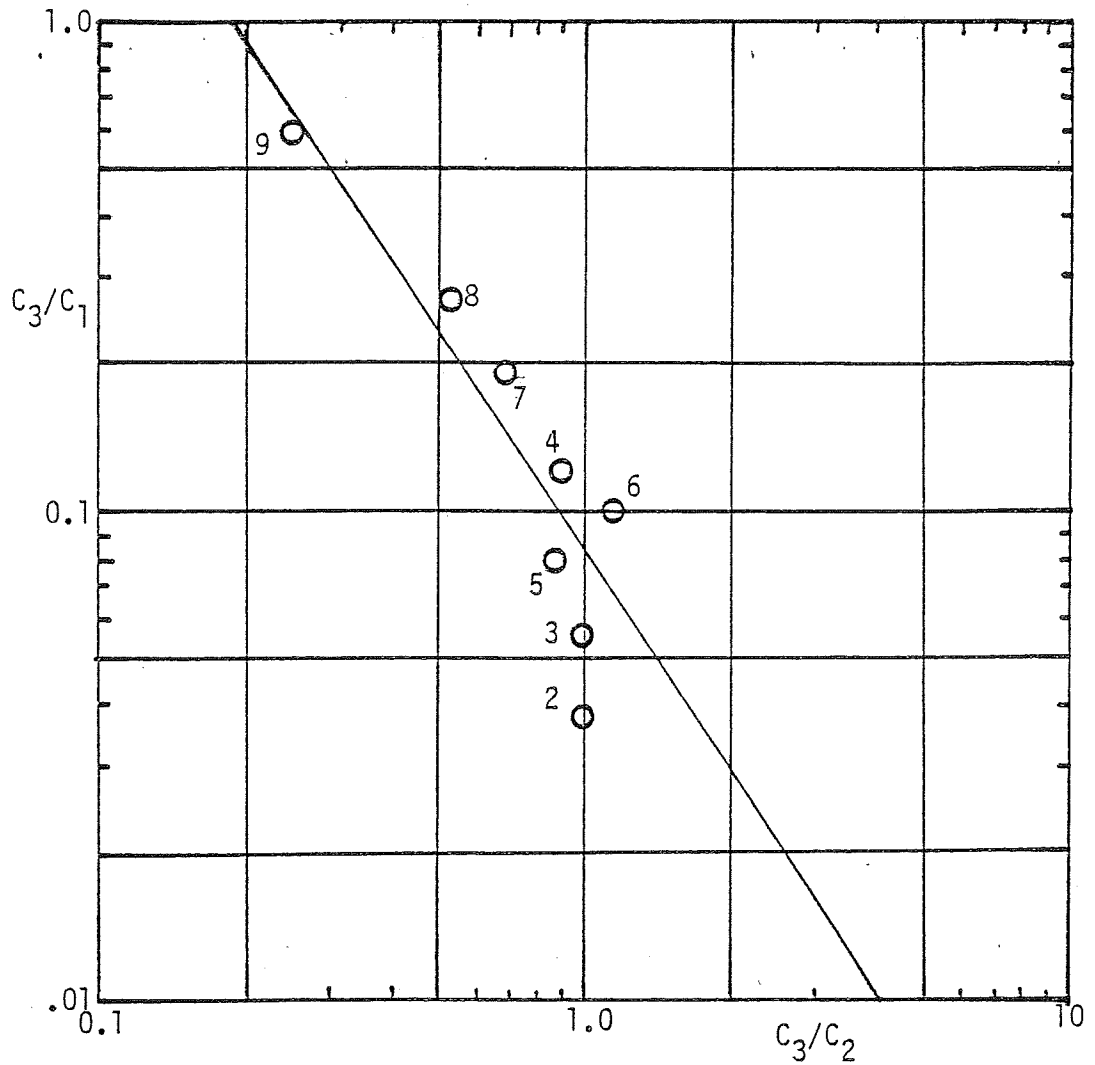FIGURE 21. TERNARY DIAGRAM OF PETROSTEP 465
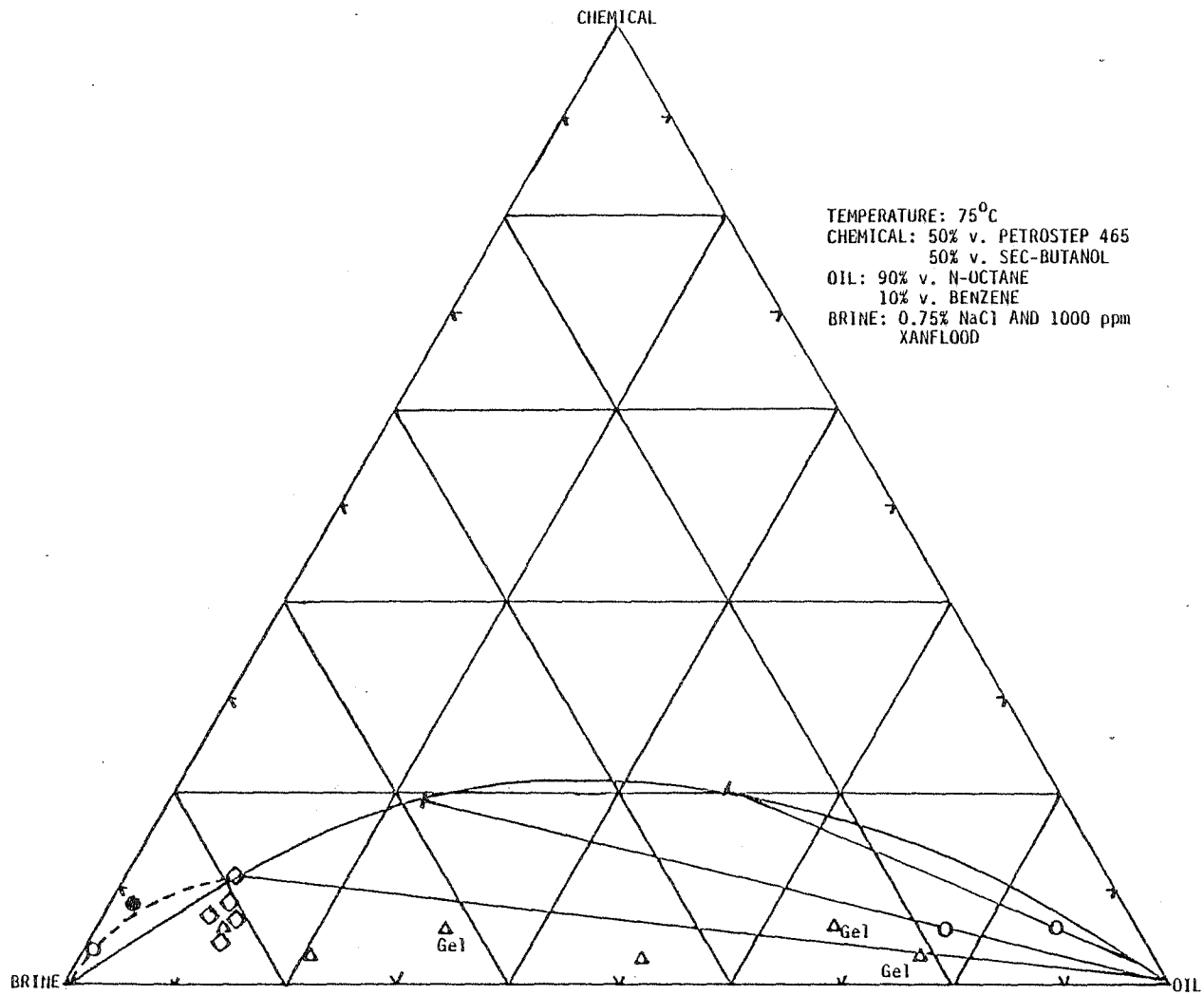
FIGURE 22. TERNARY DIAGRAM OF PETROSTEP 465

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 50% v. PETROSTEP 465
        50% v. SEC-BUTANOL
OIL: 90% v. N-OCTANE
     10% v. BENZENE
BRINE: 0.75% NaCl AND 1000 ppm
       XANFLOOD

BRINE

OIL

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 50% v. PETROSTEP 465
          50% v. SEC-BUTANOL
OIL: 90% v. N-OCTANE
     10% v. BENZENE
BRINE: 2.8% NaCl OR
       2.8% NaCl AND 1000 ppm
       XANFLOOD

BRINE

OIL

FIGURE 23. TERNARY DIAGRAM OF PETROSTEP 465

54

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 50% v. PETROSTEP 465
         50% v. SEC-BUTANOL
OIL: 90% v. N-OCTANE
     10% v. BENZENE
BRINE: 9% NaCl OR
       9% NaCl AND 1000 ppm
       XANFLOOD

BRINE

OIL

FIGURE 24. TERNARY DIAGRAM OF PETROSTEP 465

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 50% v. PETROSTEP 465
         50% v. SEC-BUTANOL
OIL: 90% v. N-OCTANE
     10% v. BENZENE
BRINE: 0.3% NaCl OR
       0.3% NaCl AND 1000 ppm
       XANFLOOD

$C_3/C_1 = 0.084(C_3/C_2)^{-1.5}$

BRINE

OIL

FIGURE 25. TERNARY DIAGRAM OF PETROSTEP 465

TEMPERATURE: 75°C   OIL: 90% v. N-OCTANE
CHEMICAL: 50% v. PETROSTEP 465   10% v. BENZENE
          50% v. SEC-BUTANOL   BRINE: 0.3% NaCl

FIGURE 26. HAND PLOT OF FIGURE 25

point #4 of Figure 25 has a $\vdash$ point with $C_1=0.8$, $C_2=0.105$, and $C_3=0.095$. C_1, C_2, and C_3 are the volume fraction of brine, oil, and chemical respectively. Therefore, $C_3/C_2=0.90$, and $C_3/C_1=0.12$. A plot of C_3/C_2 versus C_3/C_1 on a logarithmic scale for all the sample points is shown in Figure 26. The straight line was drawn in Figure 26 by the least-squares method. Since Sample #2 shows very sensitive values for C_3/C_2 and C_3/C_1, #2 was omitted. This straight line can be expressed as:

$$C_3/C_1 = 0.084 \, (C_3/C_2)^{-1.5}$$

The calculated binodal curve derived from this equation is shown on Figure 25.

Microemulsion viscosities versus oil concentration are plotted on Figure 27. The viscosity of the microemulsion increases to a maximum value and then decreases as oil fraction ranges from zero to one.

Alcolac Siponate DS-10

Figure 28 shows the Type III phase diagram of a polymer-free DS-10 system. The chemical consists 63% wt. of DS-10 and 37% wt. of sec-butanol. N-octane was used as the oil component. The salt concentration was 7% NaCl. There was no polymer. Temperature was $75^{\circ}C$. DS-10 has a very high optimum salinity, about 7% NaCl.

Witco TDA-100

TDA-100 is an nonionic surfactant. The chemical formula is $C_{13}H_{27}O(CH_2CH_2O)_{10}H$. No alcohol was used in this test. Almost all of the compositions, except the ones near the oil free line or the one at lower water content and higher chemical content, form gels at $24^{\circ}C$. Figure 29 shows a polymer-free ternary diagram of TDA-100/n-octane/distilled water at $75^{\circ}C$. No gels formed at $75^{\circ}C$.
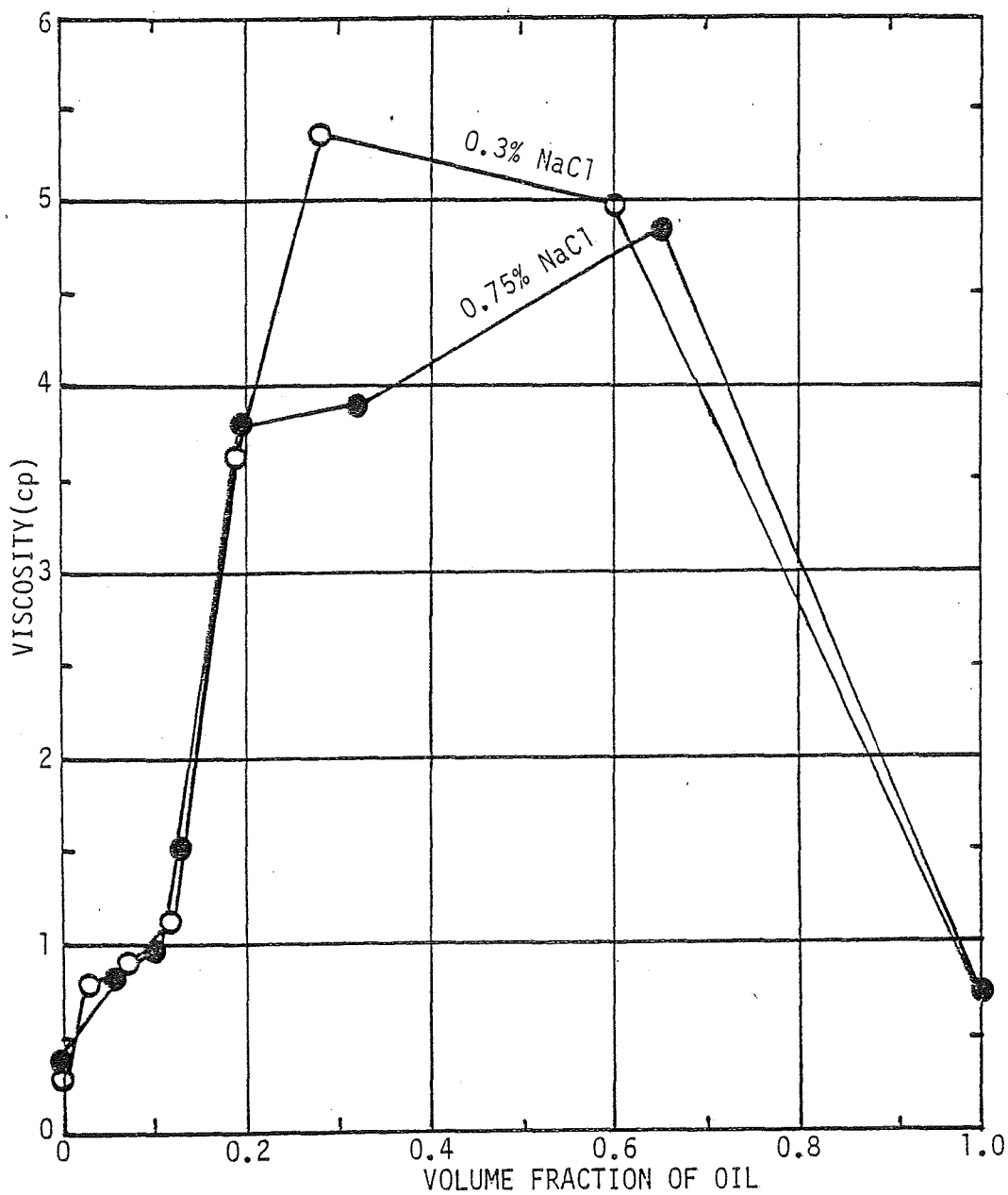
TEMPERATURE: 75°C   SHEAR RATE: 15 sec^{-1}
CHEMICAL: 50% v. PETROSTEP 465   SALT CONCENTRATION:
        50% v. SEC-BUTANOL   0.3% NaCl ⎯○⎯
OIL: 90% v. N-OCTANE   0.75% NaCl ⎯●⎯
    10% v. BENZENE

FIGURE 27. VISCOSITY OF PETROSTEP 465 MICROEMULSION

CHEMICAL

TEMPERATURE: 75°C
CHEMICAL: 63% wt DS-10
          37% wt SEC-BUTANOL
OIL: N-OCTANE
BRINE: 7% NaCl

BRINE

OIL
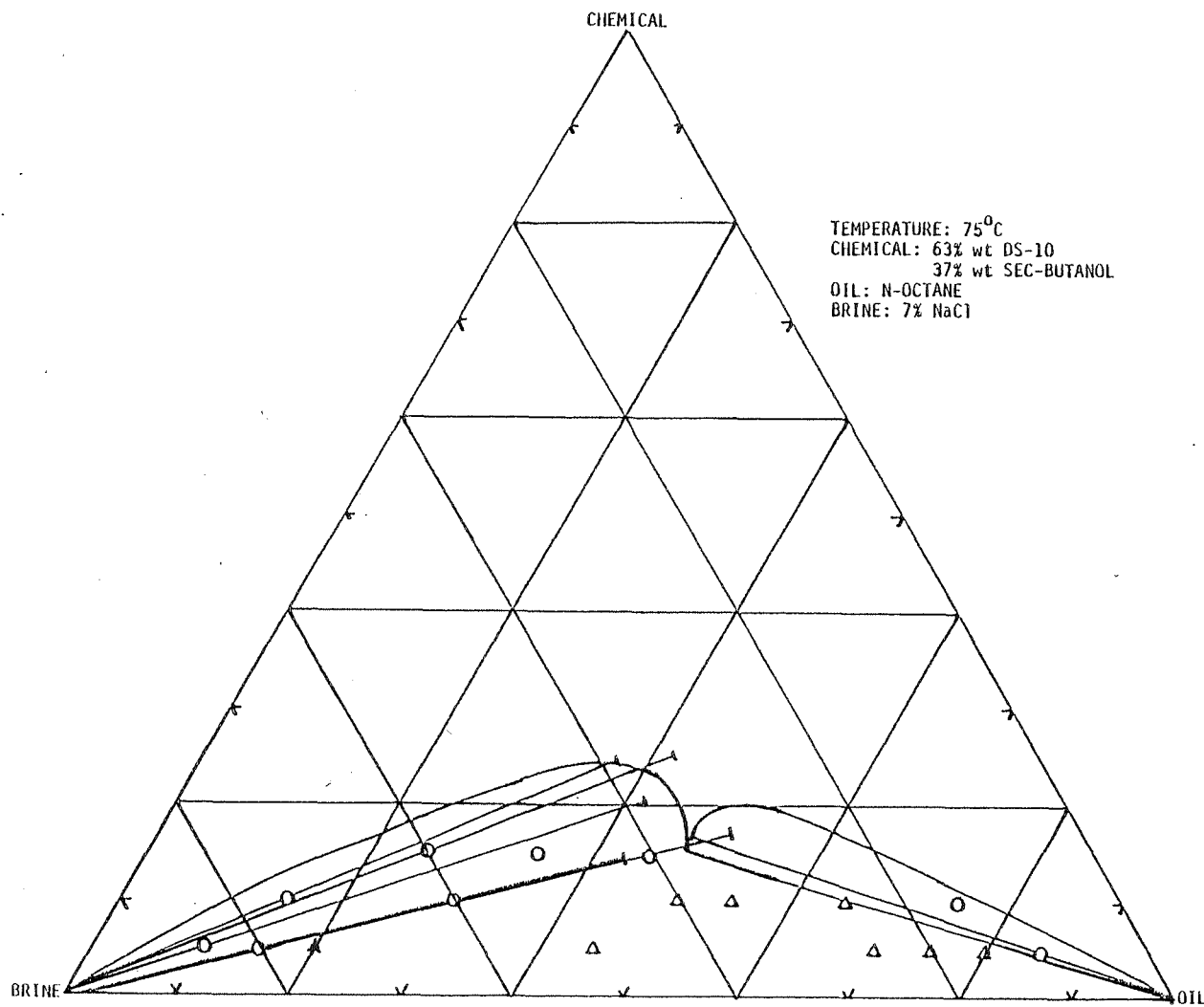
FIGURE 28. TERNARY DIAGRAM OF SIPONATE DS-10

69

TEMPERATURE: 75°C
CHEMICAL: TDA-100
OIL: 80% v. N-OCTANE
     20% v. BENZENE
BRINE: DISTILLED WATER

CHEMICAL

OIL

BRINE
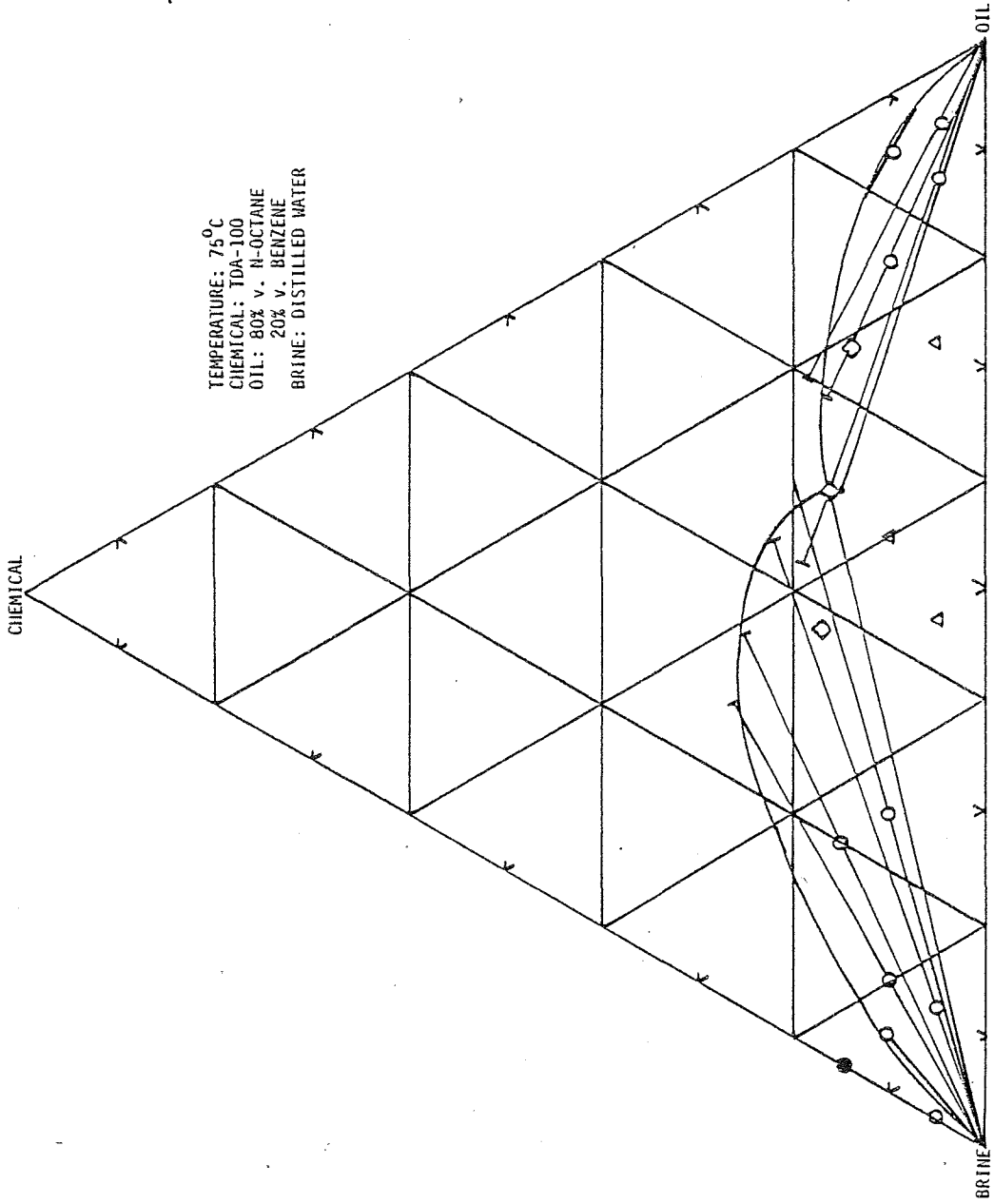
FIGURE 29. TERNARY DIAGRAM OF WITCO TDA-100

Witco TRS 10-80 in Oil-free Phase Volume Fraction System

Many combinations of various types and concentrations of surfactants and polymers in various types and concentrations of alcohols at various temperatures were studied to see how the surfactant-polymer interaction is affected by these factors by changing the electrolyte concentration.

In the TRS 10-80 system, the polymers were xanflood, Pusher 700, Calgon 800, Natrosol 250 HHR, and Polyox Coagulant. Figure 30 shows that polymer type does not affect the salinity at which separation first occurs. We will call this the critical electrolyte concentration (CEC). The bottom phase appeared to be the surfactant-rich phase due to its dark amber color. A UV spectra on a selected sample verified this. A standard TRS 10-80 (125 ppm) sample was run by UV. This sample was diluted from a mixture of 1% wt (as is) of TRS 10-80, 1000 ppm of Natrosol, 4% wt of iso-butanol, and zero percent of salt by 80 times in volume. Another sample, with 1% wt (as is) TRS 10-80, 1000 ppm of Natrosol, 4% wt of iso-butanol, and 1.4% of NaCl, was taken to be tested for the two phases in this system. The upper phase was diluted by 20 times, and the lower phase was diluted by 320 times by distilled water. Figure 31 shows that compared to the standard sample, the upper phase sample should have 89 ppm and the lower phase one should have 91 ppm of TRS 10-80. So the original concentration of the upper and lower phases are approximately 0.18% and 2.9%, respectively. Distilled water and 250 ppm of Natrosol were run by UV in the same wavelength range as before, no absorptions were found. A pure iso-butanol was run by UV, too. An absorption peak appears at wavelength about 288 nm, which is different from 268 nm, the absorption wavelength of TRS10-80. Also, the actual sample has only 0.05% wt of iso-butanol, much less than 100%. Thus, iso-butanol,
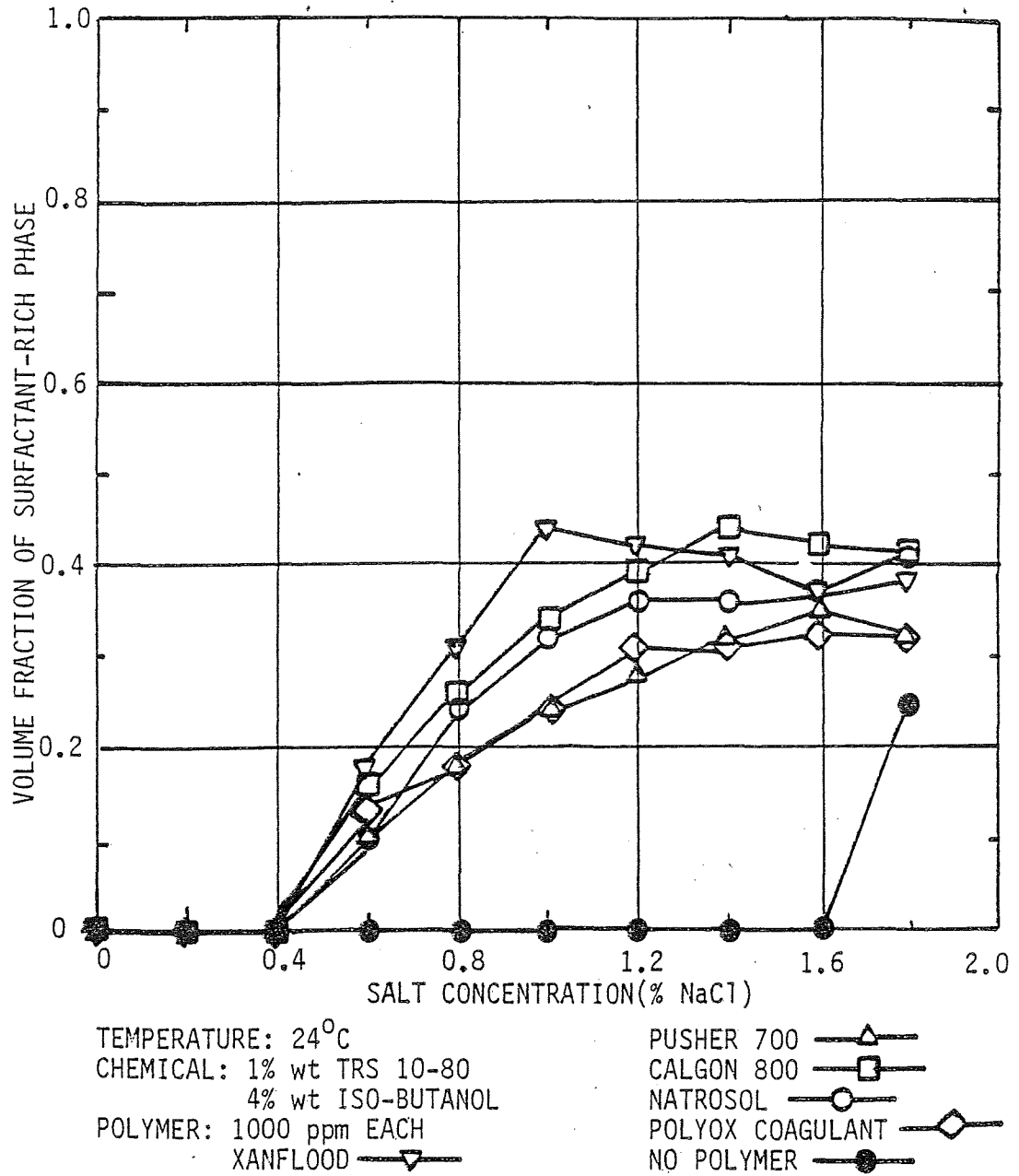
FIGURE 30. EFFECT OF POLYMER TYPE ON TRS 10-80 PHASE BEHAVIOR
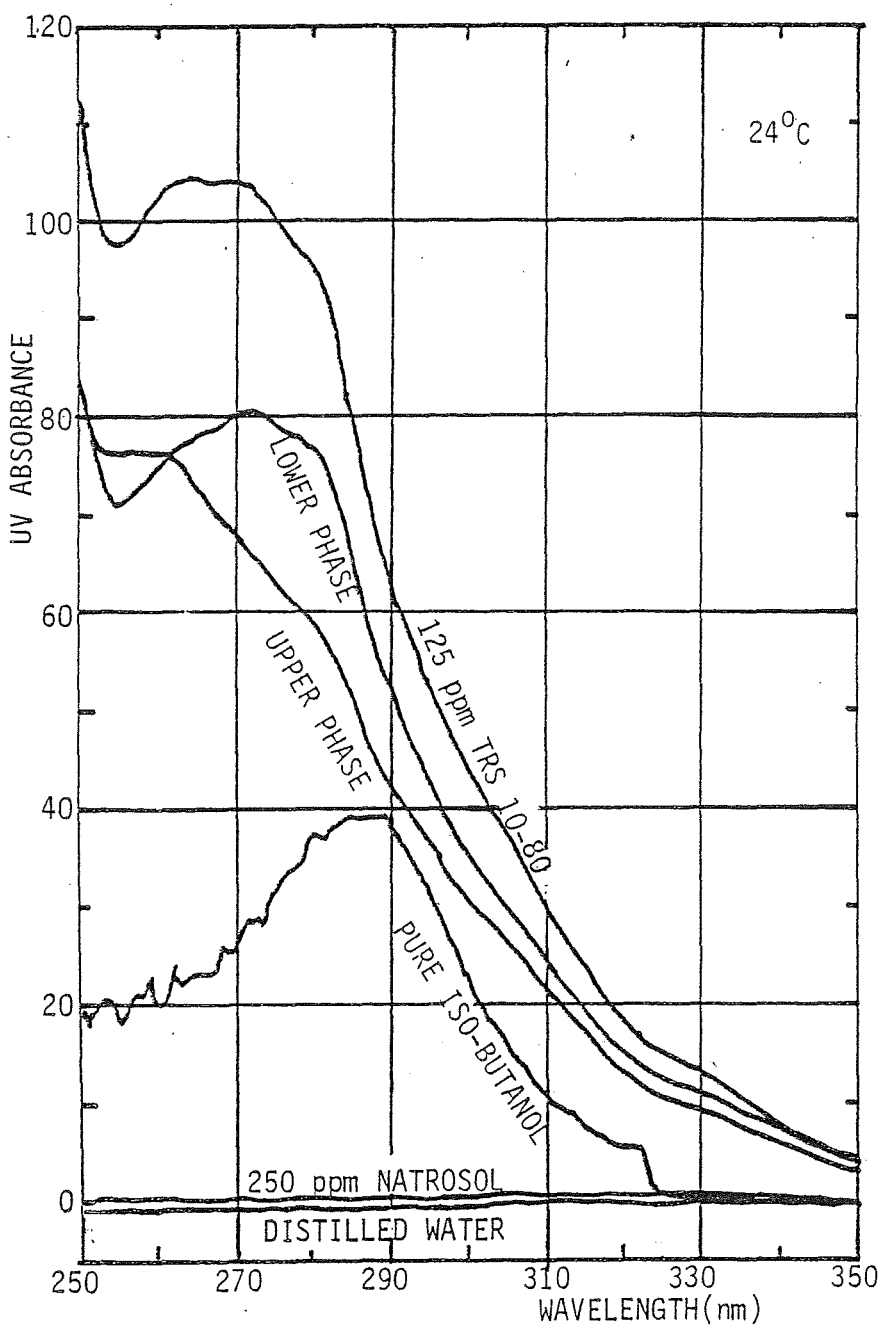
FIGURE 31. UV SPECTRA OF MIXTURE OF TRS 10-80 AND NATROSOL, DISTILLED WATER, ISO-BUTANOL, AND NATROSOL SOLUTION

like distilled water and Natrosol, should not be considered in analyzing the UV data of TRS 10-80 in Figure 31.

The CEC increased when the temperature was increased from $24^{\circ}C$ to $75^{\circ}C$ (see Figure 32). In this case, the surfactant-rich phase appears to be on the top.

Changing polymer and surfactant concentrations did not affect the CEC. Figure 33 shows two things. One is that the CEC is the same for different concentrations of polymer and surfactant, the other is that the volume of the bottom (surfactant-rich) phase seems proportional to the concentration of TRS 10-80. Two sets of surfactant-polymer mixtures were made by changing the concentraton of the surfactant in order to find out if the volume of the surfactant-rich phase increased as the concentration of the surfactant is increased. One of the sets has 3% wt. of sec-butanol, 1000 ppm of xanflood, and 0% of NaCl. The other set has the same composition except the salt concentration is 1% NaCl instead of 0% NaCl. In both sets, the TRS 10-80 concentration varied from 0% to 10% wt (see Figures 34, 35, and 36). At $24^{\circ}C$, there were no two phase samples at 0% NaCl except for the 10% wt TRS 10-80 sample. For the 1% NaCl set, the volume of the surfactant-rich phase seems proportional to the concentration of TRS 10-80 between 0% wt to 4% wt TRS 10-80. At $53^{\circ}C$, no two phase was found for 0% NaCl set. And, for the set of 1% NaCl, the volume of the surfactant-rich phase looks proportional to the concentration of the TRS 10-80 (see Figure 35). At $75^{\circ}C$, again, the 0% NaCl set has no two phases samples. The 1% NaCl set shows a proportional effect (see Figure 36).

Another study to determine which layer is the surfactant-rich phase in a 10 ml mixture of 1% wt TRS 10-80, 3% wt sec-butanol, 1000 ppm xanflood, and
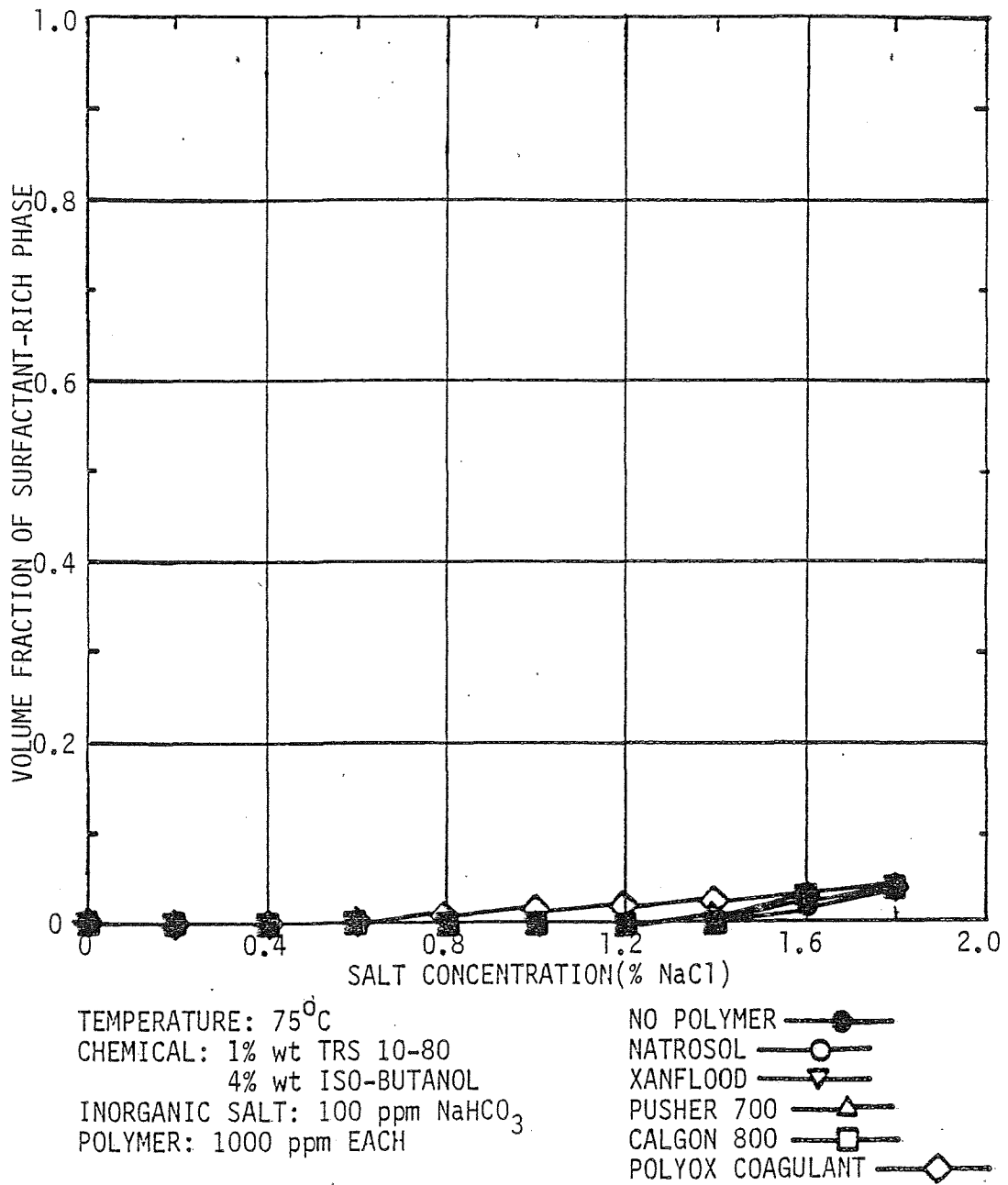
FIGURE 32. EFFECT OF POLYMER TYPE AT 75°C
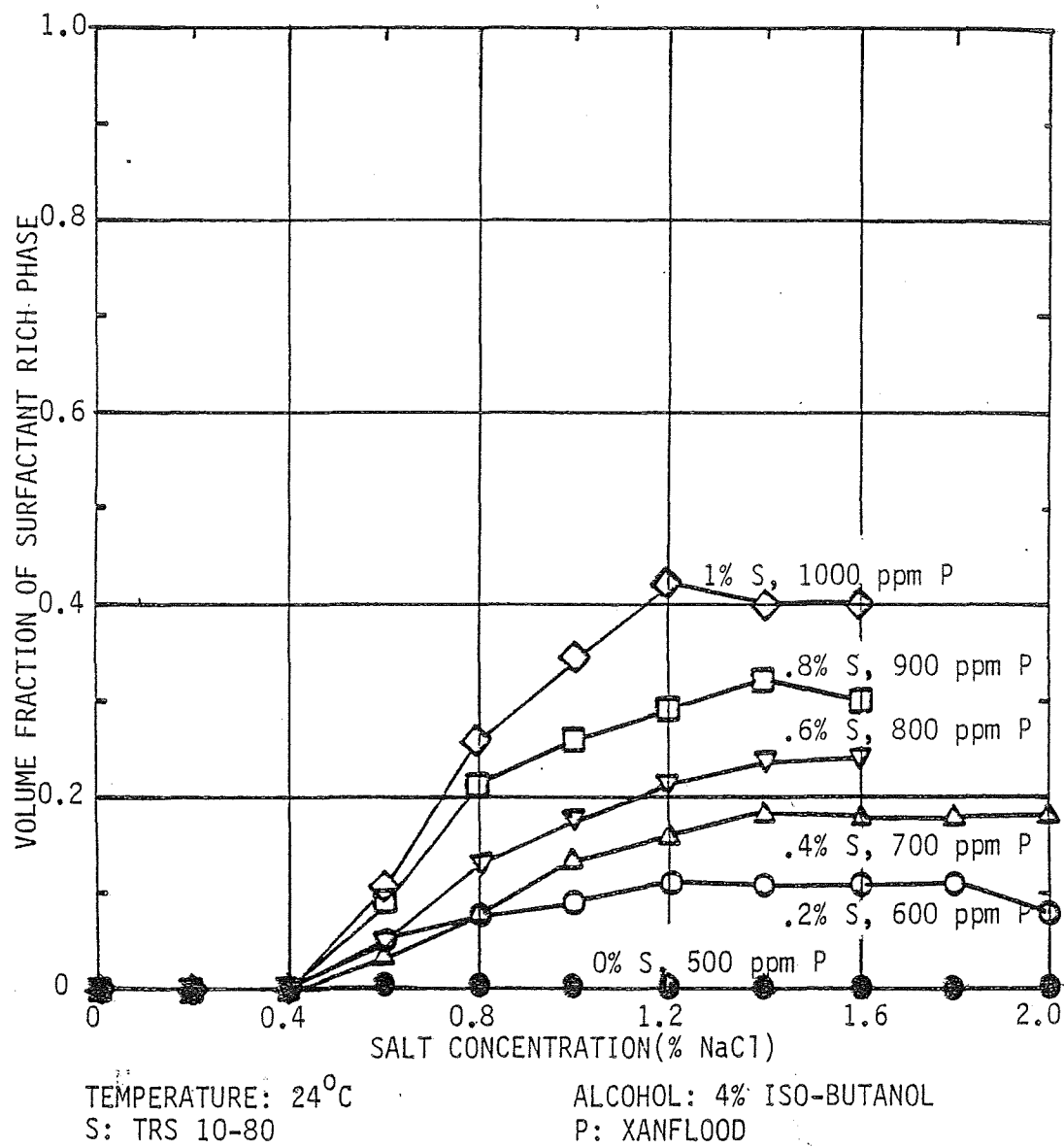
FIGURE 33. EFFECT OF TRS 10-80 AND XANFLOOD CONCENTRATIONS
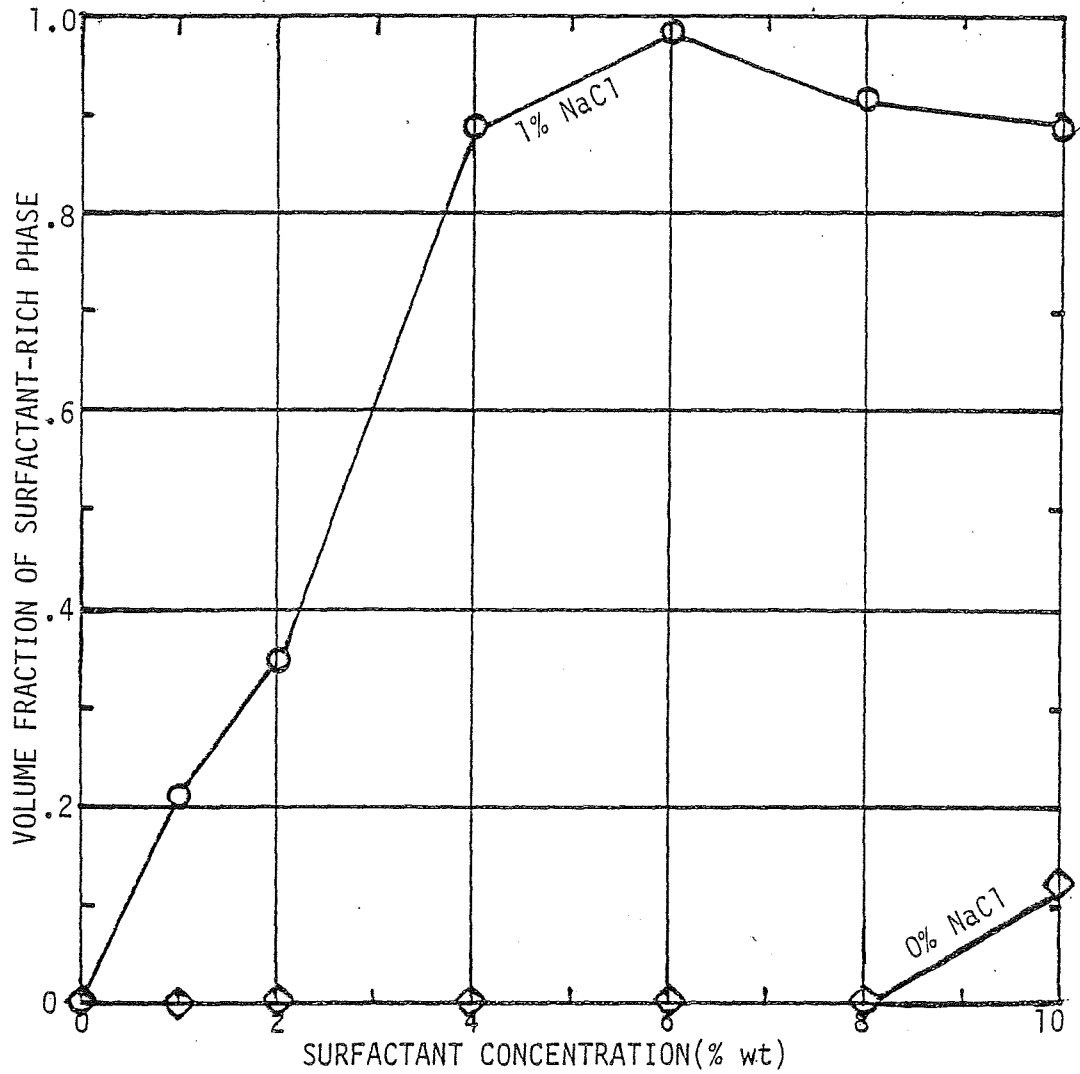
FIGURE 34. EFFECT OF SURFACTANT CONCENTRATION ON PHASE BEHAVIOR AT 24^{0}C
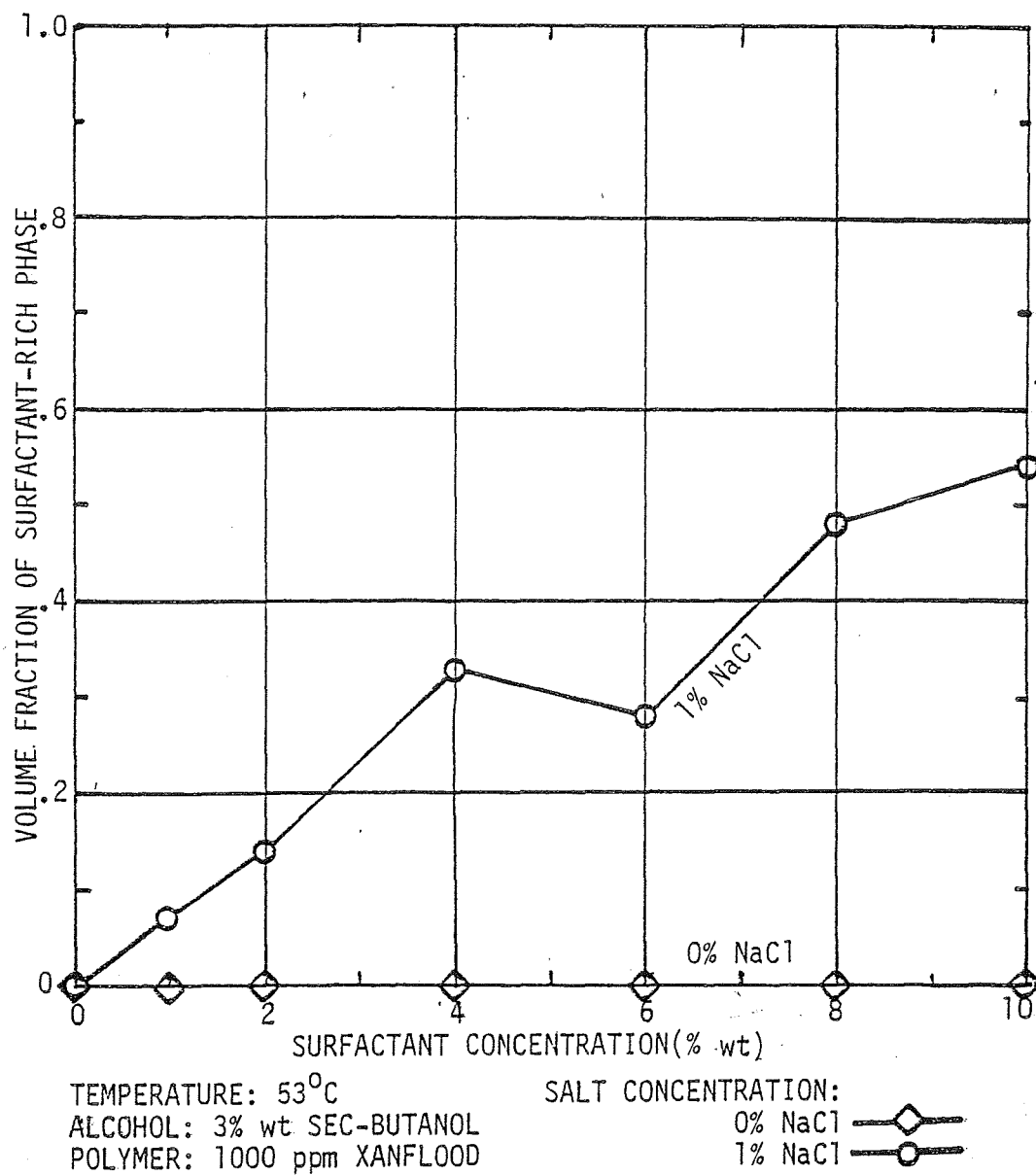
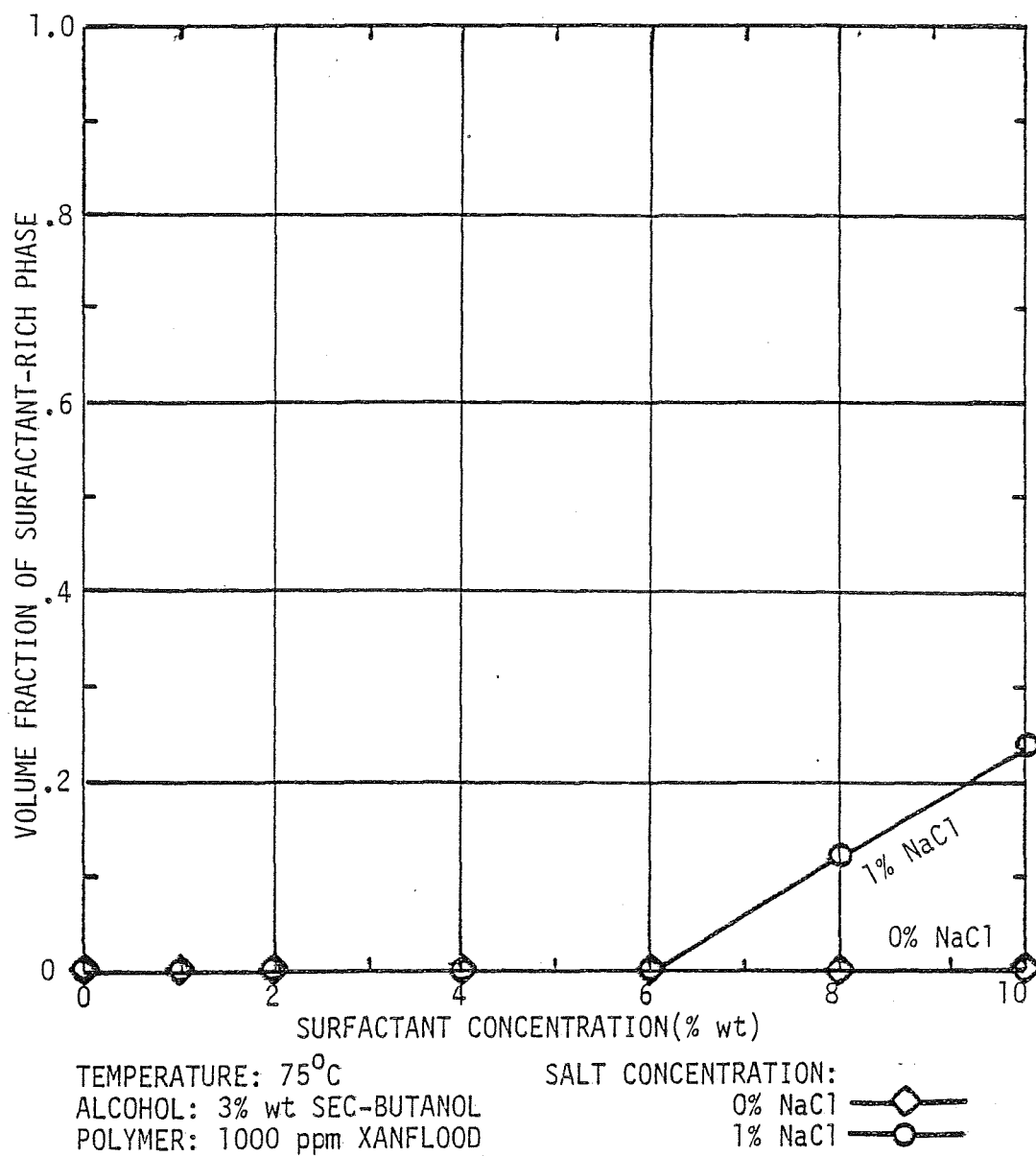FIGURE 35. EFFECT OF SURFACTANT CONCENTRATION ON PHASE BEHAVIOR AT 53°C

FIGURE 36. EFFECT OF SURFACTANT CONCENTRATION ON PHASE BEHAVIOR
AT 75°C

1% NaCl was conducted using UV Spectrometry. This sample has two phases. The volume ratio of the top layer to the bottom layer is 0.79/0.21 (see Figure 34). The top and bottom layers were diluted to 1/20 and 1/320 times, respectively, in order to give proper UV absorption peaks (see Figure 37). In Figure 9, we know that the peak of TRS 10-80 may be affected by xanflood, but not sec-butanol or brine. The effect of xanflood on the bottom layer can be neglected due to the relatively low concentration of xanflood. Therefore, the TRS 10-80 concentration of the bottom phase in Figure 37 can be calculated by 50 ppm x (164/78) x 320 = 33600 ppm = 0.0336. Because from Figure 9, a pure 50 ppm TRS 10-80 shows a peak height of 78 units and in Figure 37 the peak height of the bottom phase is 164 units. Since the volume of the bottom layer is 2.1 ml, the weight of TRS 10-80 in the bottom phase will be 0.0336 x 2.1 = 0.071 grams. And the total weight of TRS 10-80 in the 10 ml mixture is 10 x 1% = 0.1 gram, assuming the solution density is equal to one. Thus, the weight of TRS 10-80 on the top is 0.1 - 0.071 = 0.029 grams. Because the volume of the top phase is 7.9 ml., the TRS 10-80 concentration in the top is 0.029/7.9 = 0.0037 = 3700 ppm. As comparing with the bottom one, 33600 ppm, the concentration ratio of the bottom to the top is 33600/3700, or 9.08.

Alcohol concentration is very important. Adding alcohol increased the CEC. It looks like a proportional effect. Figures 38 and Figure 39 show the CEC is increased as alcohol concentration is increased. Iso-butanol, sec-butanol, and iso-propanol all had about the same effect on the CEC.

Alcolac Siponate DS-10 in Oil-free Phase Volume Fraction System

Like in the TRS 10-80 system, polymer type and concentration do not influence the value of CEC. Figure 40 shows that xanflood and Natrosol have the
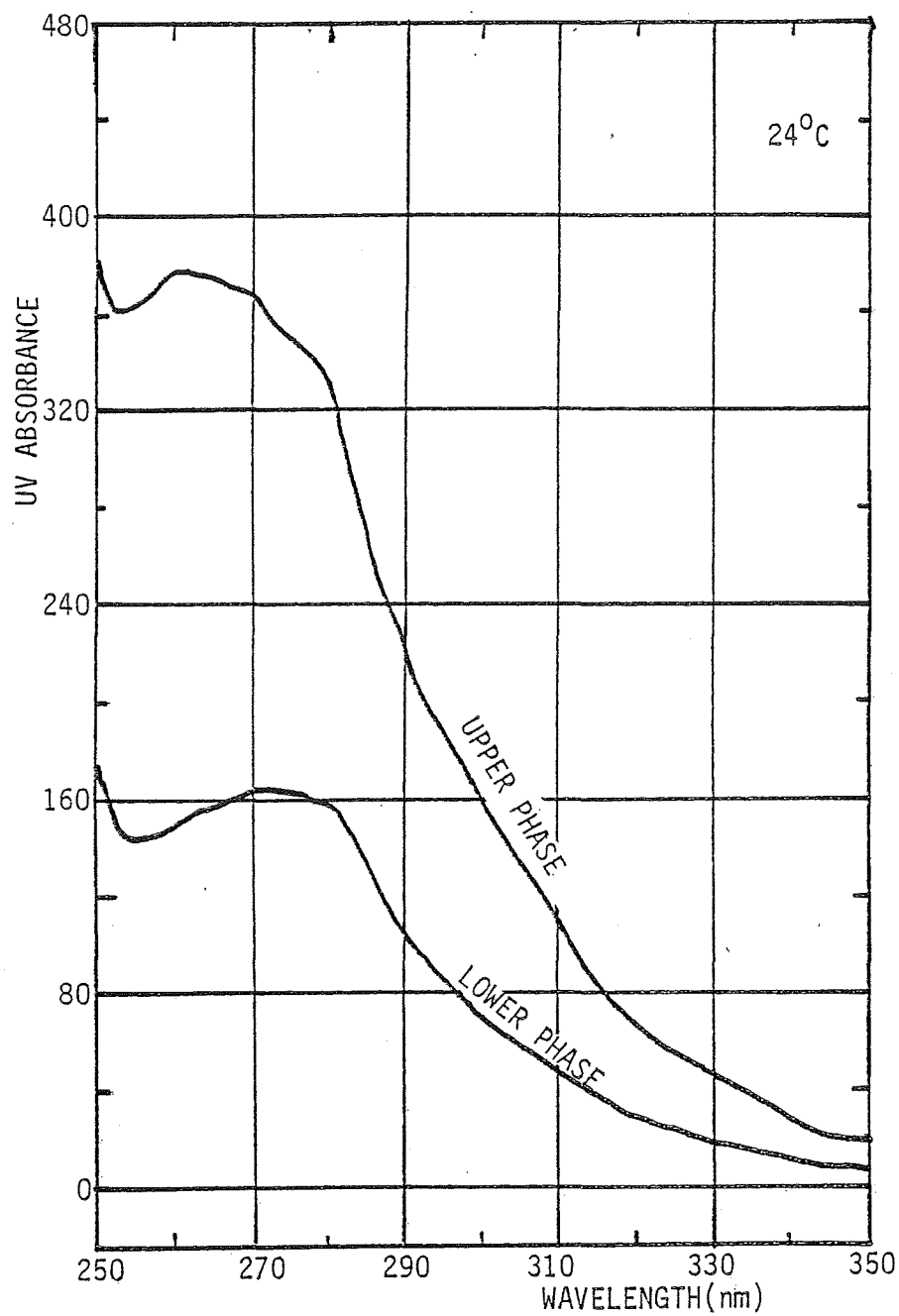
FIGURE 37. UV SPECTRA OF MIXTURE OF TRS 10-80, SEC-
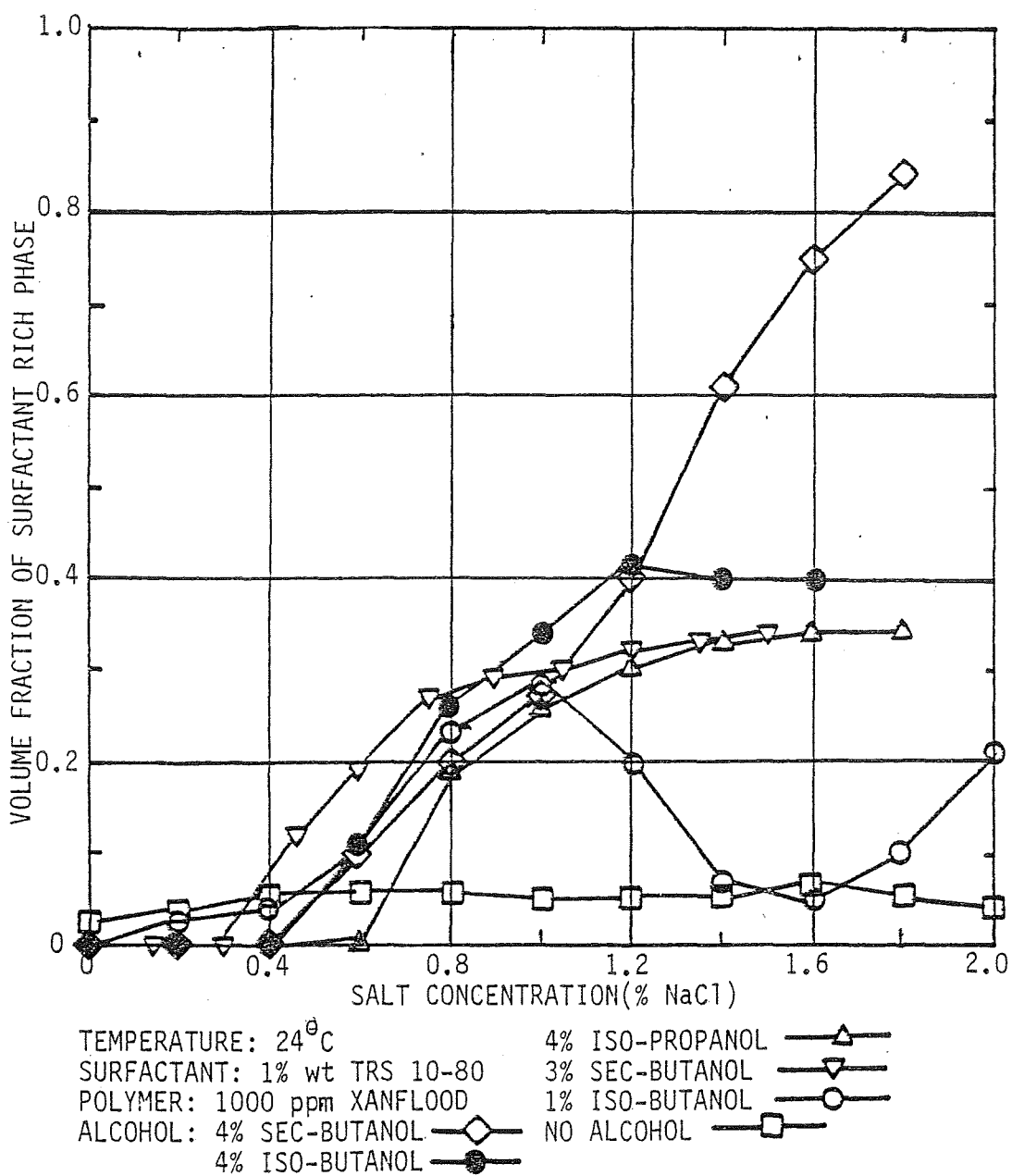BUTANOL, AND XANFLOOD IN BRINE

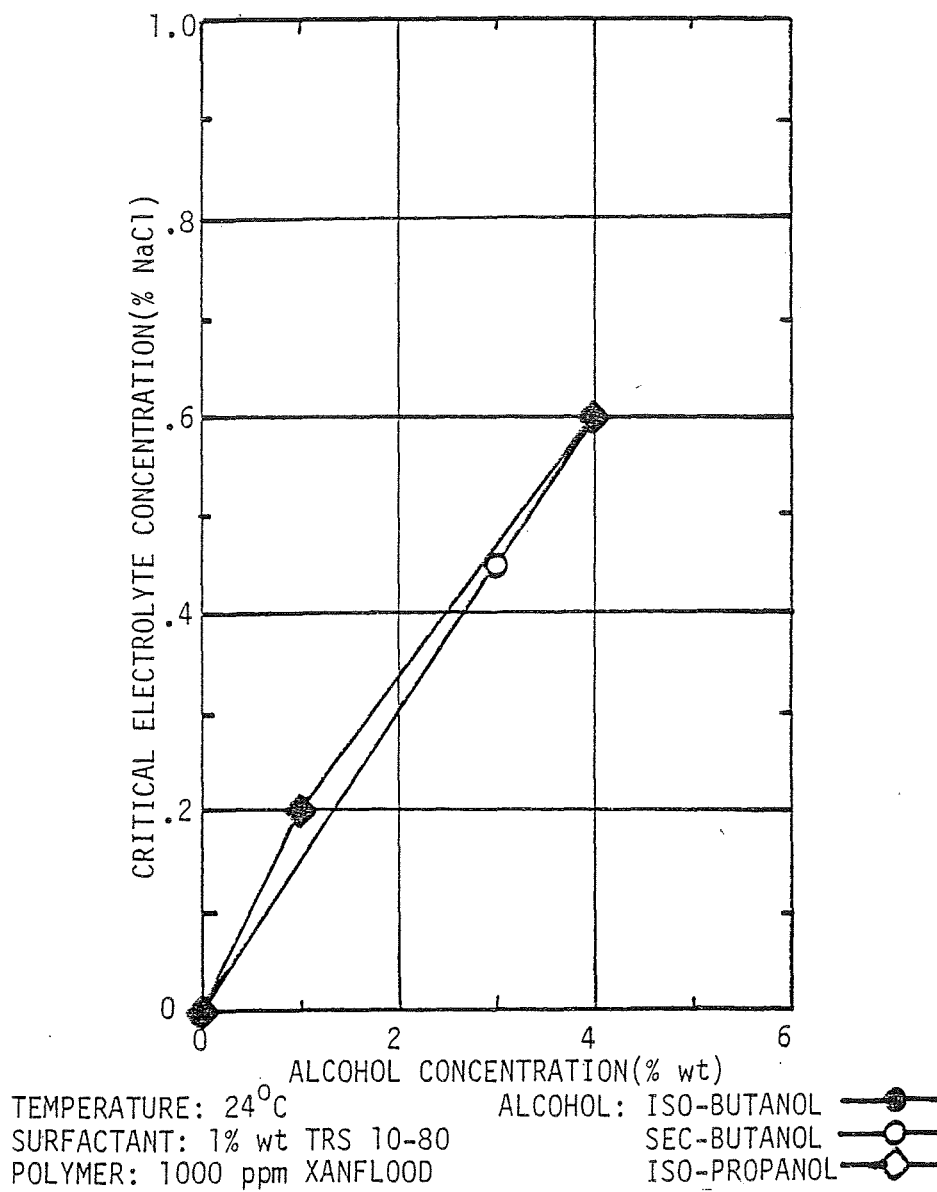FIGURE 38. EFFECT OF ALCOHOL TYPE AND CONCENTRATION ON TRS 10-80
SOLUTIONS

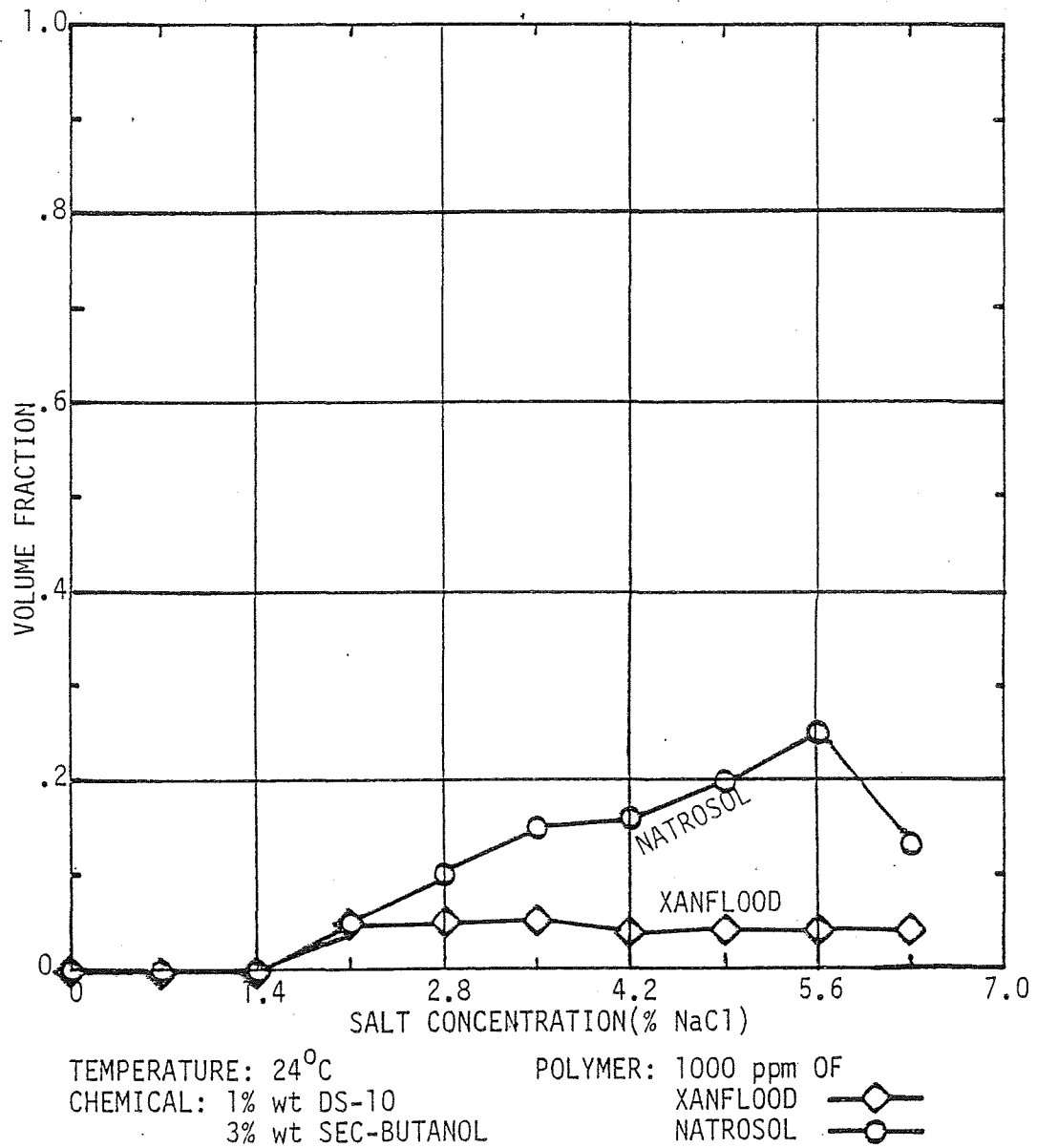FIGURE 39. ALCOHOL EFFECT ON CEC OF TRS 10-80

FIGURE 4o. EFFECT OF POLYMER TYPE ON DS-10 SOLUTIONS

same CEC value. Figure 41 shows 500 ppm of xanflood and 1000 ppm of xanflood gave about the same volume fraction with the 1% of DS-10 in 3% of iso-butanol at 24°C. All of the DS-10-rich phases are precipitate-like when sec-butanol was used. When iso-pentanol was used (see Figure 42), white solid occurred at higher salinity. But in the lower region, both of the phases were all liquid. Iso-pentanol, compared with sec-butanol, decreased the CEC (see Figure 42).

Witco TDA-100 in Oil-free Phase Volume Fraction System

3% wt of TDA-100 (without alcohol) and 1000 ppm of xanflood, Polyox Coagulant, Polyox WSR-301, and Polyox WSR N-3000 were investigated at 53°C. Figure 43 shows that the nonionic polymers (the Polyoxs) are more compatible with the nonionic surfactant (TDA-100) than the ionic polymer (xanflood). Xanflood shows a lower CEC than the Polyox.

At room temperature, 24°C, all the Polyox polymers and TDA-100 combinations gave single phases at the salinities up to 12% NaCl. For xanflood, two phases formed at 12% NaCl. The CEC is increased when temperature is decreased. This is different from the anionic surfactants. Figure 44 shows this opposite effect for TRS 10-80 and TDA-100.

GAF Igepal CO-610 in Oil-free Phase Volume Fraction System

Even in a polymer-free system, 3% wt of CO-610 and 3% wt of sec-butanol mixture in distilled water form two phases. The interface is not very clear at low salinity (less than 1% NaCl). As the salinity increased, the phase boundary became more readable, and the surfactant-rich phase was recognized at the bottom by its pale color up to 4% NaCl. Above 5% NaCl, surfactant-rich phase changed into the top phase, due to the high salt concentration. When Polyox (WSR-301 or WSR N-3000) was added, the same trend resulted except that
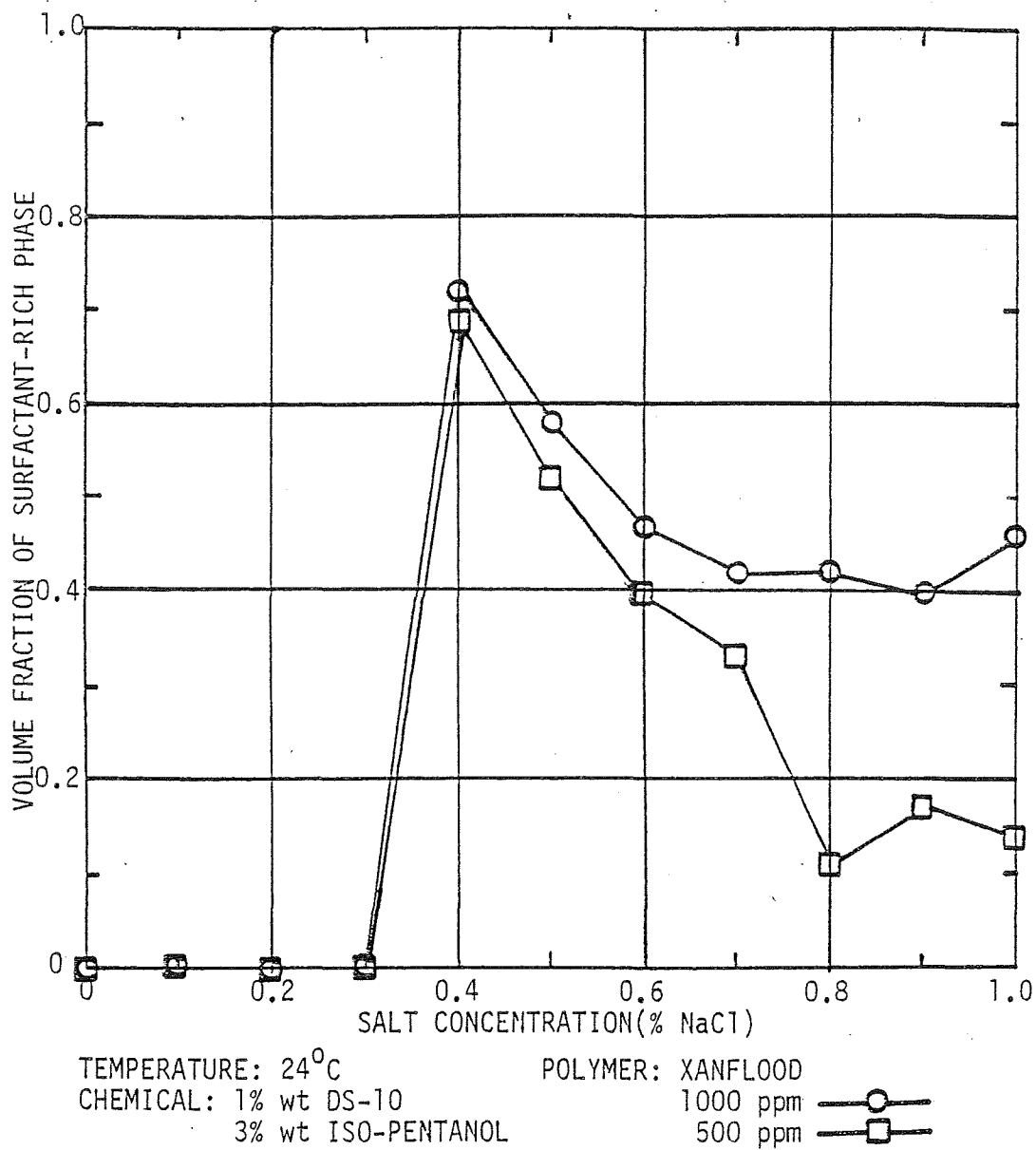
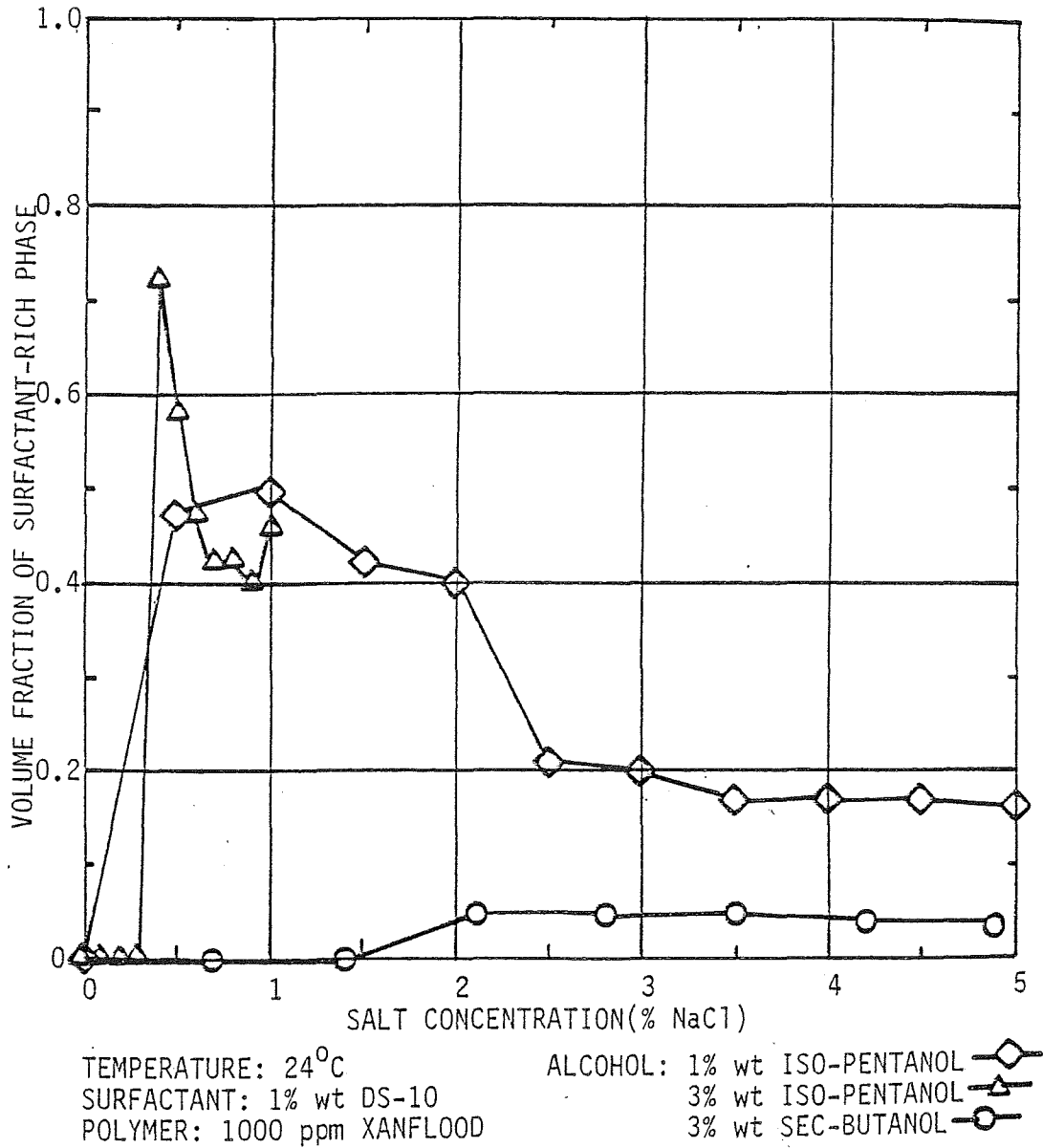FIGURE 41. EFFECT OF XANFLOOD CONCENTRATION
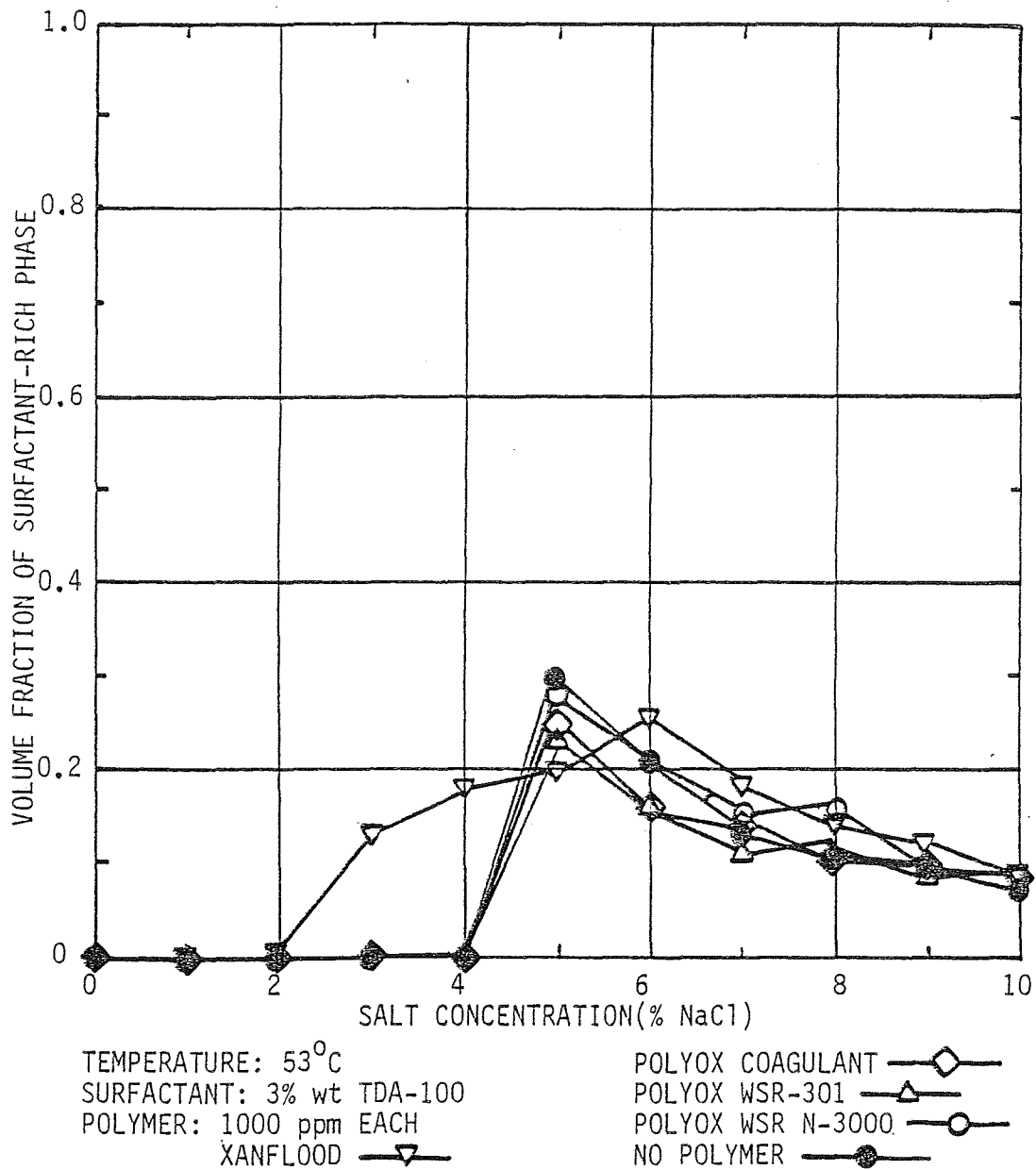
FIGURE 42. ALCOHOL EFFECT ON DS-10 SOLUTIONS

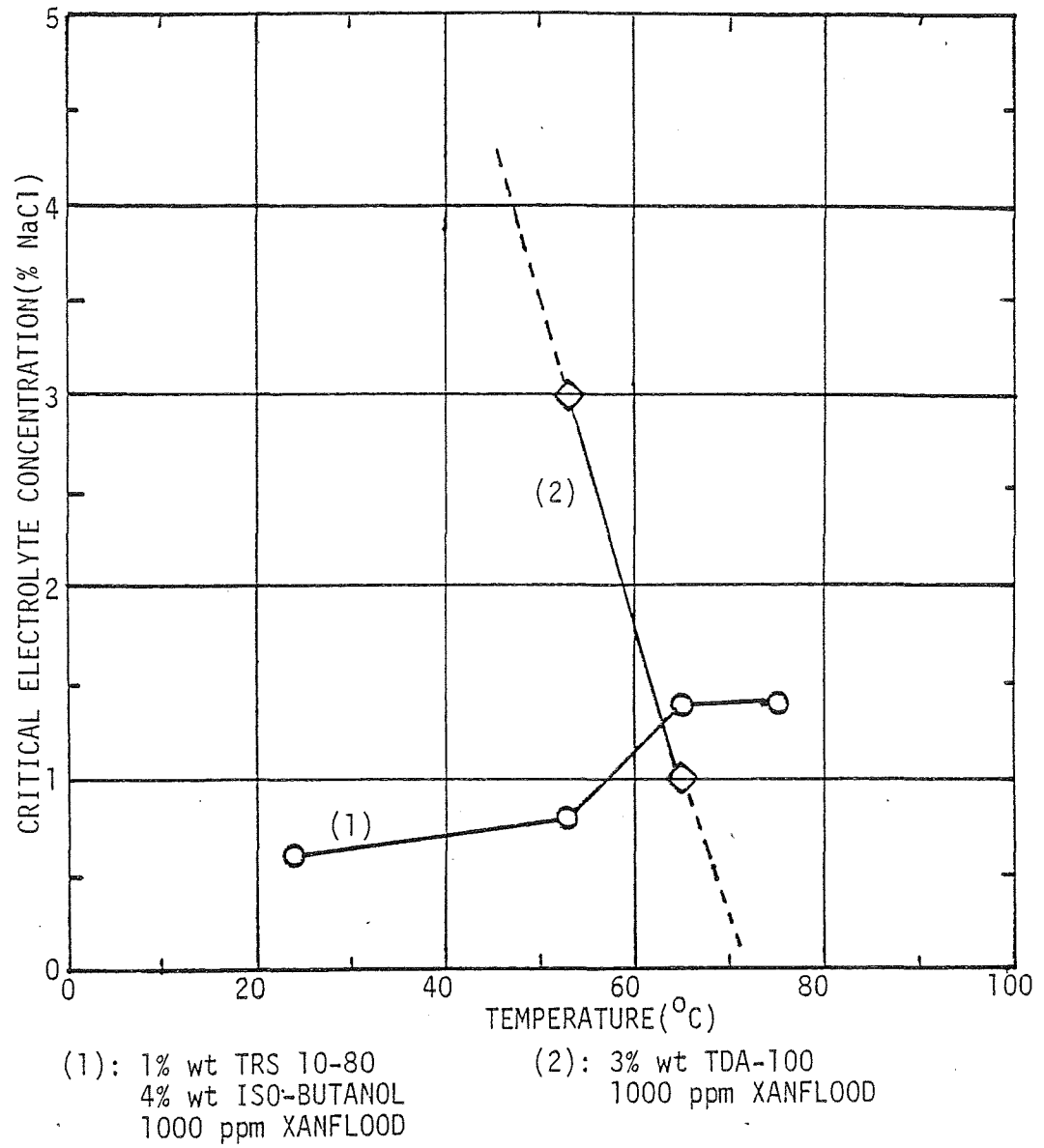FIGURE 43. EFFECT OF POLYMER TYPE ON TDA-100 SOLUTIONS

FIGURE 44. TEMPERATURE EFFECT ON CEC

the surfactant-rich phase appeared at the top when salinity was above 4% NaCl. It seems that polymer behaves as salt, which makes brine heavier than the surfactant-rich phase and goes down to the bottom at less salt concentration. It is really hard to find an interface in the xanflood case at 0% NaCl (see Figure 45). At 1% and 2% NaCl, xanflood condensed at the bottom. Surfactant-rich phase was at the bottom at 3% and 4% NaCl, and then appeared at the top at 5% NaCl or higher. Nevertheless, all the curves approach the same volume fraction value at higher salinity range (greater than 5% NaCl). The surfactant concentration was constant in every case.

Witco TRS 10-80 with Oil

Polymer-surfactant interaction was studied by changing salinity in systems containing fixed amounts of oil (20% by volume) and fixed amounts of surfactant, polymer, NaCl, and alcohol as indicated. This was to see how the type and concentration of polymer and alcohol and the addition of oil affected the phase behavior. Temperature was also varied.

20% vol. of n-octane and 80% vol. of aqueous phase which is made of 1% wt of TRS 10-80 (as is), 3% wt of sec-butanol, and variable NaCl, with or without 1000 ppm of xanflood were mixed together. Adding oil increased the CEC at 24°C and decreased the CEC at 75°C. It seems that xanflood shifts the whole three phase range in the lower salinity direction (see Figures 46, 47). Raising the temperature to 75°C did not eliminate the salinity shift caused by the polymer. Figure 48 is a more detailed study of the same system plotted in Figure 46. The oil free, polymer free, aqueous surfactant solution itself separated into two liquid phases (coacervated) at 2.5% NaCl.

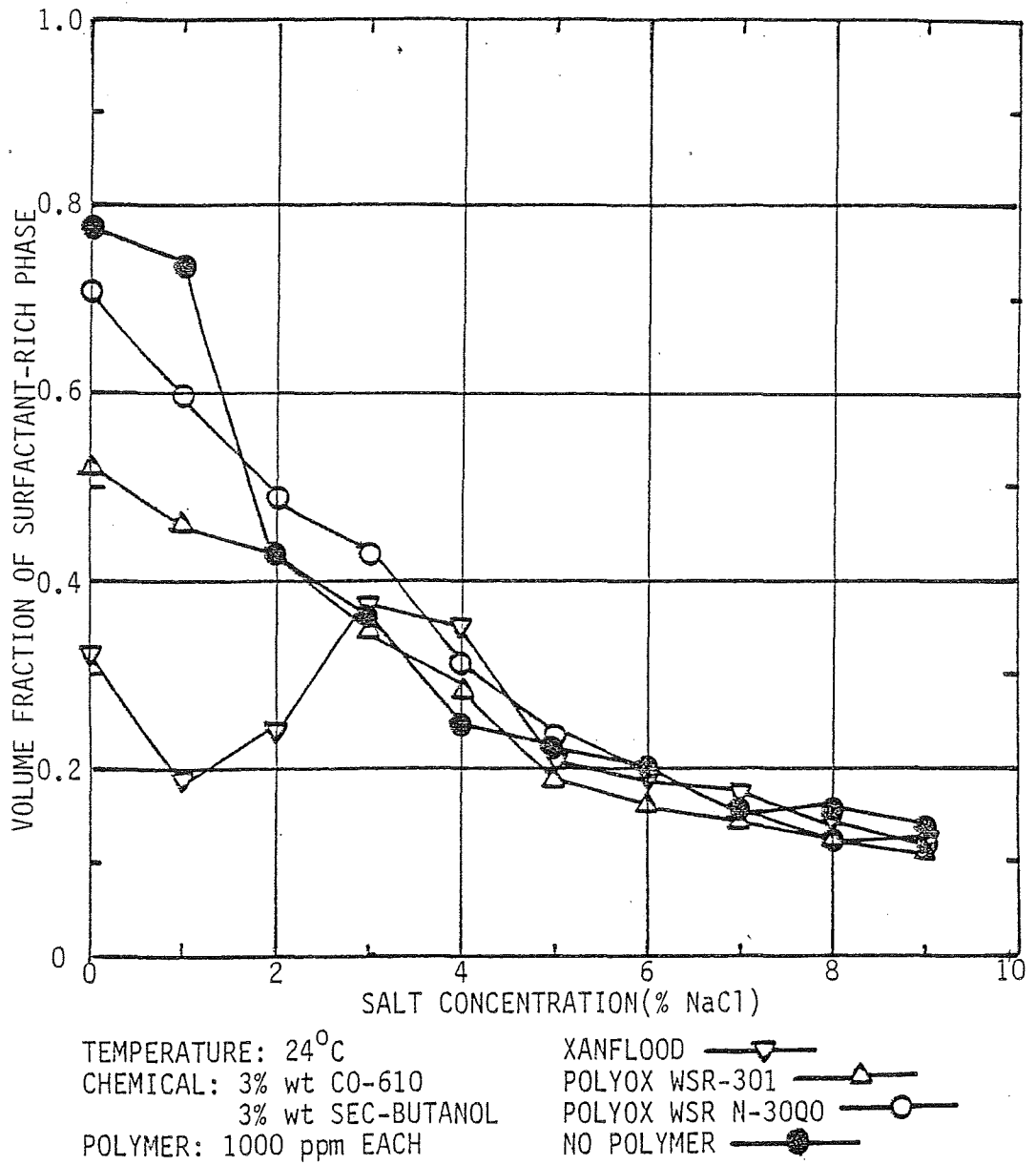The viscosity of the oil-free TRS 10-80/sec-butanol mixture versus

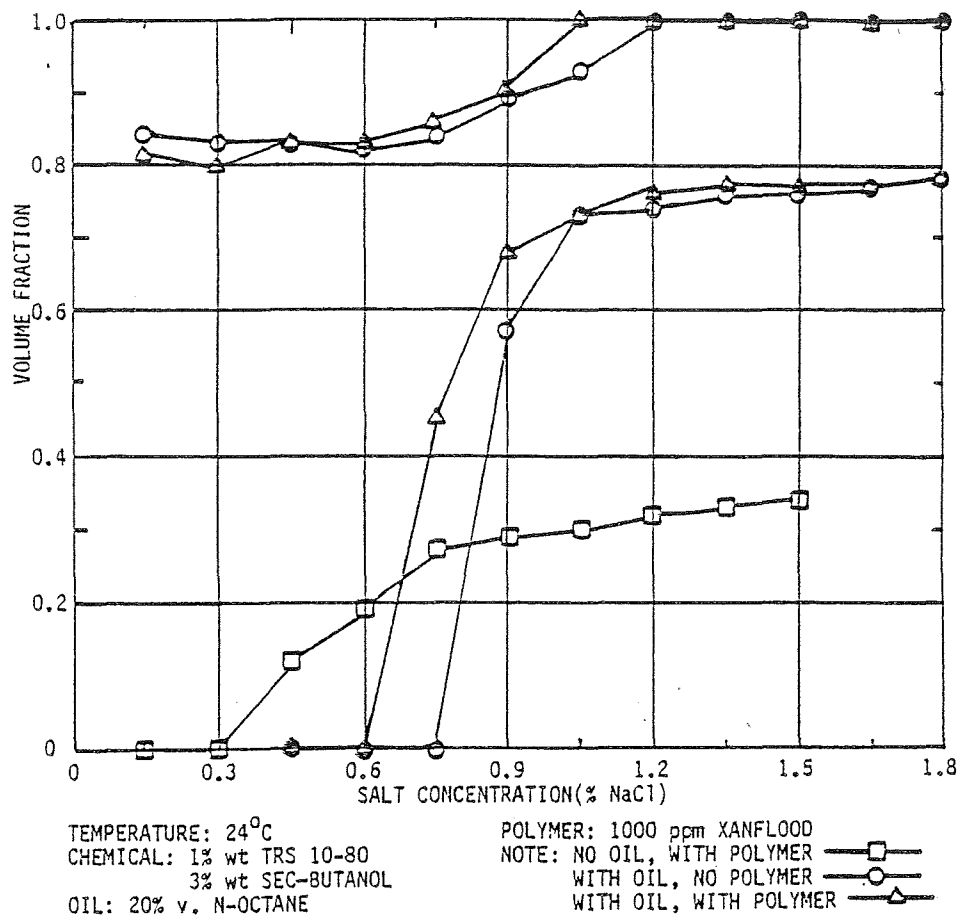FIGURE 45. PHASE BEHAVIOR OF IGEPAL CO-610 AND VARIOUS POLYMERS
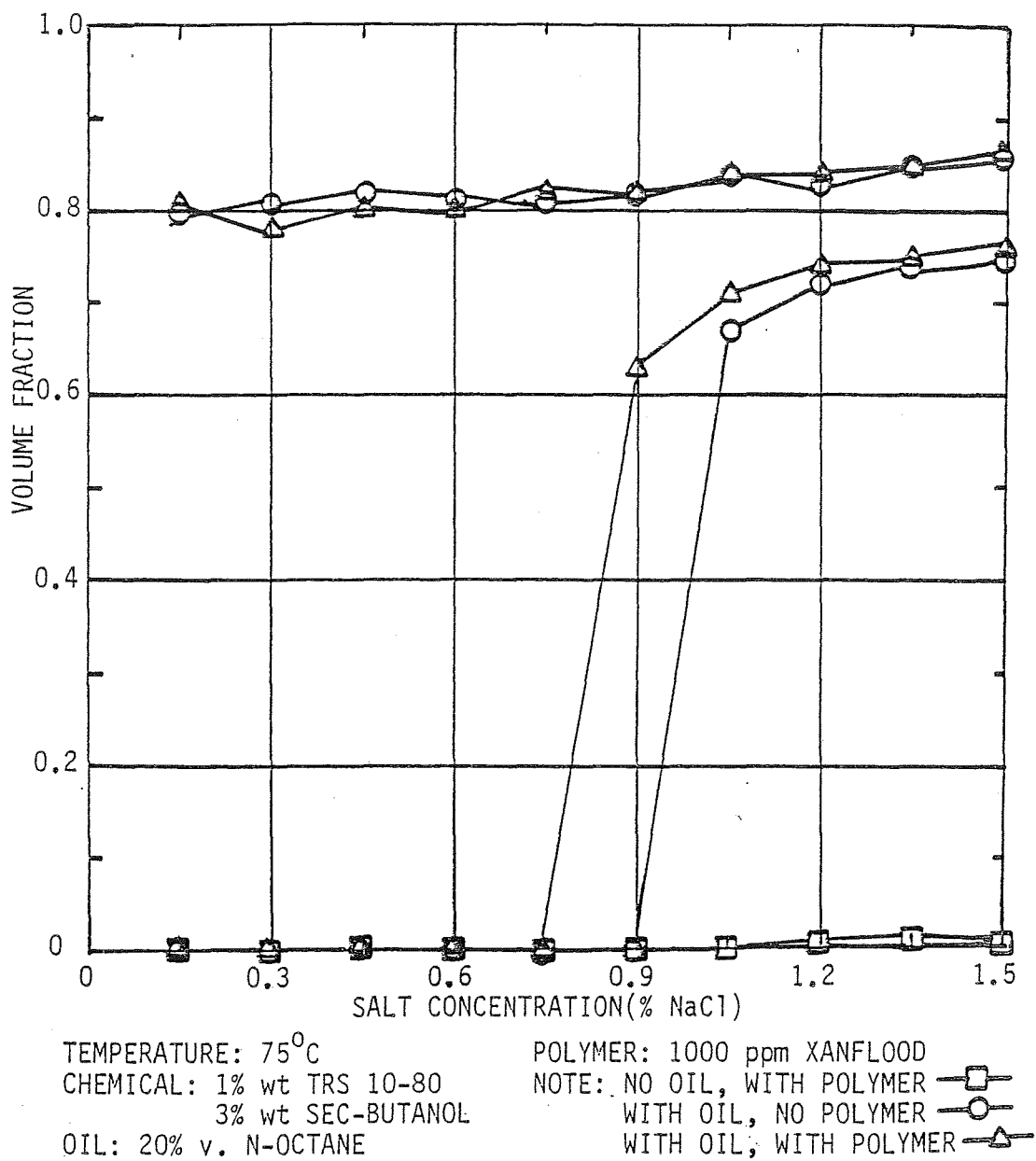
FIGURE 46. TRS 10-80 BEHAVIOR AT 24°C

FIGURE 47. TRS 10-80 BEHAVIOR AT 75°C
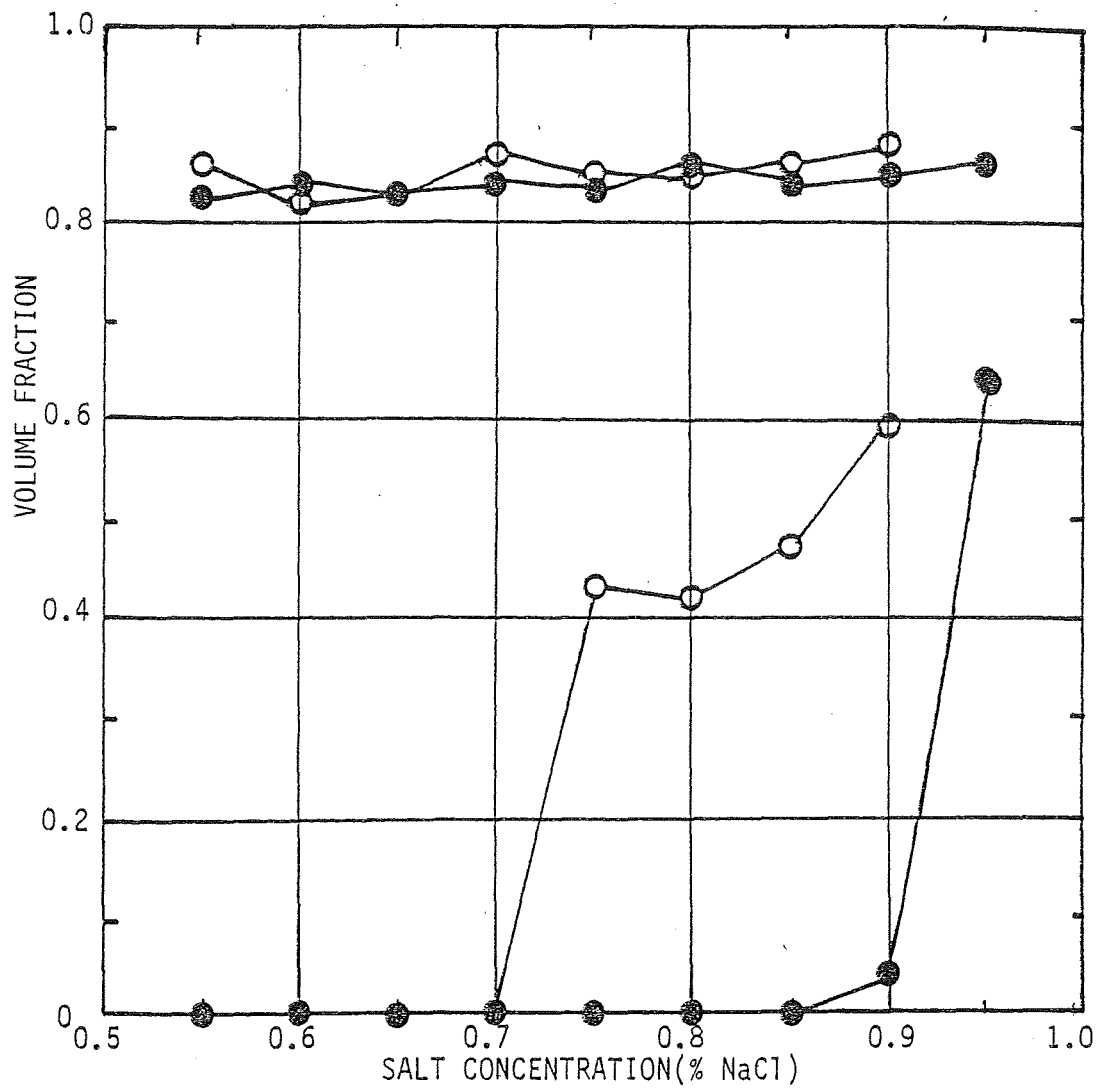
FIGURE 48. TRS 10-80 BEHAVIOR AT 24°C

salt concentration was measured by LS-30. Figure 49 shows the viscosity increased as salinity increased. When 1000 ppm of xanflood is added to this oil-free system, two layers form at 0.45% NaCl, as mentioned before. The lower phase with more surfactant and less polymer, called the surfactant-rich phase, has lower viscosity than the top layer of higher polymer content and lower surfactant content.

When oil is added, a middle, microemulsion phase forms as shown in Figure 46. Most of the surfactant is in this phase. Its viscosity is shown in Figure 50. At low salinity, below 0.75% NaCl in Figure 50, the viscosity of the microemulsion of polymer-free should be about the same as that of the oil-free, polymer-free solution (Figure 49). At 0.9% NaCl, three phases formed, and surfactant concentrated in the middle phase (microemulsion phase). Since the concentration of the surfactant is higher than that at the lower salinity, the viscosity of the microemulsion is increased. At even higher salt concentration, viscosity decreases. With polymer, the viscosity of the microemulsion at low salinity is about 30 cp. The viscosity with and without oil is the same at 0.15% and 0.3% NaCl (see Figures 49 and 50). At salt concentration of 0.45% and 0.6% NaCl, the microemulsion viscosity was still 30 cp, but surfactant-polymer mixture viscosity split into two values. The surfactant-rich phase has a viscosity lower than 30 cp. At 0.75% NaCl in Figure 50, xanflood induced an additional phase. The middle phase considered as the microemulsion phase has a viscosity much lower than 30 cp, due to the expulsion of xanflood from the microemulsion phase. There is no significant difference of viscosity in the higher salinity range even when polymer is added, because the microemulsion contains high concentrations of oil and surfactant, while most of the polymer is in the brine phase.
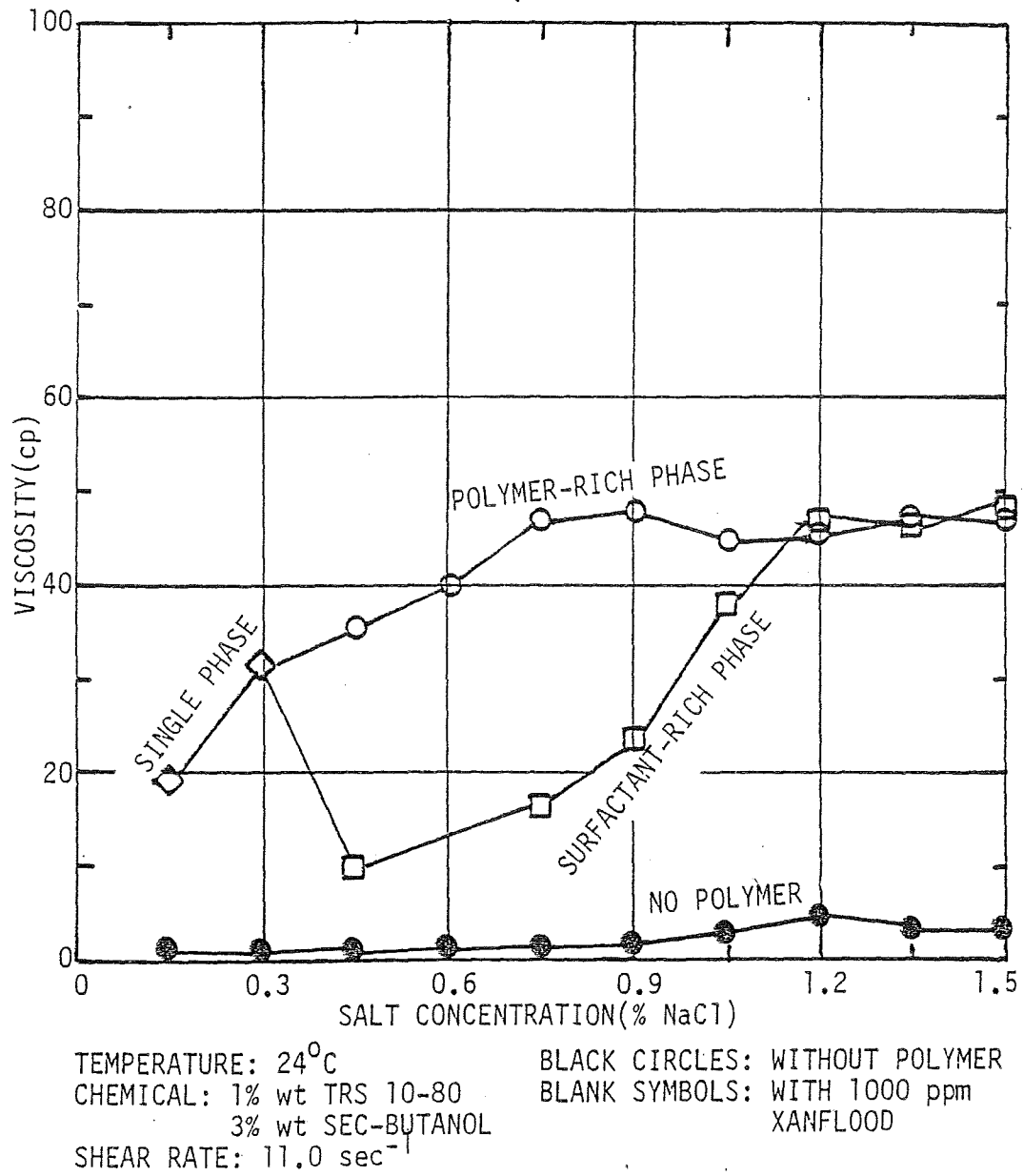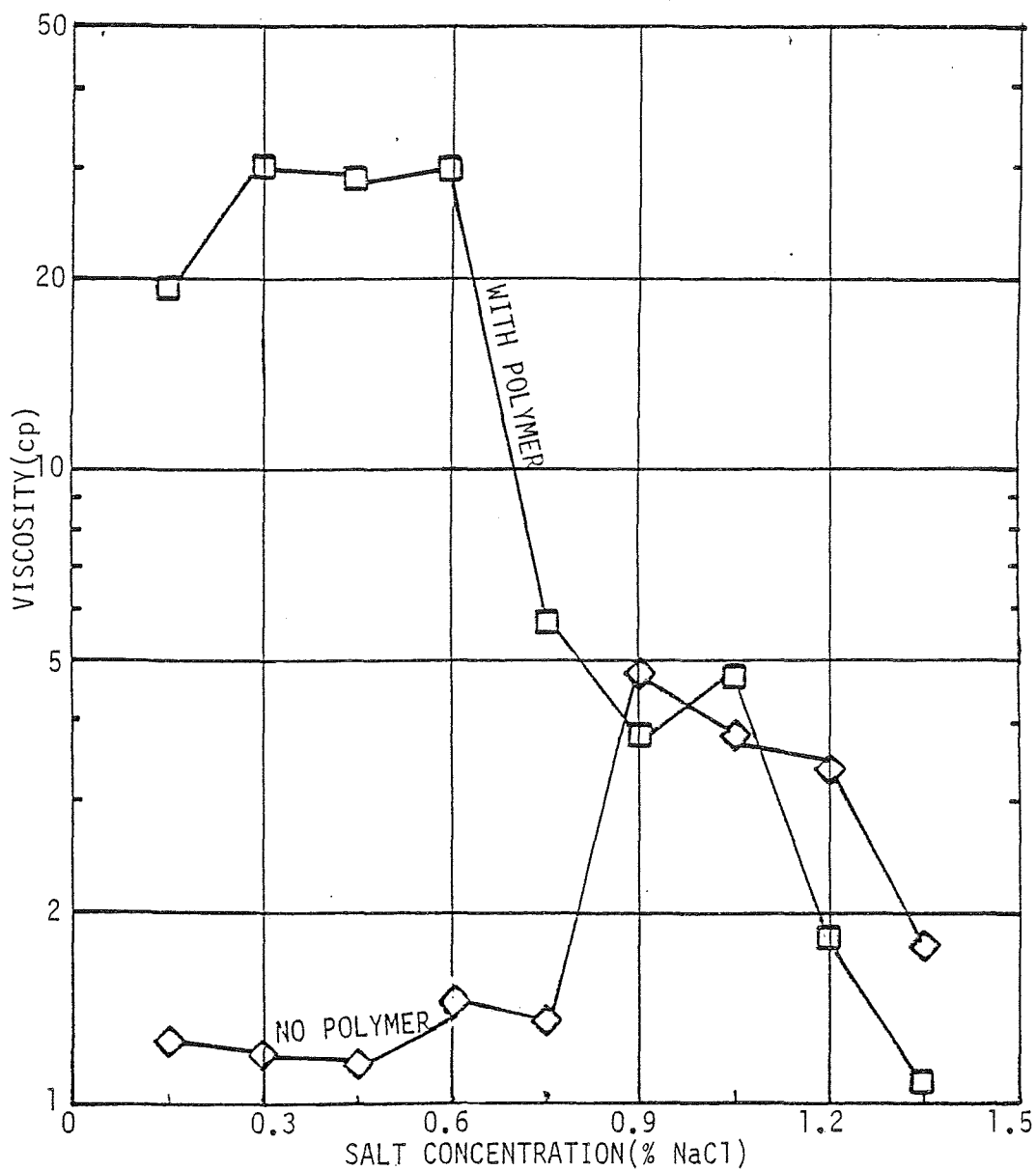
FIGURE 49. VISCOSITY OF TRS 10-80 SOLUTIONS WITHOUT ADDED OIL

FIGURE 50. VISCOSITY OF TRS 10-80 WITH OIL AT 24°C

Therefore, adding polymer did not affect the viscosity of the top (microemulsion) phase. Figure 51 shows the shear rate effect on the viscosity of microemulsion with and without xanflood.

Alcolac Siponate DS-10 with Oil

Chemicals used in this system were 1% wt of DS-10 and 3% wt of sec-butanol based on the aqueous phase. 1000 ppm of polymers, such as xanflood and Natrosol 250 HHR(HEC), may be included in the aqueous phase, too, in order to compare with the one without polymer. 80% vol. of this aqueous phase (with or without polymer) was mixed by 20% vol. of n-octane. In figure 52, the addition of oil apparently will increase the polymer-surfactant compatibility. Adding polymers seems not to make any additional phase in the oil-included system. A more detail study is needed by experiment to check the phase behavior between the salinity of 3.6% and 4.8% NaCl. Xanflood and HEC seem give the same CEC, although HEC shows an early end of three phase trend.

Stepan Petrostep 465 with and without Oil

Figure 53 shows four kinds of combination of 1% wt of Petrostep 465, 3% wt of sec-butanol, 1000 ppm of xanflood, and 20% vol. of oil mixture of 90% v. of n-octane and 10% v. of benzene. Again, polymer induced an additional phase in the oil-free system but not in the oil-included system. A further study of the oil-included system is necessary to find out if SPI occurs somewhere between 0.45% and 0.6% NaCl. Adding oil increases CEC, too.

Exxon MEAC12OXS with Oil

The aqueous phase of this test contained 1% wt of MEAC12OXS, and 3% wt of sec-butanol. Two sets of experiment, one without polymer, the other with 1000 ppm of xanflood in the aqueous phase, were done by mixing the aqueous
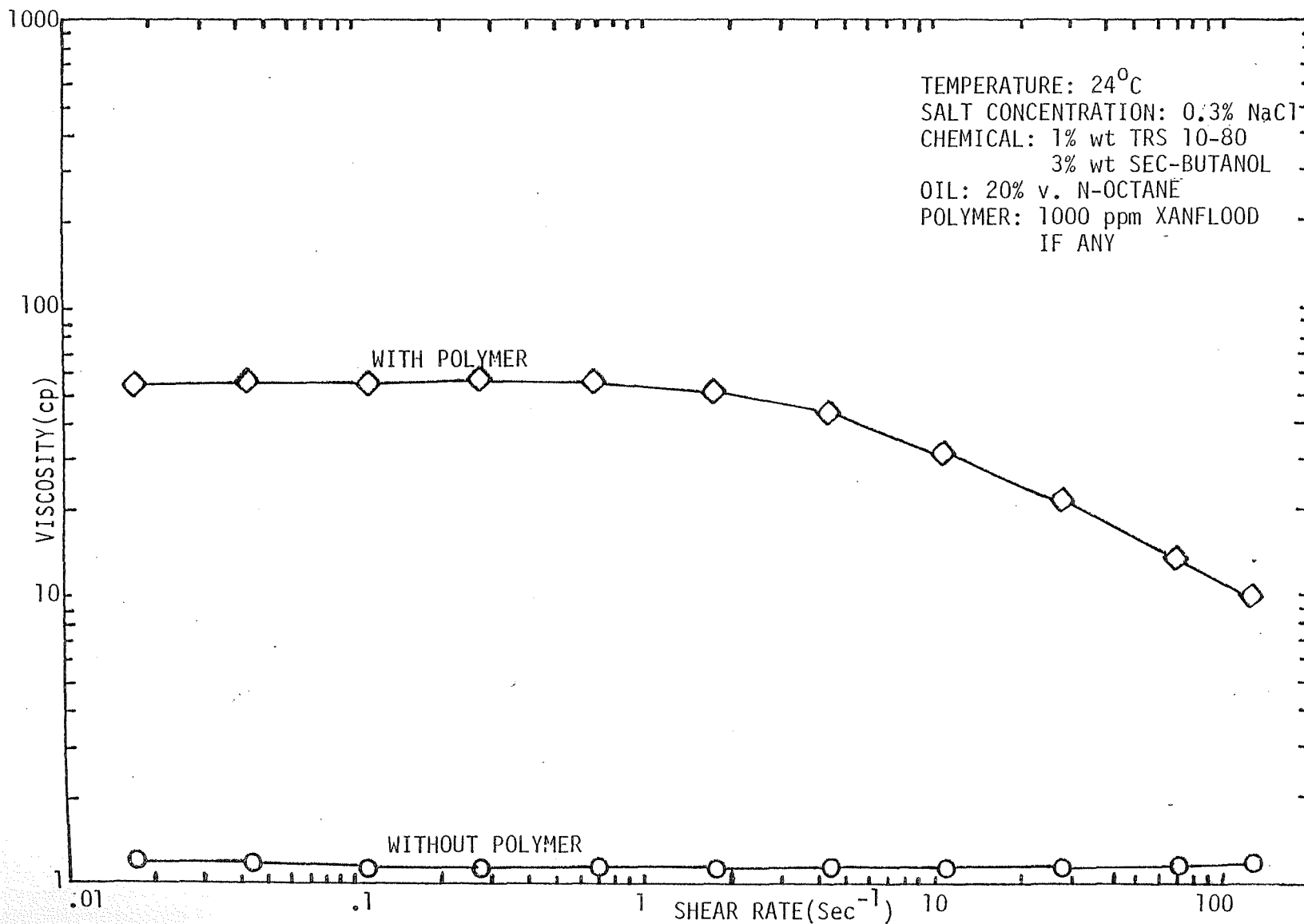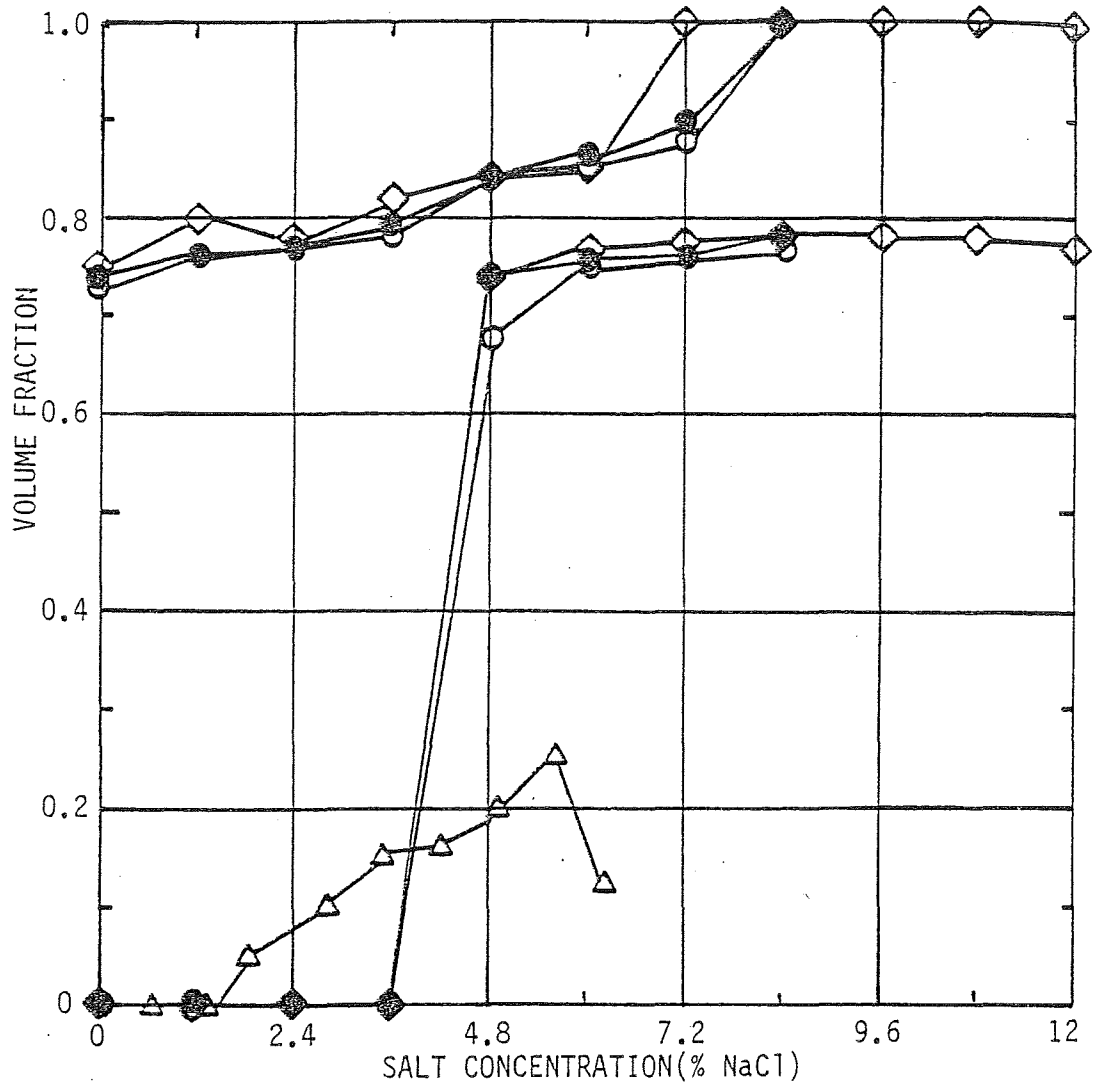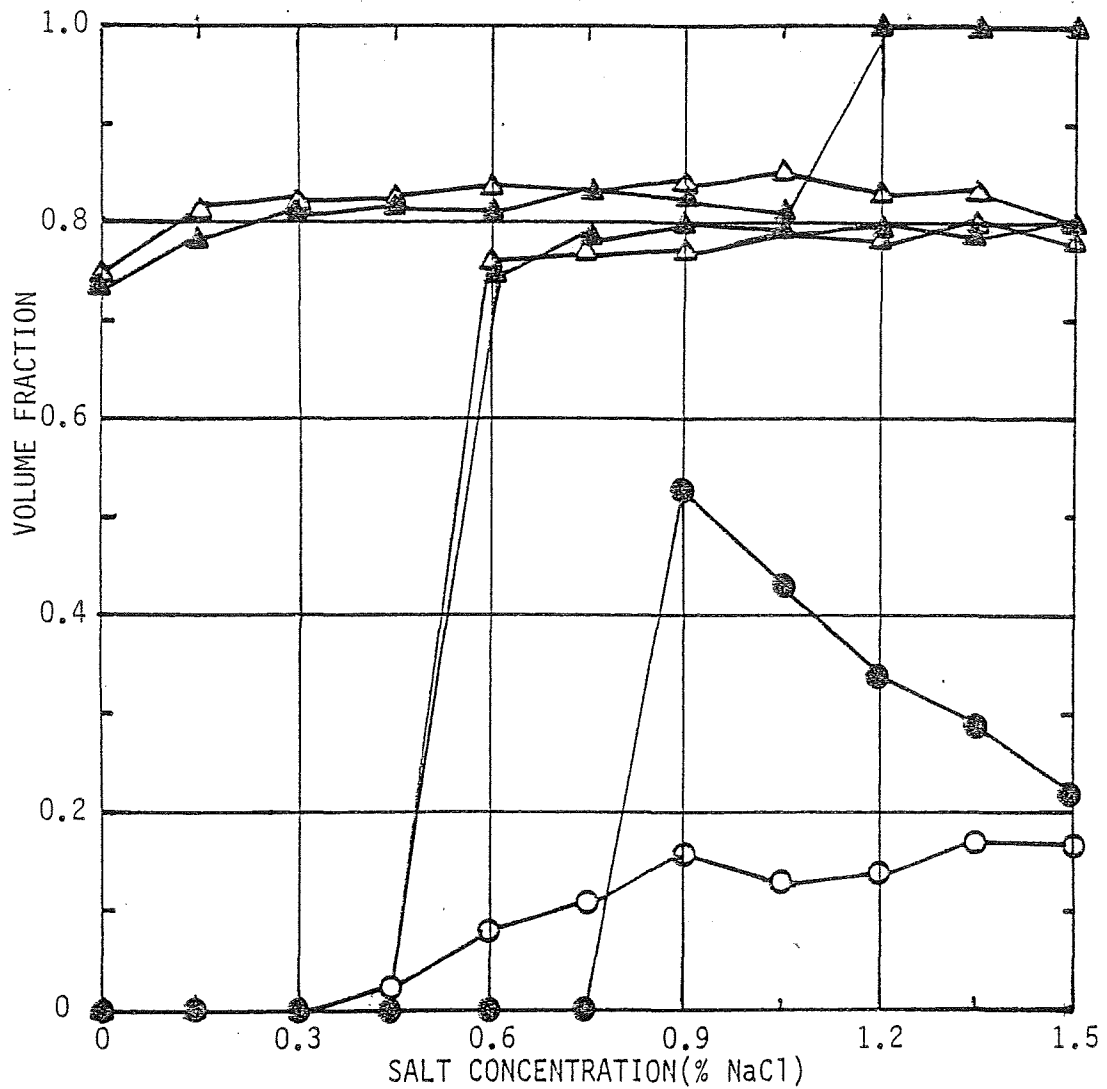
FIGURE 51. VISCOSITY OF MICROEMULSION WITH AND WITHOUT XANFLOOD

TEMPERATURE: 24°C
SALT CONCENTRATION: 0.3% NaCl
CHEMICAL: 1% wt TRS 10-80
             3% wt SEC-BUTANOL
OIL: 20% v. N-OCTANE
POLYMER: 1000 ppm XANFLOOD
             IF ANY

WITH POLYMER

WITHOUT POLYMER

VISCOSITY(cp)

SHEAR RATE(Sec^{-1})

FIGURE 52. EFFECT OF POLYMER TYPE AND POLYMER ADDITION ON DS-10
SOLUTIONS

TEMPERATURE: 24°C   POLYMER: 1000 ppm XANFLOOD
CHEMICAL: 1% wt PETROSTEP 465   NO OIL, NO POLYMER
        3% wt SEC-BUTANOL   NO OIL, WITH POLYMER
OIL: 20% v. OF 90% v. N-OCTANE   WITH OIL, NO POLYMER
       10% v. BENZENE   WITH OIL, WITH POLYMER

FIGURE 53. EFFECT OF POLYMER ON PETROSTEP 465 SOLUTIONS

phase with n-octane in a volume ratio of 4:1. Figure 54 shows that xanflood induced an additional phase at salinity 1.25% NaCl.

Witco TDA-100 with Oil

3% wt of TDA-100 was used as the chemical, no alcohol was included in the aqueous phase. 1000 ppm of xanflood, and Polyox Coagulant, may be contained in the aqueous phase. 80% vol. of this aqueous phase and 20% vol. of oil (80% vol. of n-octane and 20% vol. of benzene) were mixed together. Higher temperature, $53^{\circ}C$, was set instead of $24^{\circ}C$. Because only two phases, one is oil phase on the top and the other is microemulsion phase at the bottom, were obtained in the salinity range of 0% to 12% NaCl. Increasing temperature will shift the three phase region from the left to the right.

At $53^{\circ}C$, adding oil will increase CEC for xanflood (compare Figures 43 and 55), but not for the Polyox Coagulant.

It seems that Polyox shows a more compatible result than xanflood. Because the molecular structure of Polyox is pretty like the structure of TDA-100. Both of them are nonionic and have polyethylene oxide chains. Like Polyox Coagulant, Polyox WSR-301 and polyox WSR N-3000 gave the same CEC and phase diagrams as Polyox Coagulant.

GAF Igepal CO-610 and CO-530 with Oil

Igepal CO-610 is a clear, transparent, liquid-type, nonionic surfactant with an average of 7.5 ethoxylated groups and an average molecular weight of 595. Pure CO-610 is a Newtonian fluid with a viscosity of 275 cp at $24^{\circ}C$.

3% wt of CO-610 was used in the aqueous phase for this study. The oil is a mixture of 80% vol. of n-octane and 20% vol. of benzene. Several combinations of alcohol were used to check the effect of alcohol. Anionic and
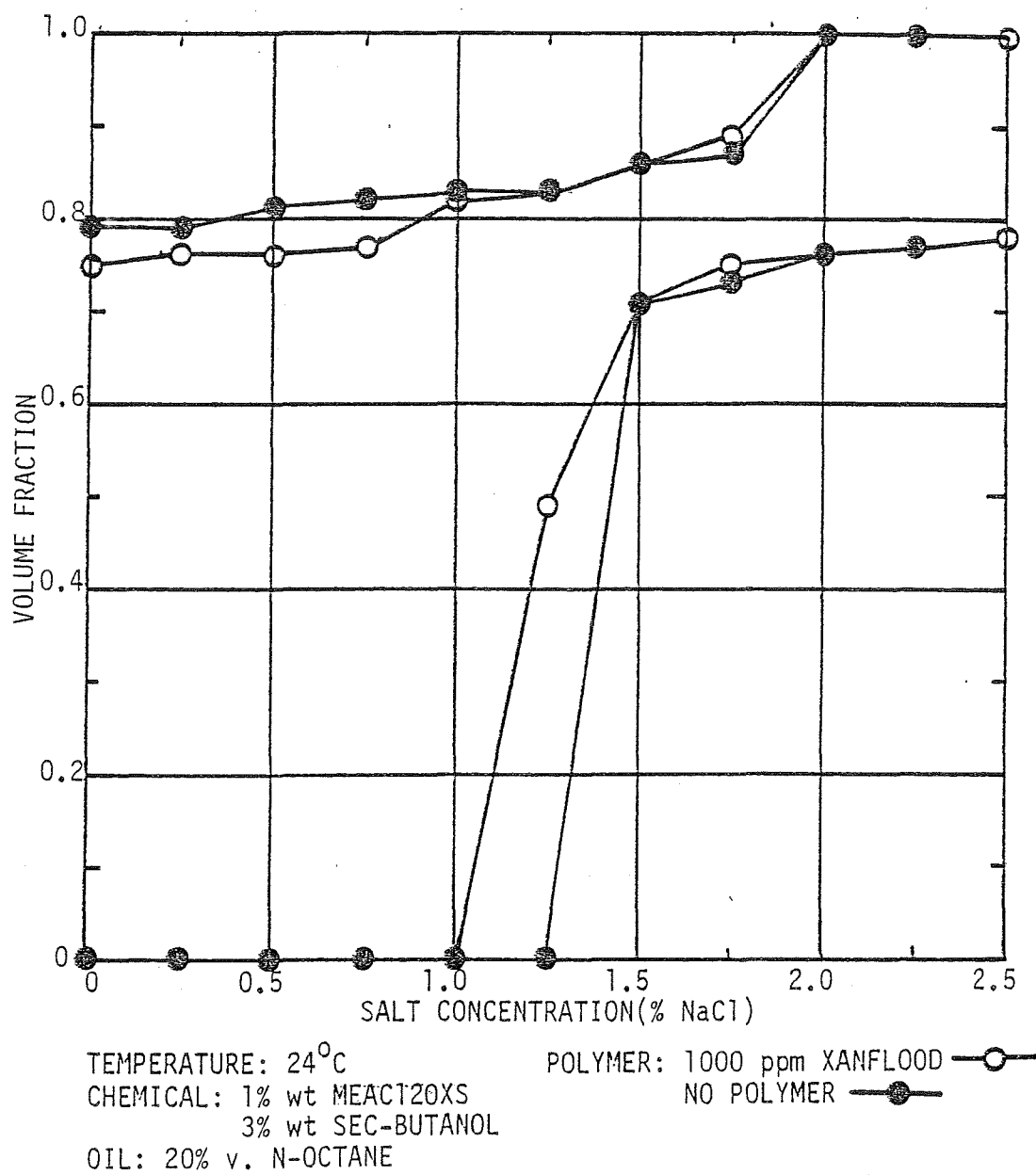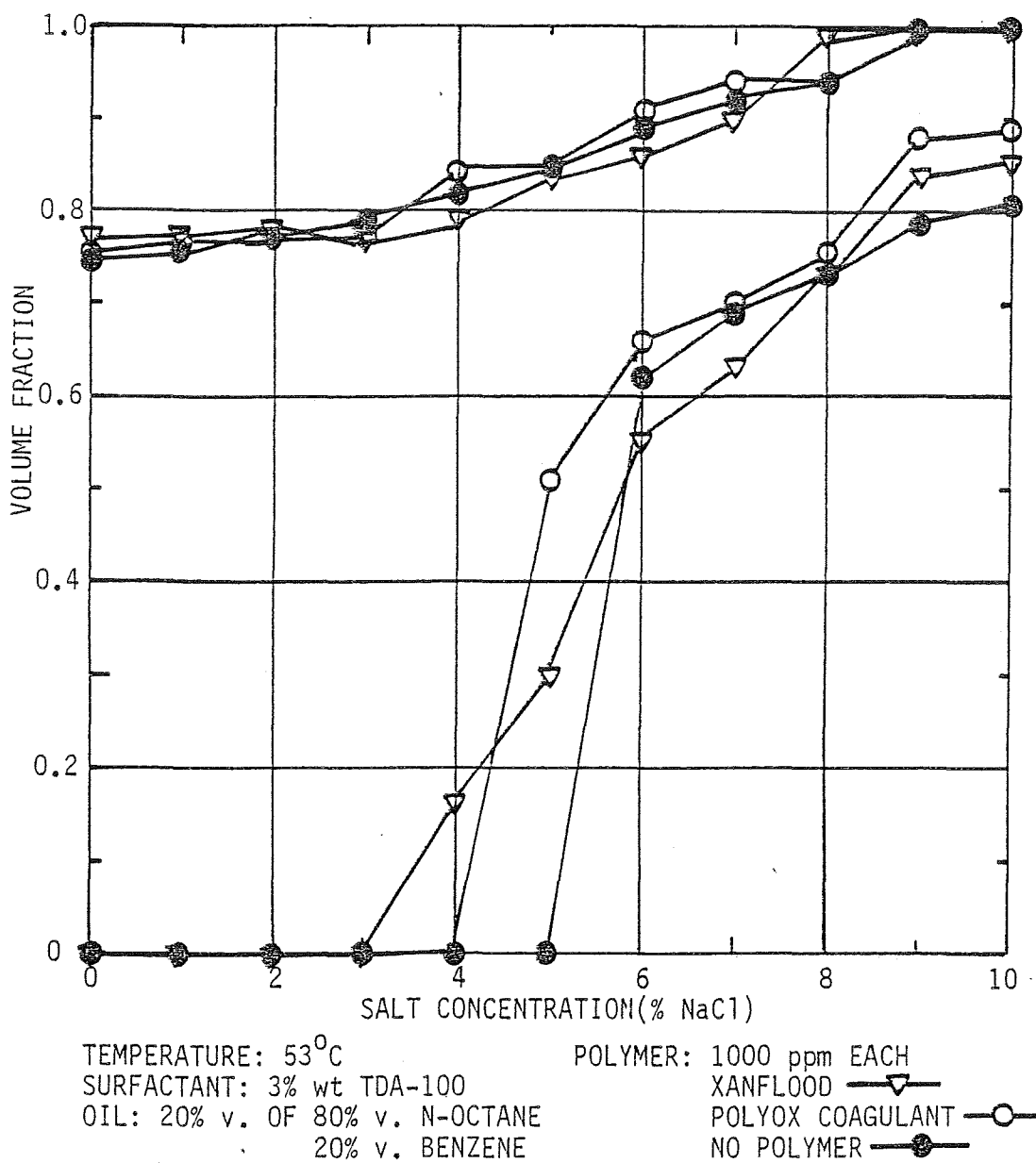
FIGURE 54. MEAC120XS BEHAVIOR AT 24°C

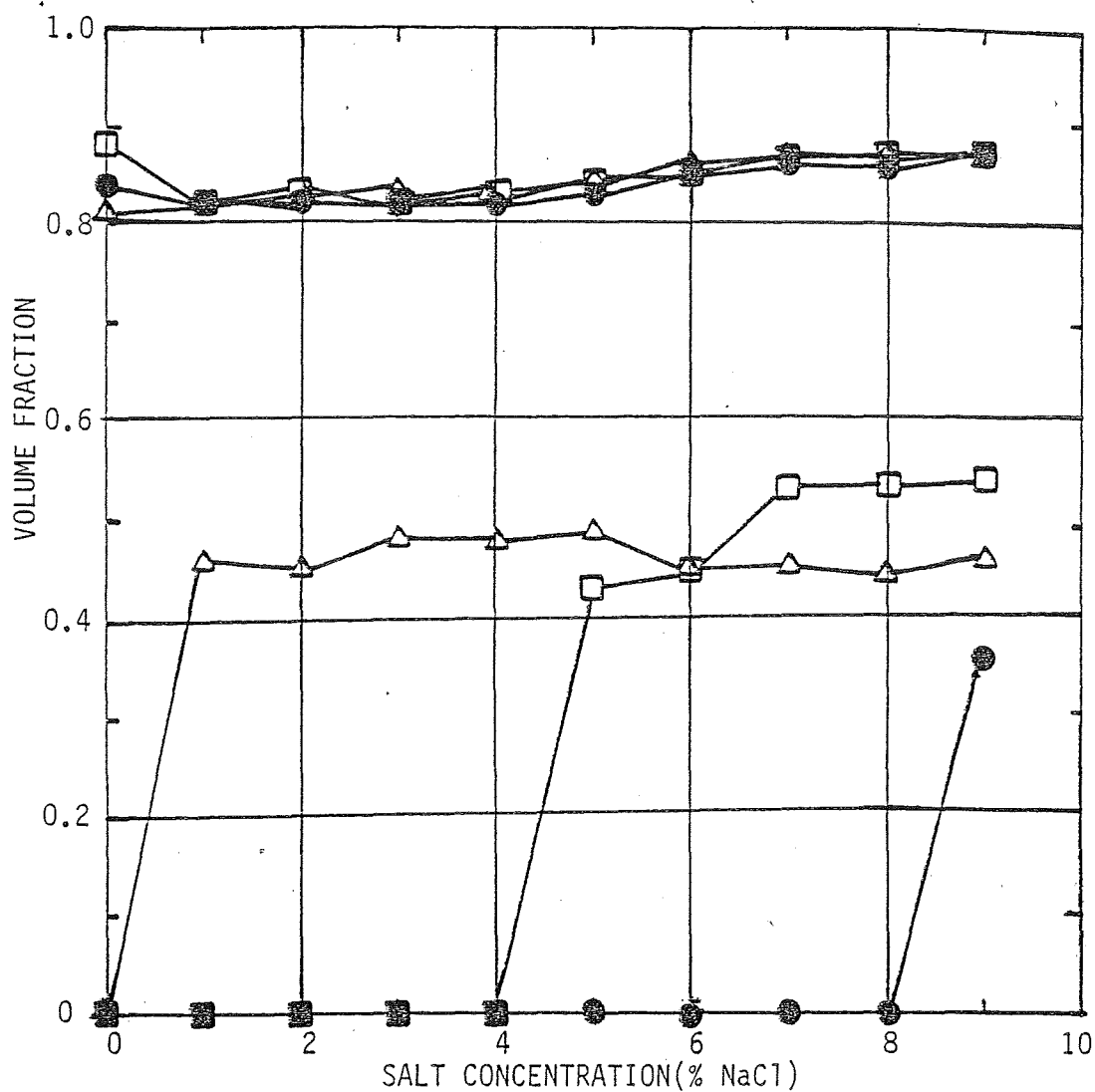FIGURE 55. EFFECT OF POLYMER TYPE ON TDA-100 SOLUTIONS

nonionic polymers were also included in the aqueous phase. 80% vol. and 20% vol. of aqueous phase and oil were mixed.

When no alcohol was added, the polymers made a big difference in the phase behavior, especially the xanflood (see Figure 56). When alcohol was added, xanflood and Polyox, like for TDA-100, show different behavior with CO-610. In Figure 57, the concentration of sec-butanol was 3% wt (oil free basis). Polyox WSR N-3000 was the most compatible with CO-610. As seen by comparing Figures 57, 58 and 59, heavier alcohol reduce the difference between systems with and without polymer. For 1% wt of iso-pentanol, 3% wt of sec-butanol, and 1% wt of iso-pentanol plus 3% wt of sec-butanol, the difference in the CEC is 1%, 2%, and 3% NaCl respectively for Polyox Coagulant.

A nonionic surfactant mixture, 2.3% wt of Igepal CO-530 and 0.7% wt of Igepal CO-610, based on the aqueous phase, was also used. The molecular weight of CO-530 is 484, and it has six ethoxylated groups. 1% wt of iso-pentanol was selected. The oil is n-octane. Various polymers, all at 1000 ppm, were used in the aqueous phase. This mixture of surfactants gave the same trend as before. All of the high molecular weight polymers show a less compatibility with the nonionic surfactant mixture (see Figure 60) than Polyox WSR N-3000.

Figure 61 (see Table 4 also) shows a plot of CEC with xanflood versus CEC without xanflood. All the cases were measured at 24°C. Anionic and nonionic surfactants were investigated. Both of the lines for anionic and nonionic surfactants have slopes greater than one. Also, the slope of the nonionic surfactant line is greater than that of the anionic line. Therefore, xanflood is less compatible with the nonionic surfactants than the anionic surfactants.

Viscosity of Xanflood Solution

FIGURE 56. EFFECT OF POLYMER TYPE ON CO-610 SOLUTIONS WITHOUT ALCOHOL

TEMPERATURE: 24°C

SURFACTANT: 3% wt CO-610

OIL: 20% v. OF 80% v. N-OCTANE
          20% v. BENZENE

POLYMER: 1000 ppm EACH
XANFLOOD ————△————
POLYOX COAGULANT—□—
NO POLYMER ——●——

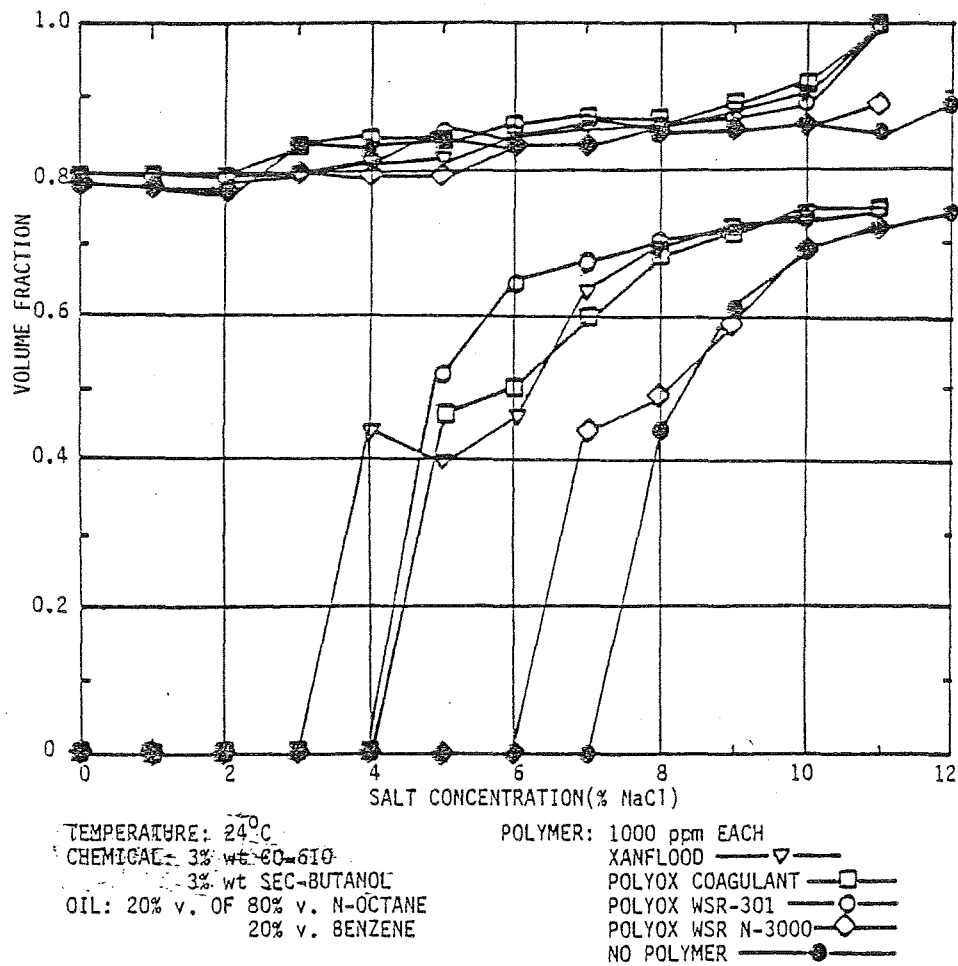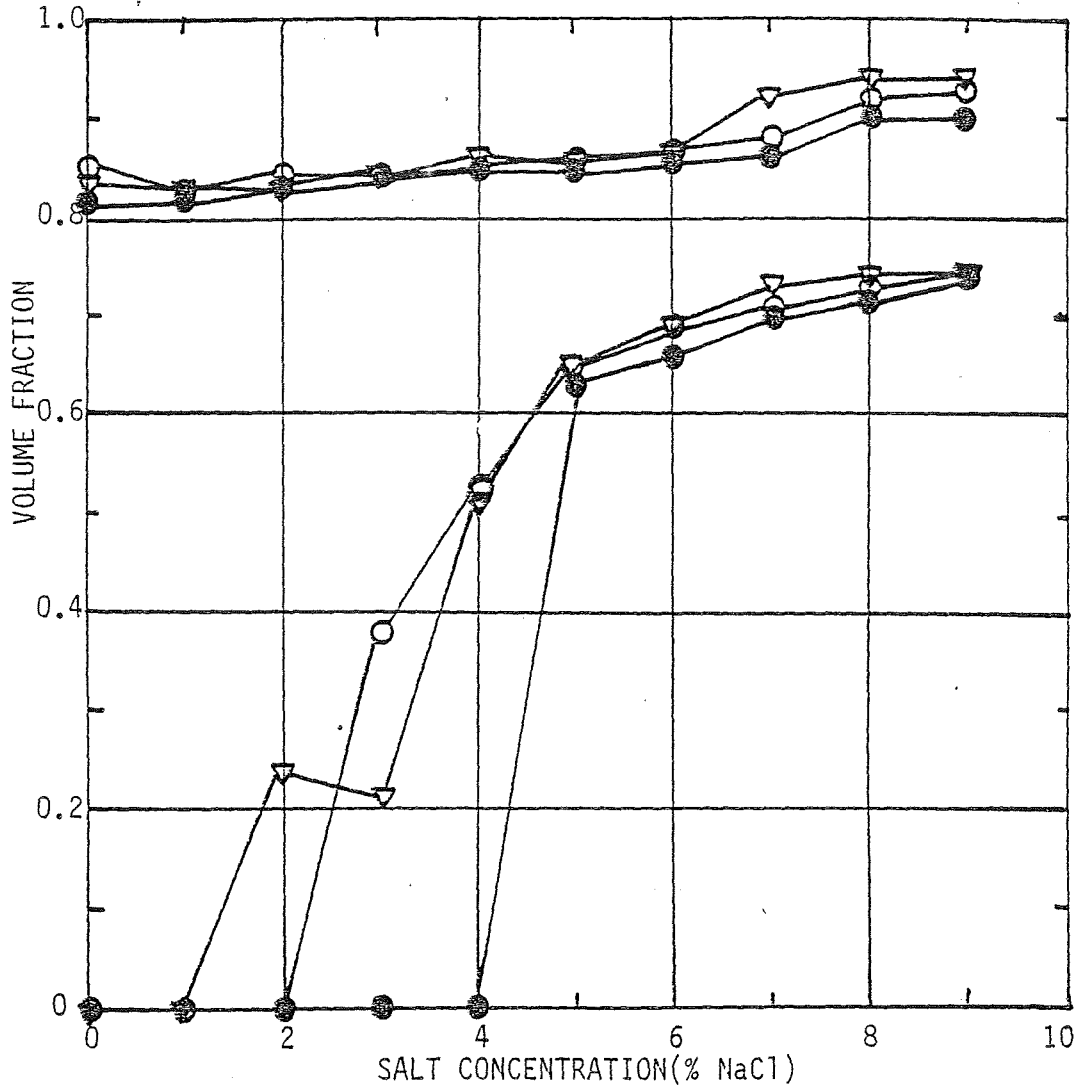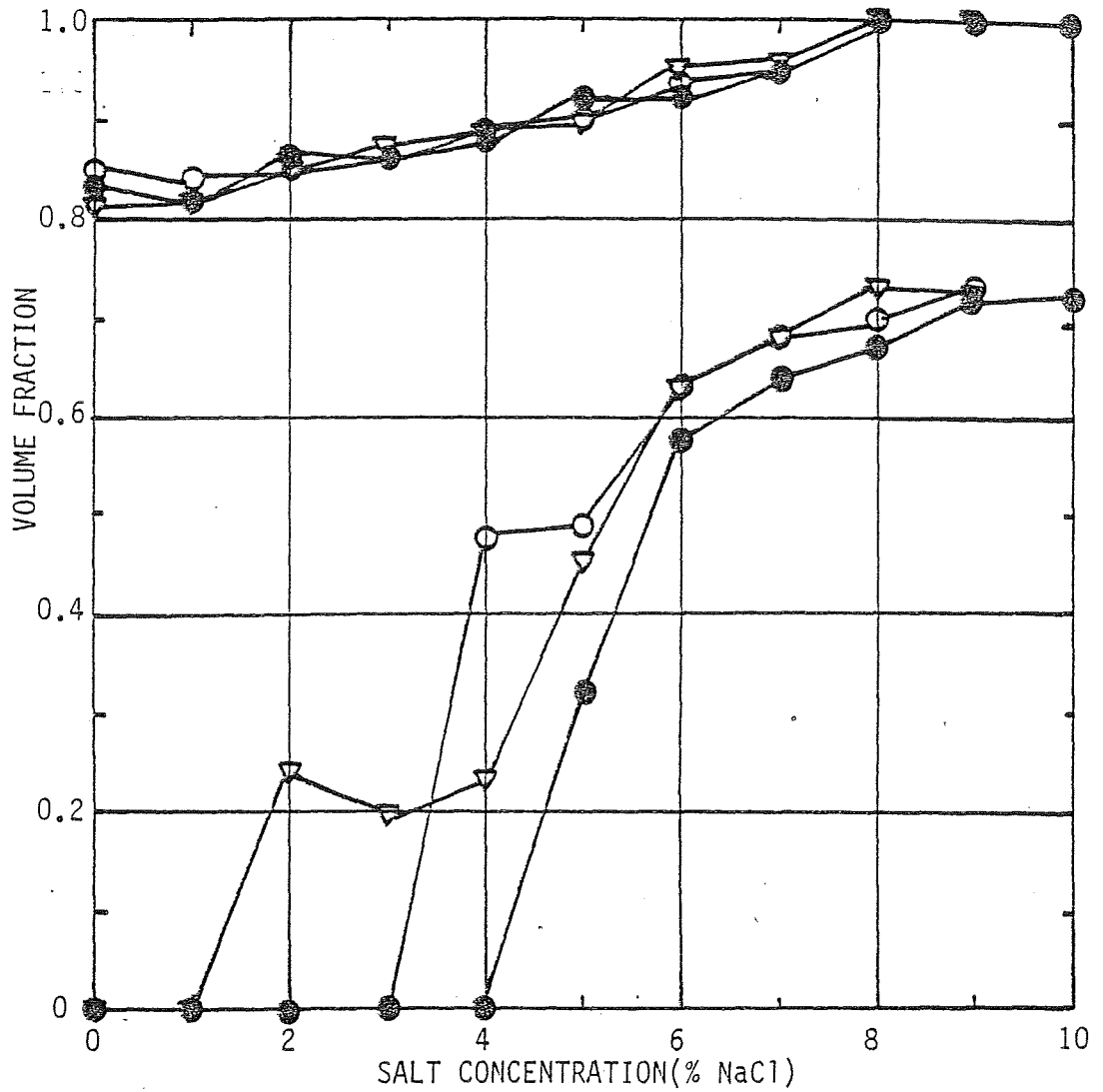FIGURE 57. EFFECT OF POLYMER TYPE ON CO-610 SOLUTIONS WITH SEC-BUTANOL

TEMPERATURE: 24°C   OIL: 20% v. OF 80% v. N-OCTANE
CHEMICAL: 3% wt CO-610   20% v. BENZENE
         3% wt SEC-BUTANOL   XANFLOOD
         1% wt ISO-PENTANOL   POLYOX COAGULANT
POLYMER: 1000 ppm EACH   NO POLYMER

FIGURE 58. EFFECT OF POLYMER TYPE ON CO-610 SOLUTIONS WITH MIXTURE
             OF SEC-BUTANOL AND ISO-PENTANOL

FIGURE 59. EFFECT OF POLYMER TYPE ON CO-610 SOLUTIONS WITH ISO-PENTANOL

FIGURE 60. EFFECT OF POLYMER TYPE ON MIXTURE OF IGEPAL CO-610 AND CO-530 WITH ISO-PENTANOL
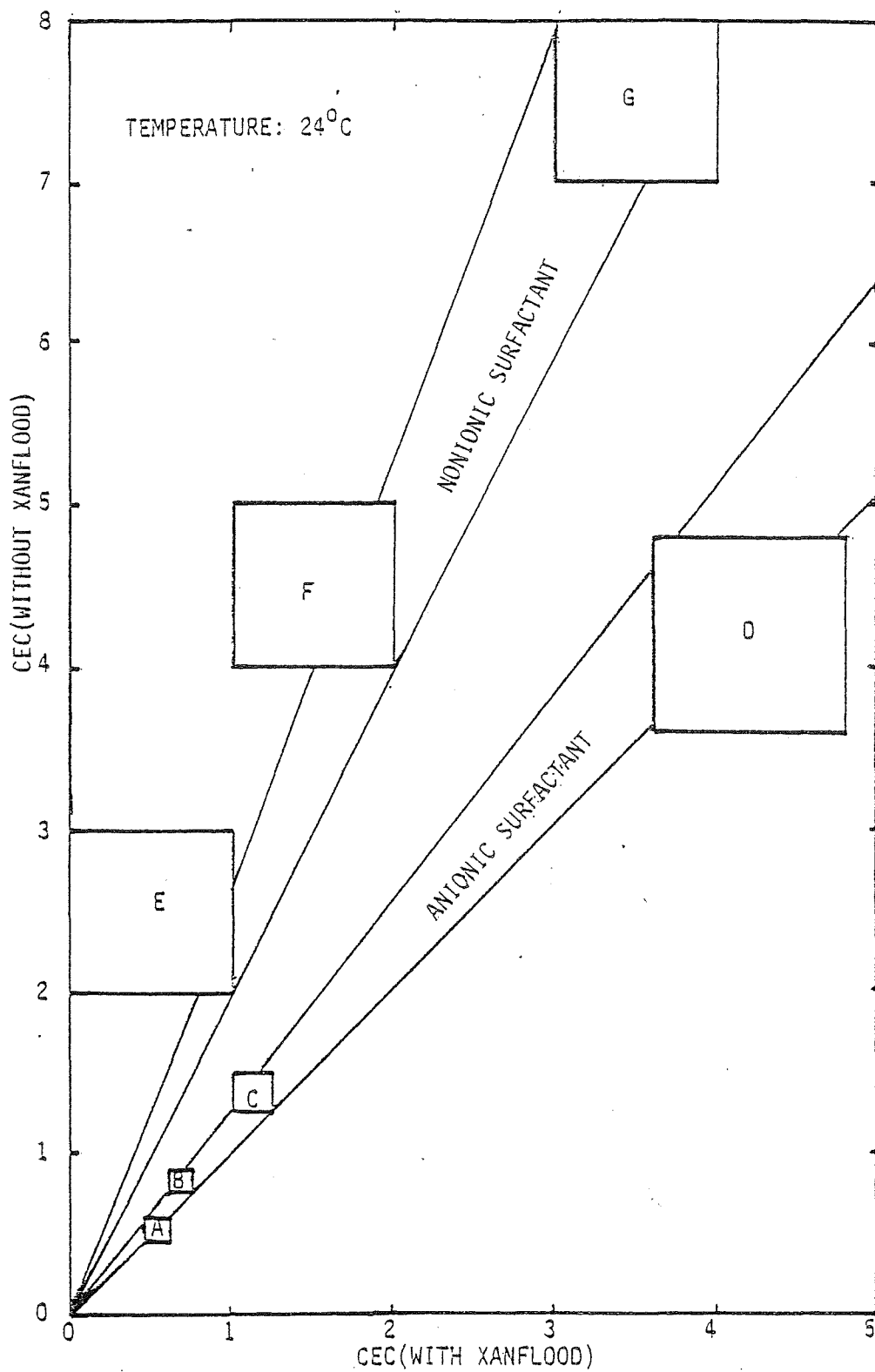
FIGURE 61. CEC PLOT WITH AND WITHOUT XANFLOOD

TABLE 4

SYSTEM NOMENCLATURE FOR FIGURE 61

System	Composition of Oil Free System* (weight %)	Composition of Oil** (volume %)
A	1% Petrostep 465 3% Sec-butanol	90% N-octane 10% Benzene
B	1% TRS 10-80 3% Sec-butanol	N-octane
C	1% MEAC120XS 3% Sec-butanol	N-octane
D	1% DS-10 3% Sec-butanol	N-octane
E	2.3% CO-530 0.7% CO-610 1% Iso-pentanol	N-octane
F	3% CO-610 1% Iso-pentanol With or Without 3% Sec-butanol	80% N-octane 20% Benzene
G	3% CO-610 3% Sec-butanol	80% N-octane 20% Benzene

*   80% of final volume

**   20% of final volume

As mentioned in Chapter V, some additives were always used in the xanflood solutions. A list of the company names and addresses which supply these additives is shown in Table 5. The ratio of Alcalase/Dowicide B/sodium bicarbonate/xanflood is 4.0/120/100/1000. For example, in a 1000 ppm of xanflood solution, there will be 4 ppm of Alcalase P1.5, 120 ppm of Dowicide B, and 100 ppm of $NaHCO_3$. For convenience, these chemicals will not be noted in the Figures.

A typical viscosity v.s. shear rate diagram for various xanflood concentrations is shown in Figures 62. The higher the xanflood concentration, the higher the viscosity (see Figures 63 and 64). In the low shear rate range, it behaves as a Newtonian fluid. Increasing shear rate makes viscosity drop. The LS-30 was used to measure the viscosity.

Xanflood viscosity is decreased if temperature increased. Figure 65 shows the temperature effect on various concentrations of xanflood solution. Salt also affected the viscosity of xanflood. Figure 66 shows that viscosity increased as the salinity increased. This is unusual behavior for a polyelectrolyte. 0.5% of calcium chloride did not have a significant influence in a 1% NaCl solution of xanflood at $50^{\circ}C$. The viscosity of two 1500 ppm xanflood samples, one with 3% wt of sec-butanol, the other without alcohol, both in 1% wt NaCl, was measured. No signficant difference was observed at $24^{\circ}C$. The addition of alcohol did not affect the viscosity of this xanflood solution.

Viscosity of Pusher 700 Solution

Viscosity of Pusher 700 solutions is affected by the polymer concentration, shear rate, and electrolyte concentration. The higher the polymer concentration, the higher the viscosity (see Figure 67). Increasing shear rate will

TABLE 5

POLYMER ADDITIVES

Company Name and Address	Chemical Name or Trade Name
American Drug and Chemical Co. Culver City, CA 90230	Sodium Bicarbonate
Nova Laboratories Incorporated P. O. Box 189 Mamaroneck, NY 10543	Prill Alcalase 1.5 P (TiO_2 free)
Dow Chemical Company Midland, Michigan 48640	Dowicide B
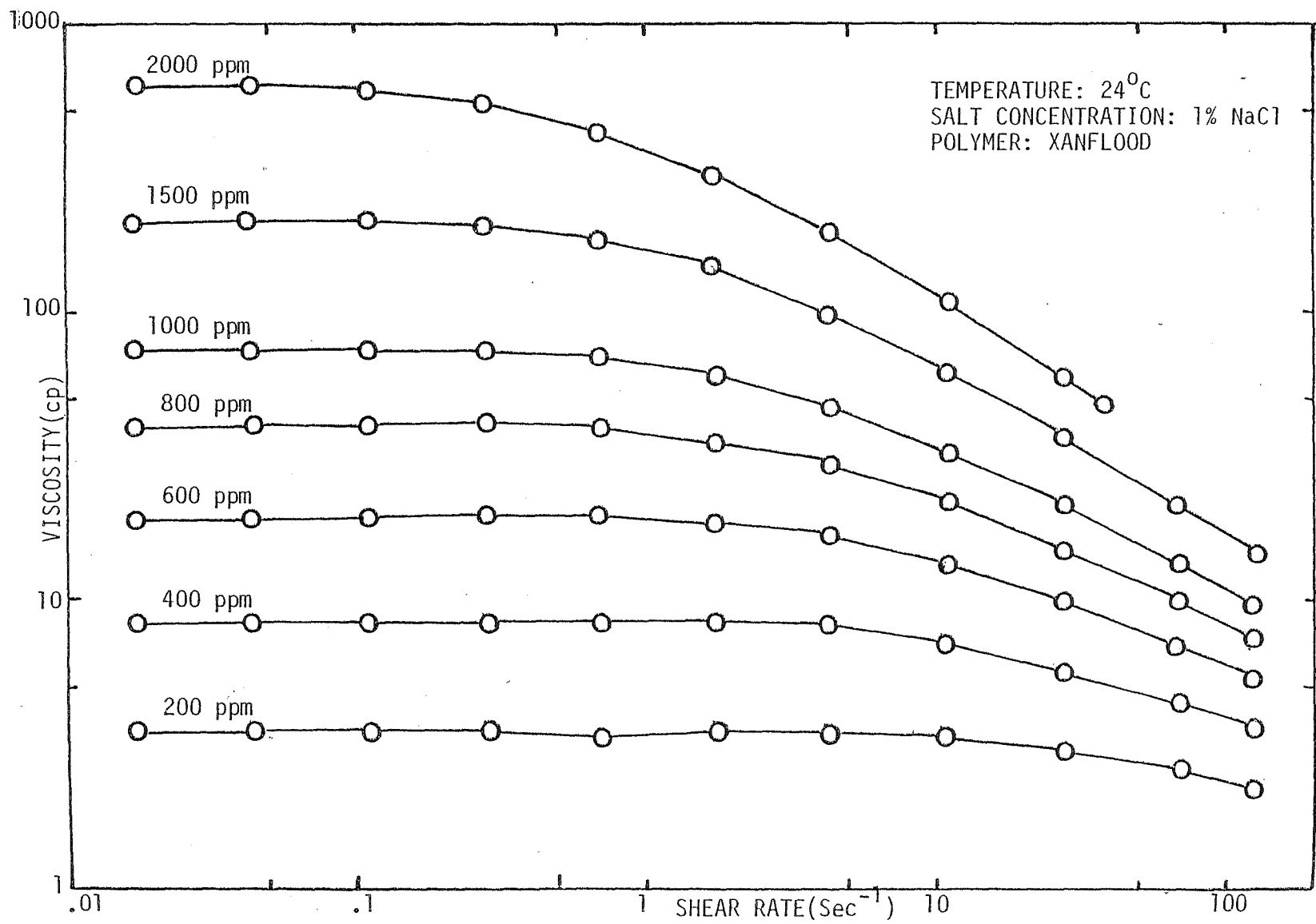
FIGURE 62. VISCOSITY OF XANFLOOD POLYMER IN BRINE

FIGURE 63. XANFLOOD VISCOSITY VERSUS CONCENTRATION IN
1% NaCl BRINE

TEMPERATURE: 24°C   SALT CONCENTRATION: 10% NaCl
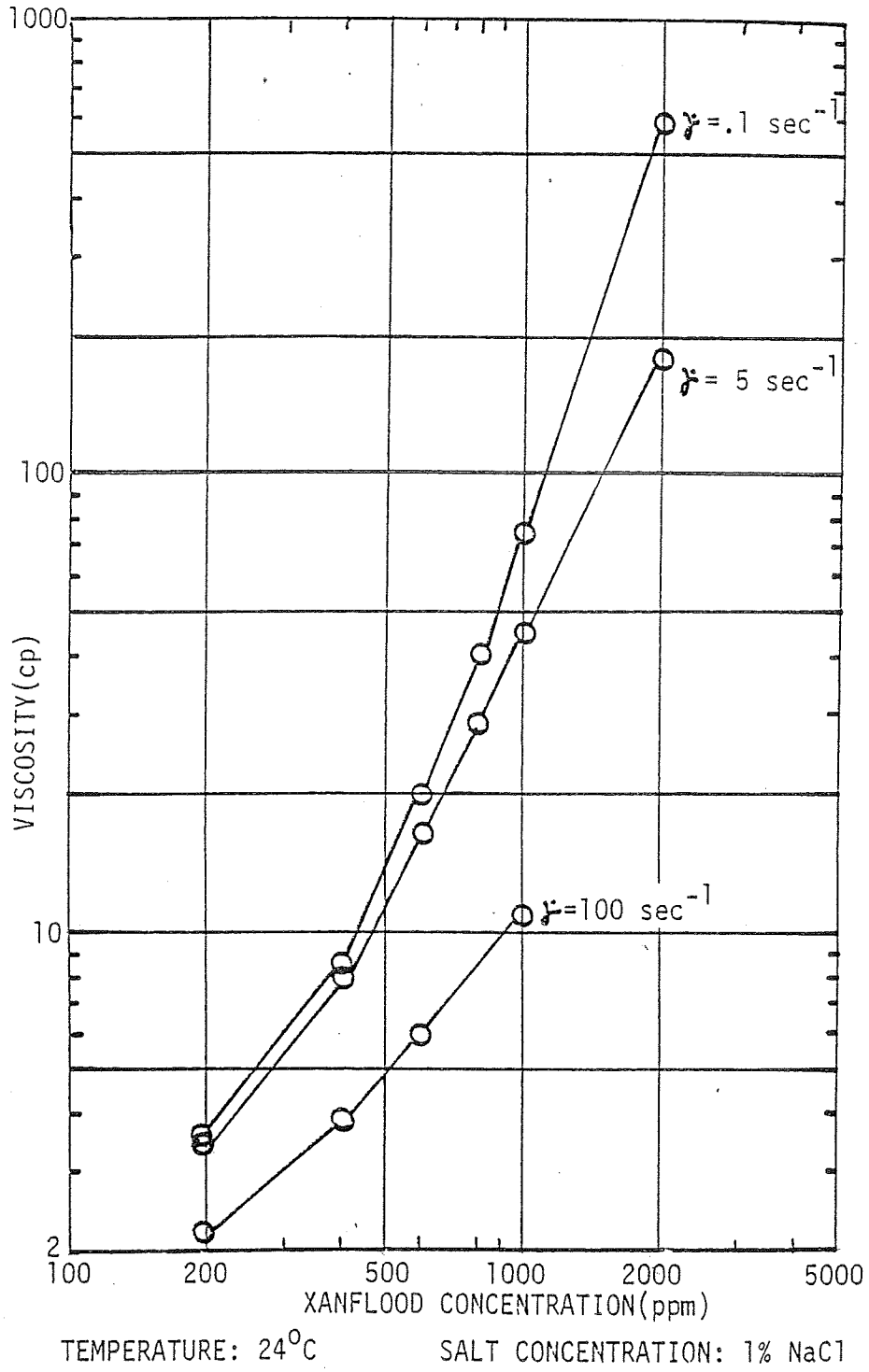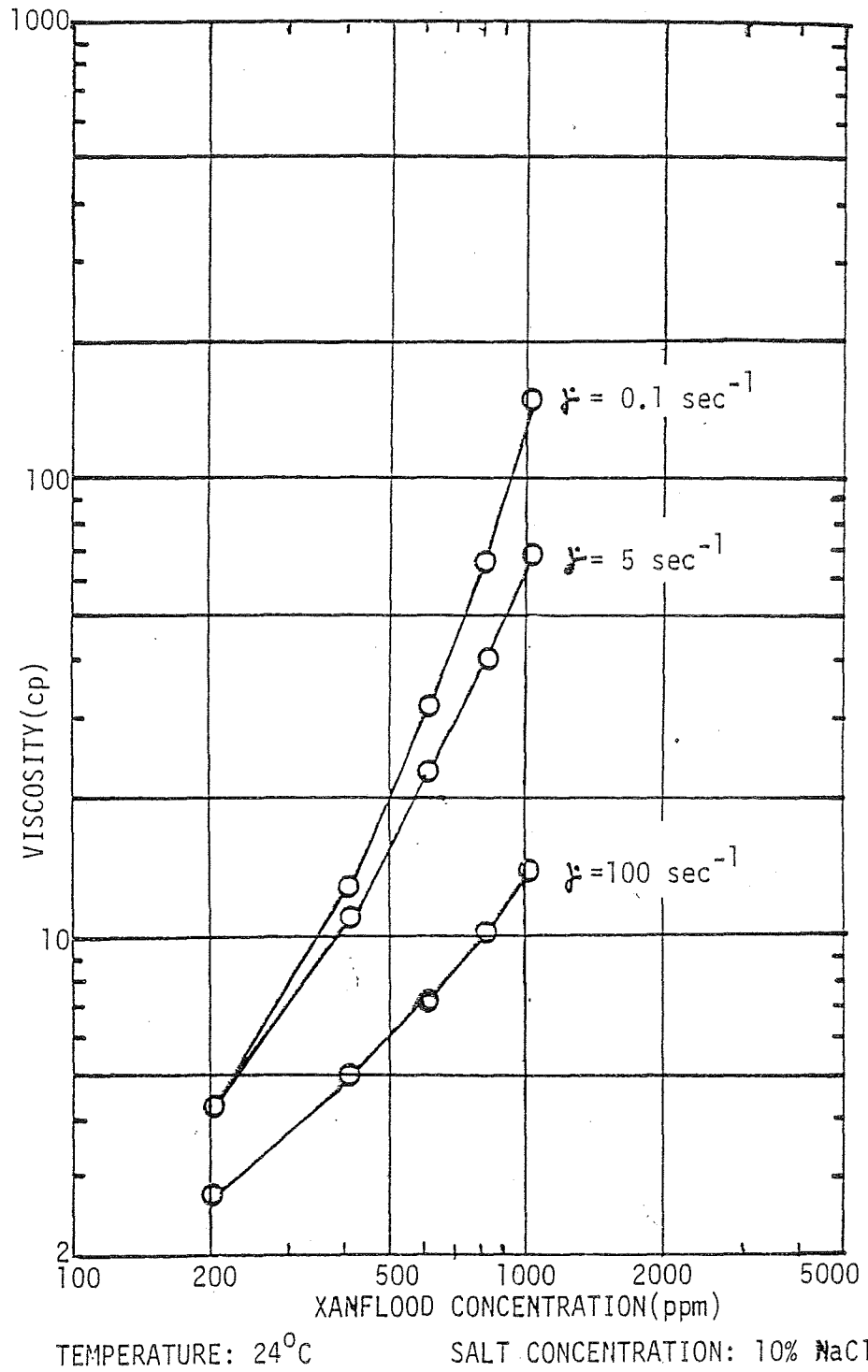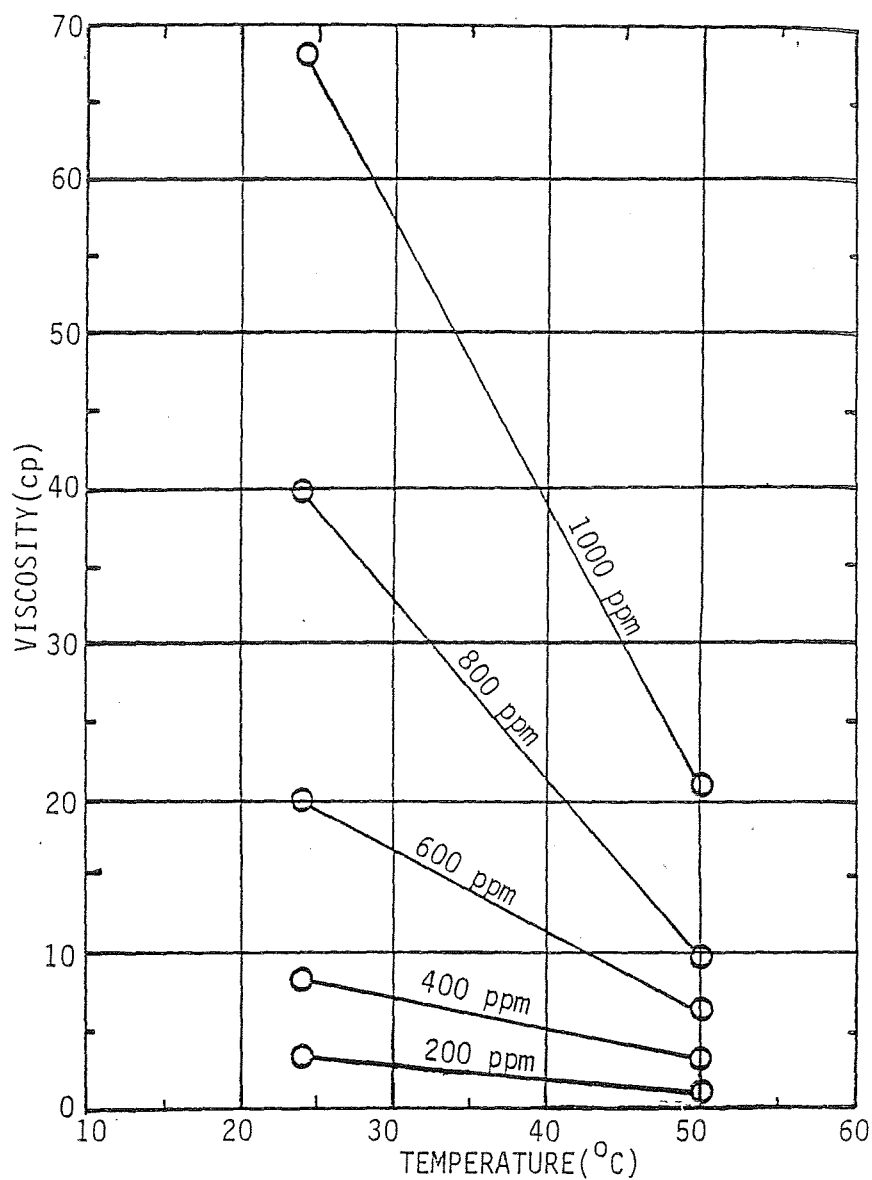
FIGURE 64. XANFLOOD VISCOSITY VERSUS CONCENTRATION IN
            10% NaCl BRINE

POLYMER: XANFLOOD   SALT CONCENTRATION; 1% NaCl
SHEAR RATE: 1 sec^{-1}

FIGURE 65. VISCOSITY OF XANFLOOD VERSUS TEMPERATURE
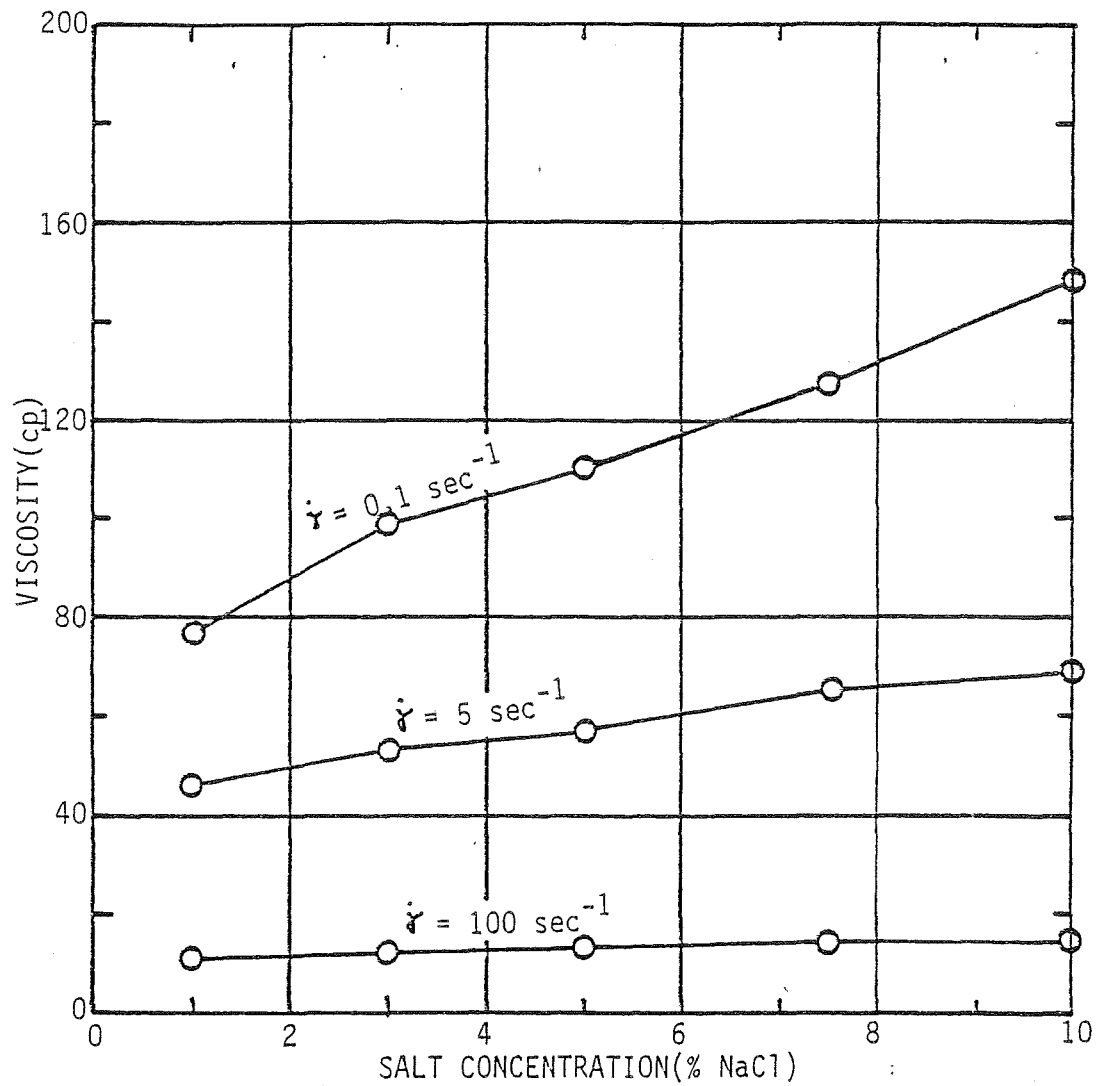
FIGURE 66. VISCOSITY OF XANFLOOD VERSUS SALINITY
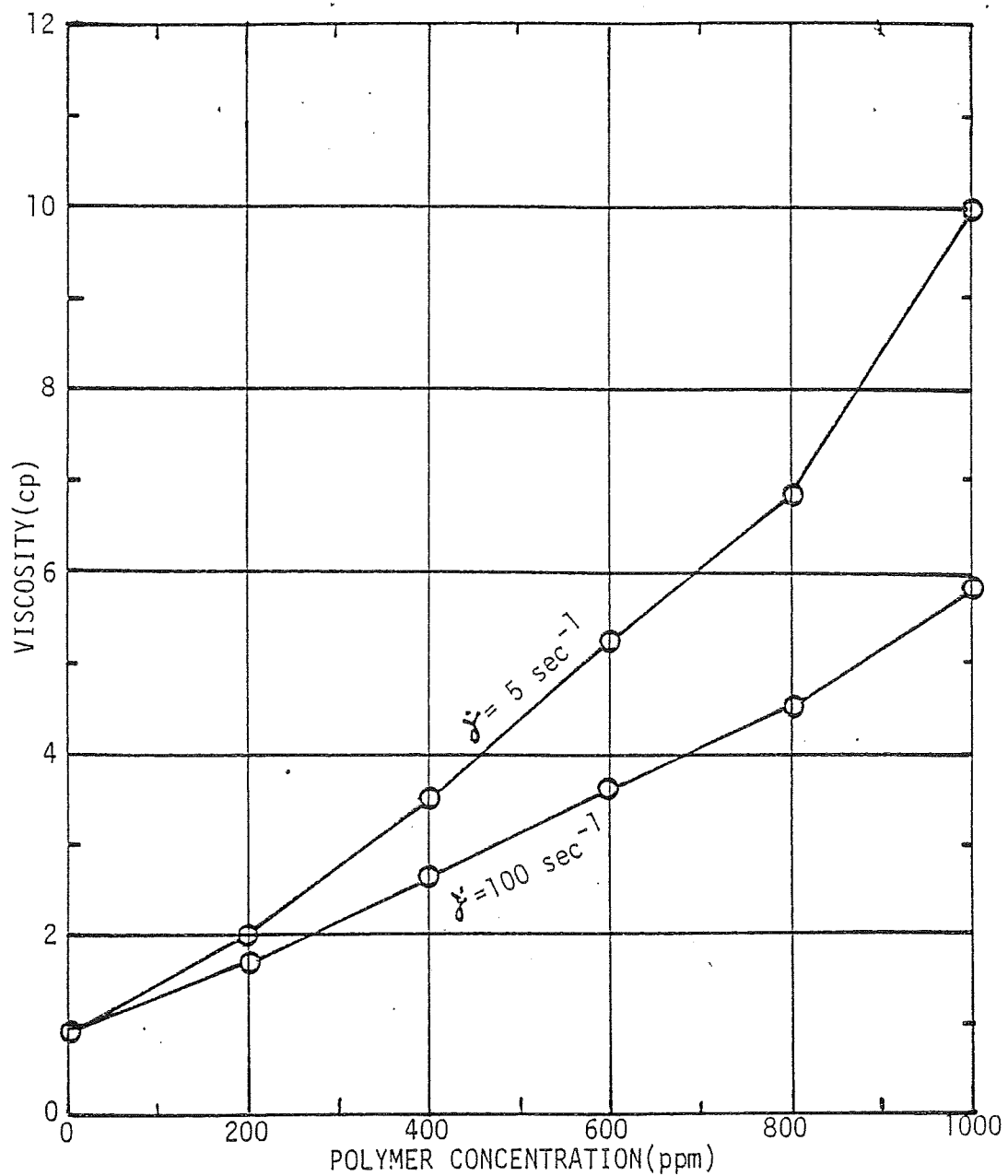
FIGURE 67.   VISCOSITY OF PUSHER 700 IN BRINE

decrease the polymer viscosity (see Figure 68). Viscosity is also decreased by increasing the salt concentration (see Figure 69). This decrease is opposite that for xanflood but typical of polyelectrolytes.

Viscosity of Polyox Solution

Polyox has lower viscosity compared with xanflood and Pusher 700 solutions of the same concentration. The molecular weight of Polyox WSR N-3000, WSR-301, and Coagulant are approximately 400,000, 4,000,000, and 5,000,000, respectively. The higher the molecular weight of the Polyox, the higher the viscosity (see Figures 70, 71 and 72). Increasing temperature causes a decrease in viscosity (see Figure 73). Electrolyte does not affect the viscosity of Polyox solutions very much (see Figure 74).
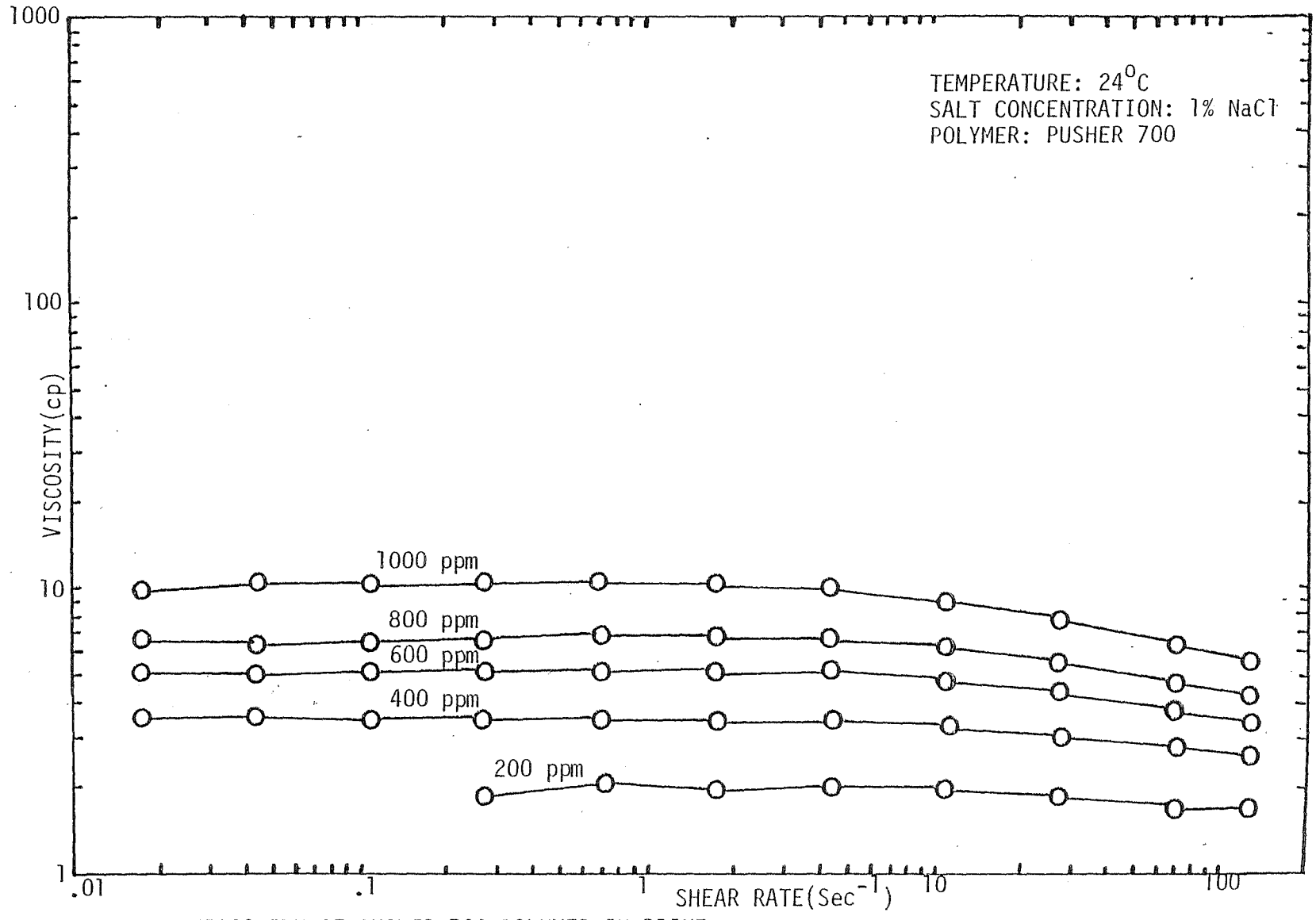
FIGURE 68. VISCOSITY OF PUSHER 700 POLYMER IN BRINE
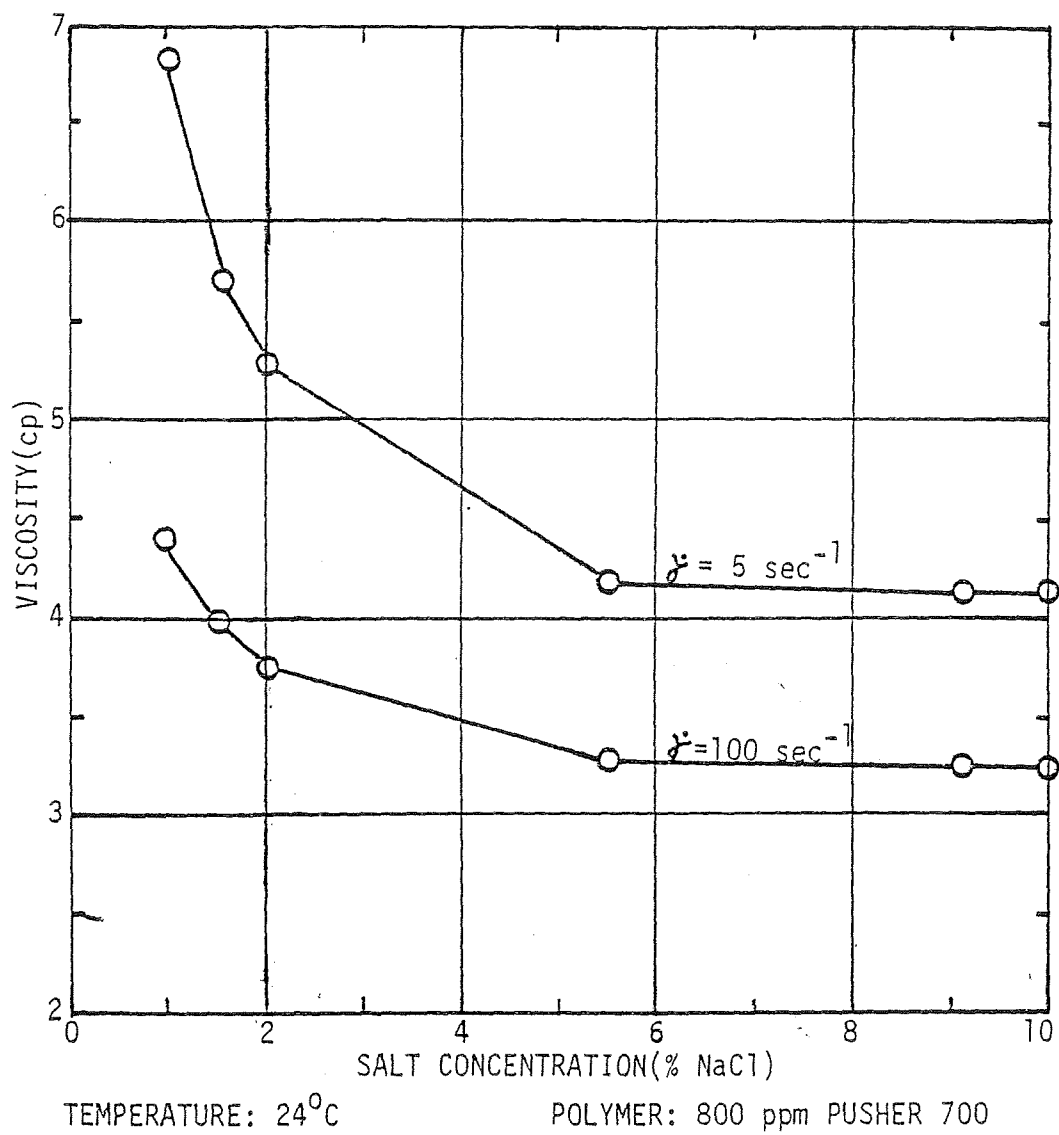
FIGURE 69. VISCOSITY OF PUSHER 700 VERSUS SALINITY

FIGURE 70. VISCOSITY OF POLYOX WSR-301
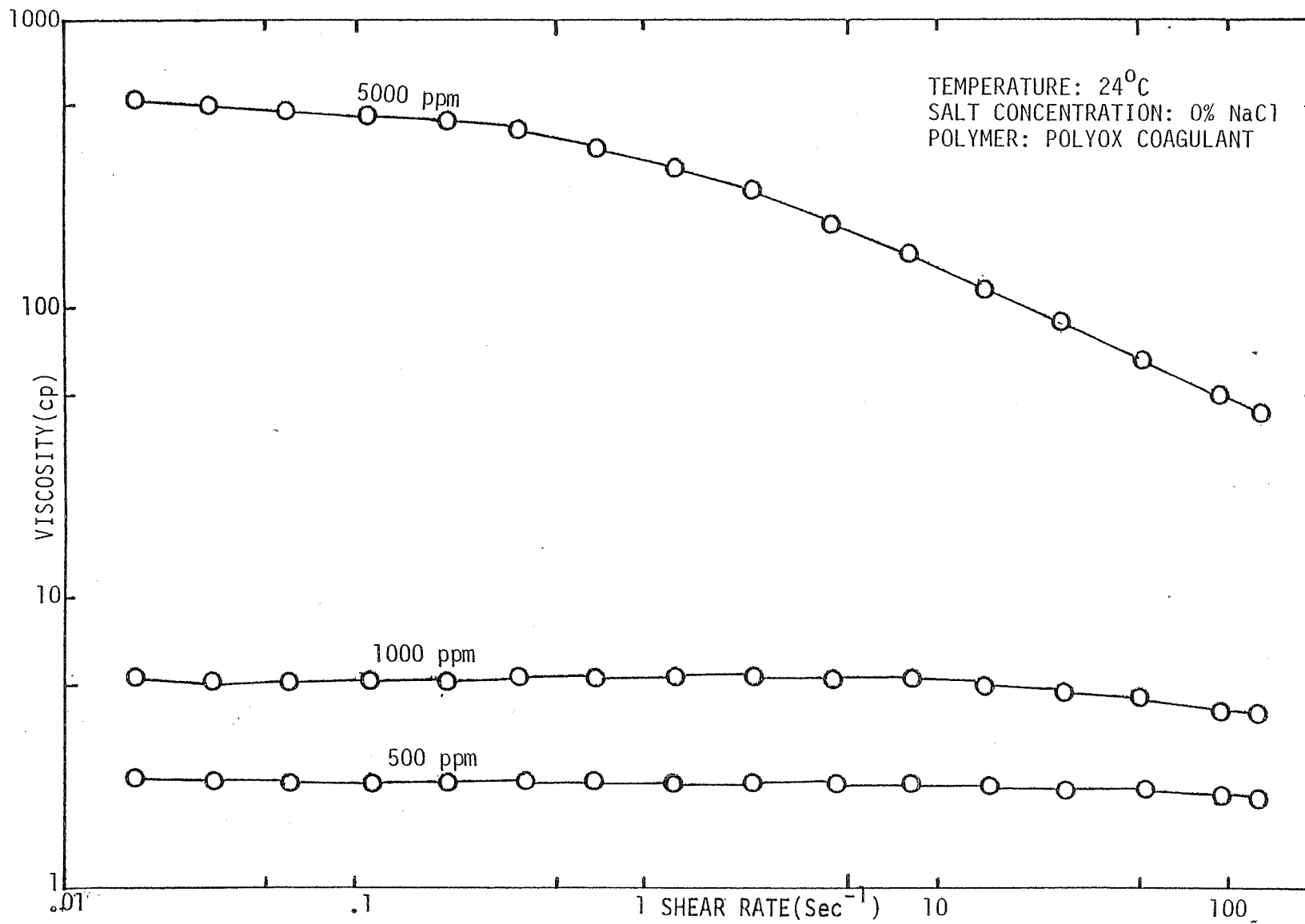
FIGURE 71. VISCOSITY OF POLYOX COAGULANT

TEMPERATURE: 24°C
SALT CONCENTRATION: 0% NaCl
POLYMER: POLYOX WSR N-3000

25000 ppm
20000 ppm
15000 ppm
10000 ppm
5000 ppm
1000 ppm
500 ppm

VISCOSITY(cp)
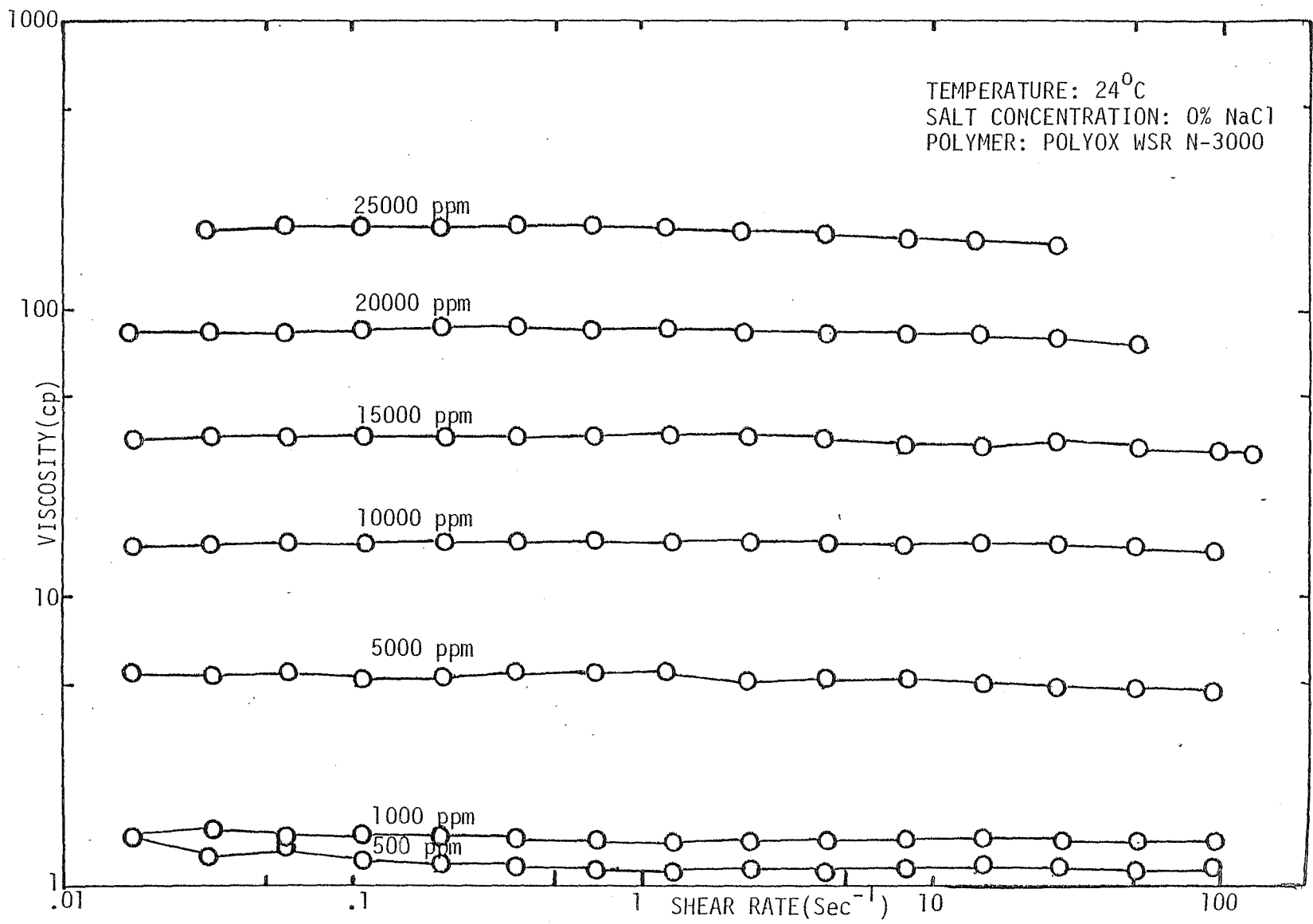
SHEAR RATE(Sec^{-1})
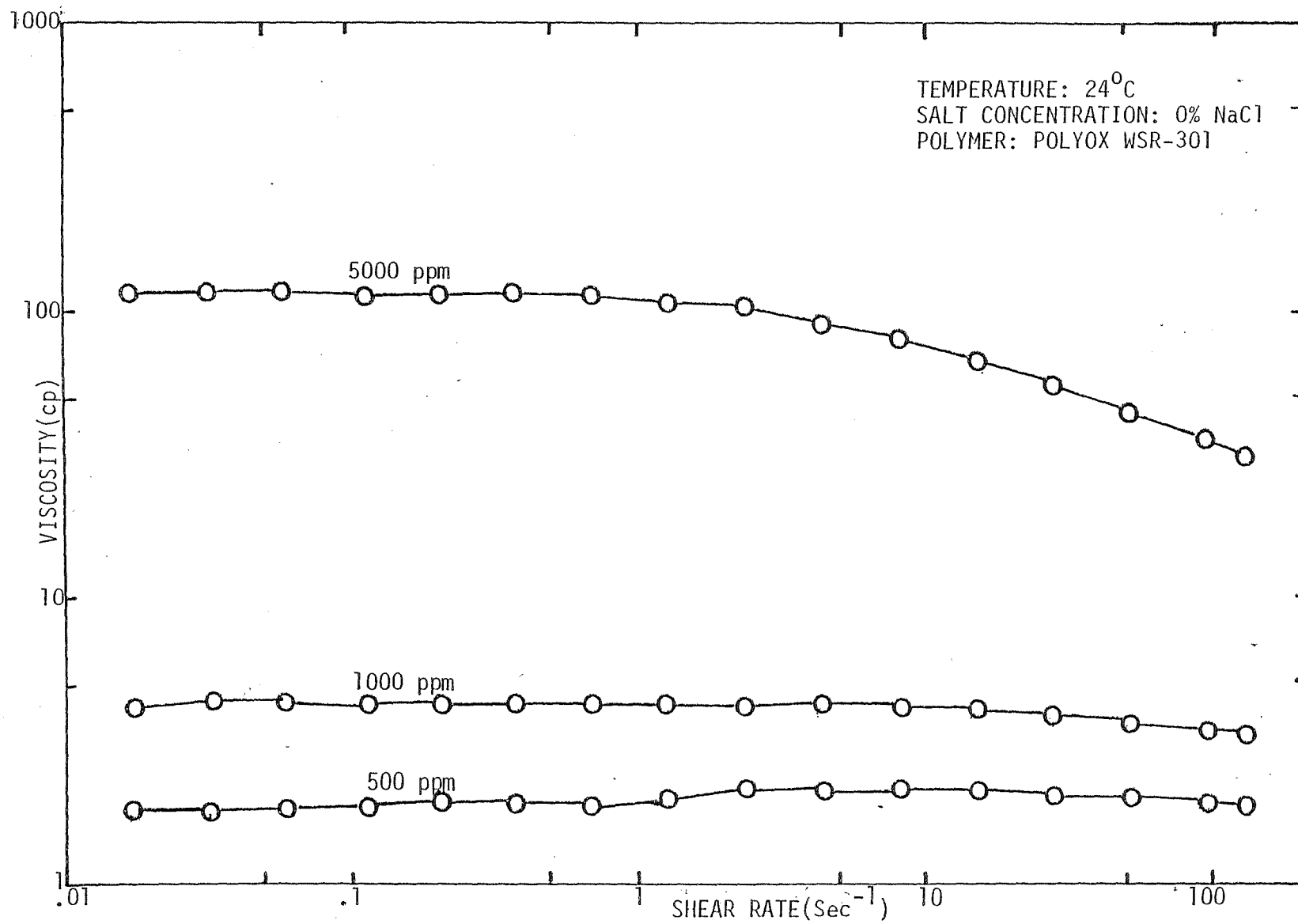
FIGURE 72. VISCOSITY OF POLYOX WSR N-3000
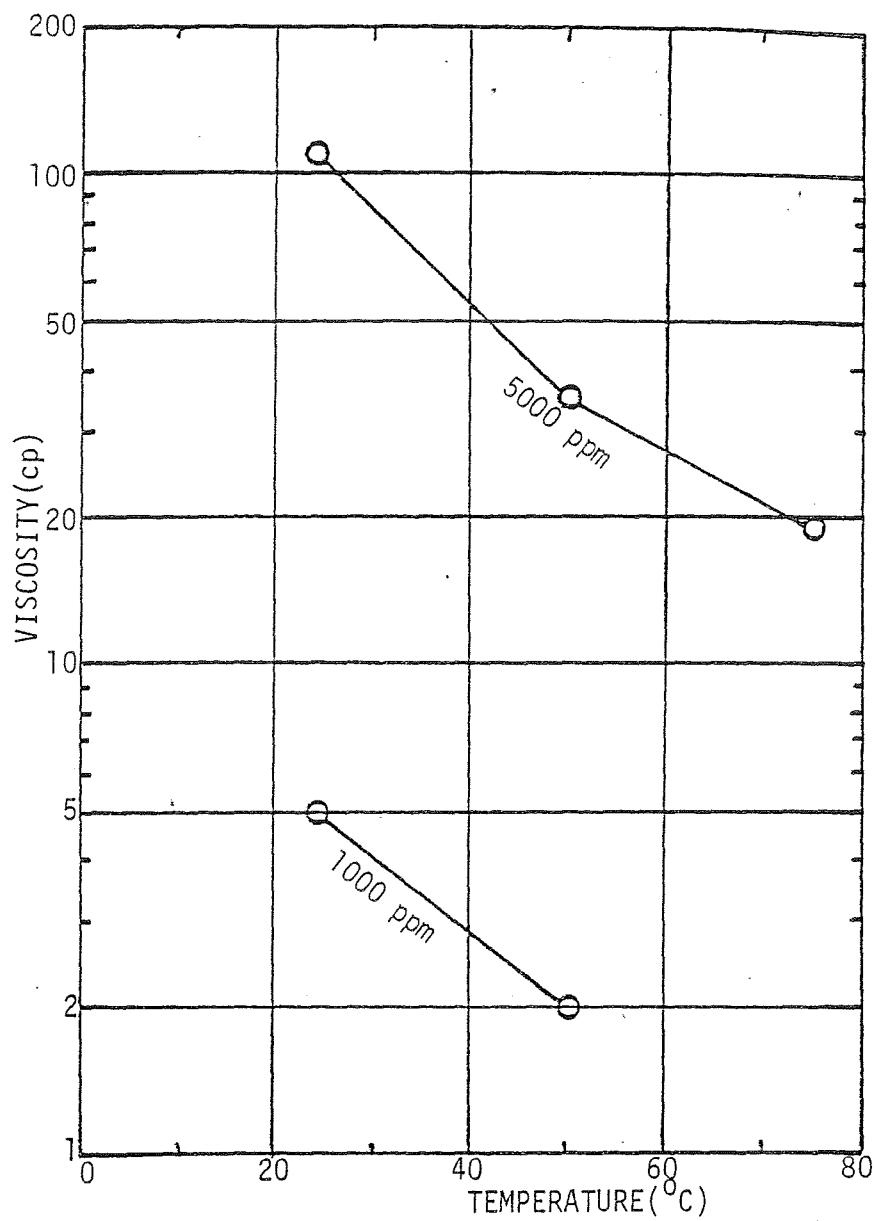
FIGURE 73. VISCOSITY OF POLYOX WSR-301 VERSUS TEMPERATURE
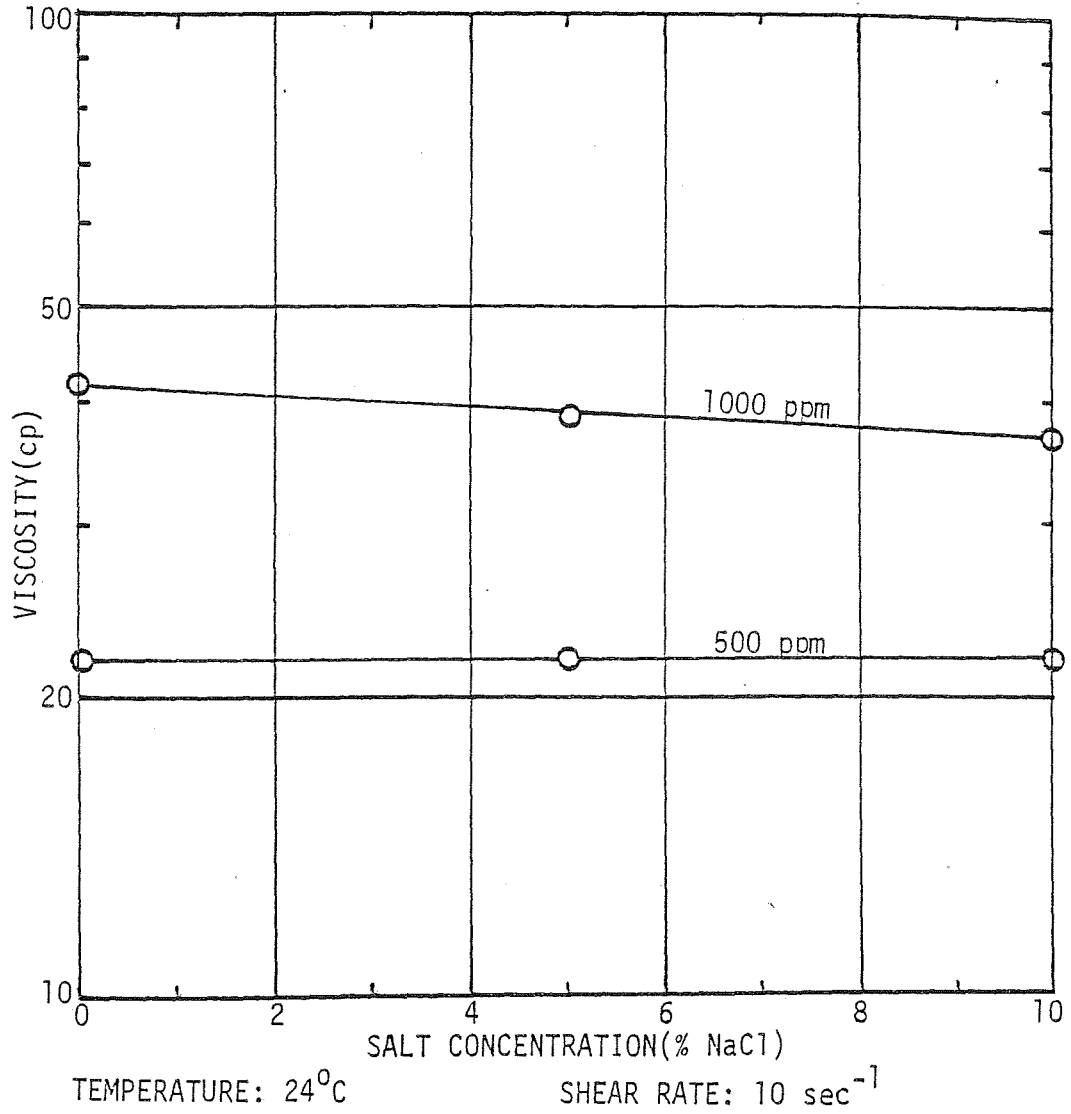
FIGURE 74. VISCOSITY OF POLYOX WSR-301 VERSUS SALINITY

CHAPTER VII

CONCLUSIONS

1. All combinations of anionic and nonionic surfactants with all anionic and nonionic polymers studied showed regions of composition which were compatible and regions of composition which were not compatible.

2. In aqueous systems, there is a well defined critical electrolyte concentration (CEC) where a separate polymer-rich phase forms. The CEC is the same for all polymers and a given surfactant.

3. The CEC increases with temperature for anionic surfactants and decreases with temperature for nonionic surfactants.

4. The CEC increases with alcohol concentration. There is little difference between iso-propanol, iso-butanol, and sec-butanol.

5. The CEC is independent of surfactant and polymer concentration in the range studied.

6. The CEC increases or decreases in the same direction as optimal salinity (for any given ACN). Thus, the CEC, for example, can be increased by lowering the molecular weight of the anionic surfactants, but the optimal salinity also goes up, in fact even more relatively.

7. When oil is added, the usual sequence of phase behavior is observed with all combinations of chemicals with and without polymer. The sequence is II(-), III, II(+). The polymer has its most dramatic effect just before the electrolyte at which three phase form and just above the electrolyte at which II(+) behavior forms.

8. The volume of the surfactant-rich aqueous phase increases more or less

proportionately with the total surfactant concentration.

9. The anionic surfactants appear to be somewhat more compatible with the polymers than the nonionics. Solubility of the surfactant/alcohol is probably the determining factor.

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