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LOW INTERFACIAL TENSION AND MISCIBILITY STUDIES FOR SURFACTANT TERTIARY ENHANCED OIL RECOVERY PROCESSES

Final Report, December 1980–September 1981

Work Performed for the Department of Energy
Under Contract No. DE-AS19-79BC10007

Date Published—July 1982

Carnegie-Mellon University
Pittsburgh, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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Final Report, December 1980-September 1981

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UNITED STATES DEPARTMENT OF ENERGY

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OBJECTIVE

The main purpose of this project is to develop an improved basic understanding of how ultralow interfacial tensions arise in oil-brine-surfactant systems. Such tensions must be achieved and maintained during tertiary oil recovery processes if they are to be successful.

ABSTRACT

The effects of temperature and of divalent ion concentration on the structure of aqueous surfactant solutions have been determined. As temperature increases, the salinity range where liquid crystalline phases exist is narrowed. At sufficiently high temperatures the liquid crystal "melts" and only isotropic phases are observed. These are an aqueous phase and, when partial immiscibility of alcohol and brine occurs, an alcohol-rich phase as well.

The effect of divalent ions on aqueous solution structure is basically the same as that of monovalent ions, but smaller quantities of divalent ions are needed to bring about the same phase changes. In the particular system studied addition of one mole of Ca^{+2} was equivalent to addition of about 11.5 moles of Na^{+}.

We have extended our model of drop size in microemulsions to include the effect of drop dispersion. A hard sphere model was used to describe dispersion effects. With dispersion, drop size is slightly smaller for both oil-continuous and water-continuous microemulsions than predicted by the previous analysis which considered film properties alone.

Further work on our proposed scheme for reducing microemulsion sensitivity to salinity changes is included in an Appendix.*

SUMMARY OF PROGRESS

In previous reports we have described observations of the liquid crystalline structure of aqueous surfactant solutions in the composition range proposed for injection in enhanced oil recovery processes. Emphasis was on how structure varied with salinity and alcohol content. In this report we present data on structure variation with temperature in two systems, one containing a petroleum sulfonate and one a pure sulfonate surfactant.

It is found that the liquid crystalline phases "melt" when exposed to sufficiently high temperatures - about 60°C in the systems studied. Above this temperature a single isotropic phase exists except at high salinities when an alcohol-rich phase appears owing to partial immiscibility between alcohol and brine. Below about 60°C we find that the lamellar liquid crystalline phase "melts" at a lower temperature than the isotropic phase which scatters light and exhibits streaming birefringence described in our previous reports. Near room temperature this phase, which may be a liquid crystalline phase of the cubic type, occurs at higher salinities than the lamellar phase.

In another set of experiments the effect of calcium ion concentration on liquid crystalline structures was investigated in a system containing a mixture of a petroleum sufonate and an ethoxylated sulfate. The sequence of structures found on addition of $CaCl_2$ was the same as that found on addition of NaCl. Calcium ions are much more effective in causing the phase changes, however, with addition of one mole of calcium being equivalent to addition of about 11.5 moles of sodium.

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*The appendix is not available for publication at this time. For more information, contact Min K. Tham, technical project officer.

Our theory of drop size in microemulsions has been extended to include the effect of the dispersion entropy of the drops. Using a hard sphere model, we find that drop size is somewhat smaller than that reported previously based entirely on the properties of the surfactant films at the drop surfaces.

Experimental work has begun to measure the electrical charge of microemulsion drops using electrophoretic light scattering. This work is being done in collaboration with Professor G.C. Berry of Carnegie-Mellon University. Some key experimental problems have been resolved, and initial data are expected soon.

I. EFFECT OF TEMPERATURE ON PHASE BEHAVIOR OF AQUEOUS SURFACTANT SOLUTIONS.

(W.J. Benton)

The effect of temperature on the phase behavior and phase structures of aqueous solutions of two sulfonate surfactants has been studied. The systems and compositions investigated were a) 1.5 wt.% Texas 1, 10.0 wt.% n-propanol, 0.0 - 5.0 wt.% NaCl and b) 5.0 wt.% TRS 10-410 (Witco Chemical Corp.), 3.0 wt.% iso-butanol and 0.0 - 2.4 wt.% NaCl. The temperature range was 5 - 75°C for the Texas 1 scan and 5 - 85°C for the TRS 10-410 scan.

Phase diagrams were generated by polarized light screening using the PLS II which has been described in detail previously(1). Solutions were kept submerged in the water bath at constant temperature (± 0.5°C) for periods of one day to several weeks. Once the desired temperature had been reached the solutions were either gently rocked back and forth by hand or mixed with a vortex mixer and then allowed to equilibrate. On other occasions the temperature was raised or lowered to the desired temperature without mechanically disturbing the solutions. Equilibrium was considered to have been achieved when no further change was observed in the birefringent textures and phase volumes of the solutions.

The effect of temperature and salinity on the phase behavior and structures of 1.5 wt.% Texas 1 and 10.0 wt.% n-propanol is shown in Figure 1. Several 10 wt.% solutions at 0.2 wt.% NaCl increments were formulated by the procedure previously described(2). Between temperatures of about 30° and 50°C the usual progression of structural changes was found i.e. $I_1 \rightarrow S \rightarrow L \rightarrow C$(3). Here I_1 is an isotropic, aqueous micellar solution, S is a dispersion of liquid crystalline particles (spherulites) in brine, L is a lamellar liquid crystalline phase, and C is an isotropic phase which scatters light and exhibits streaming birefringence and may be a cubic liquid crystalline phase.

At temperatures below the dotted line marked as the Kraft line in Figure 1 the surfactant chains freeze and a precipitate was observed. At salinities higher then 2.5 wt.% NaCl the precipitate rises to the top of the solutions. At salinities lower than 2.5 wt.% NaCl the precipitate settles to the bottom of the solutions. This behavior indicates a possible discontinuity in liquid crystal density at 2.5 wt.% NaCl and thus a possible phase change. We note that this salinity is the same as that of the previously reported structural change in solutions at 35°C in this system(3). The solutions are composed of a predominantly S structure below 2.5% NaCl and a predominantly L structure above 2.5% NaCl.

Above around 50°C the phase behavior and structures are more complex. Because surfactant solubility increases with increasing temperature, the I_1 phase extends to higher salinities at higher temperatures. The dispersions characteristic of the S and S + L regions separate into two phases, I_1 and L, with I_1 having the greater density.

Above about 3 wt.% NaCl the "cubic" phase (C) predominates. Moreover, this phase persists to higher temperatures than does the lamellar phase, i.e., its melting temperature is higher. It is of interest that the C phase can co-exist simultaneously with the aqueous I_1 phase and an alcohol-rich I_2 phase. The latter forms at sufficiently high temperatures and salinities because of partial immiscibility between n-propanol and brine(4). Above about 65°C the C phase melts and one observes the I_1 phase at low salinities and both I_1 and I_2 at high salinities.

Between 55° and 65° a number of single-phase and multiphase regions exist. In this region Figure 1 is incomplete because more data points at more closely spaced salinities and temperatures than chosen here would be required for an accurate mapping.

Figure 2 shows the effects of temperature and salinity in a petroleum sulfonate system containing 5.0 wt.% TRS 10 - 410 and 3.0 wt.% iso-butanol. The salinity was varied in 0.1 wt.% increments up to 2.4 % NaCl. Here enough data points were obtained to locate the various two-phase and three-phase regions at higher temperatures. Despite TRS 10 - 410 being only 60% active and having a distribution of various surface active components, its behavior is basically the same as that observed in the pure quaternary Texas 1 system. For purposes of comparsion with microemulsion behavior we note that the optimum salinity at 22°C is about 1.4 % NaCl for dodecane - corresponding to the middle of the (S + L) region in Figure 2.

The phase behavior below around 50°C shows the same sequence of structures with salinity variation as the Texas 1 system. At high salinities and low temperatures a freezing of the surfactant chains occurs as indicated by the dotted line. The precipitate observed at conditions below this line is a yellowish oily mixture rising to the top of the solutions. In the Texas 1 system, in constrast, the precipitate had a definite crystalline appearance. The difference is probably due to the impurities such as oil which are known to be present in the petroleum sulfonate. Below 1.5 wt.% NaCl the solutions remained homogeneous even at the lowest temperatures studied.

Above 50°C the phase behavior becomes complex with one, two and three phase regions involving the predominant C phase. At the apex of the C phase, all the thermodynamically expected phases occur. The phase diagram of Figure 2 is constructed from close to five hundred points.

Figures 3, 4, and 5 are a series of volume fraction (V_f) versus salinity plots for the TRS 10-410 system at temperatures of 85, 80, 75, 70, 65, 60, 55, 50, and 35°C. Further details of the phase behavior can be seen quite clearly. For example in Figure 5 (a) at 50°C the S and L phases separated except at 1.5 wt.% NaCl. This behavior is further indication of a liquid crystal phase transformation between S and L regions (see above). It should be noted that at no other time in the past five years in any systems studied have the S and L phases been observed to macroscopically separate in a test tube. Perhaps the reduction in viscosity caused by increased temperature and the reduction in natural convection produced by improved temperature control allow the separation to take place in this system.

With decreasing temperature from 85° to 65° the growth of the C phase is clearly seen with the appearance of I_1 + C + I_2, I_1 + C and C + I_2 regions. The alcohol-rich phase I_2 would not be expected to appear as a single phase at the low alcohol content of the present system. At 65°C and near 1.5 wt.% NaCl the C phase was seen to split into C and C' possibly indicating that the formulation is not too far from a criticality condition between I_1 and C.

Mention should also be made of the region that appears at low salinities which we call "turbid" (T). It occurs between 0.0 and 0.1 wt.% NaCl at low temperatures, increasing to 0.4 wt.% NaCl at 75°C, the highest temperature at which data were recorded. But it appears to be bending more strongly to higher salinities at the higher temperatures. Further comment on the structure of this region will be made after it has been studied by microscopy.

A more detailed explanation and interpretation of these experiments is presently being prepared for presentation and publication.

II. EFFECT OF Ca^{+2} ON LIQUID CRYSTALLINE STRUCTURES AND MICRO-EMULSION BEHAVIOR (W.J. Benton, J.H. Wagner)

Liquid crystalline structures of aqueous surfactant solutions were determined by

the polarized light screening (PLS) technique in systems containing brines with various ratios of NaCl and $CaCl_2$. Each sample contained 3.5% by weight on an active basis of the petroleum sulfonate TRS 10-410, 1.5% by weight on an active basis of the ethoxylated sulfate Neodol 25-3S, and 3% isobutanol by weight. Brines ranged from pure NaCl to a mixture containing 75% NaCl and 25% $CaCl_2$ on a weight basis (5.8 moles of Na^+ per mole of Ca^{+2}).

Figure 6 shows the results of these experiments. Basically the liquid crystalline structures and the sequence of phases observed are the same as found previously in systems containing no divalent ions. The structures of primary interest for injection are (1) a stable dispersion S of liquid crystalline particles in brine, (2) a single lamellar liquid crystalline phase L, and (3) a mixture (S+L) of these two. Transition occurs in the direction S → S + L → L as either NaCl or $CaCl_2$ is added but much more rapidly in the latter case. Indeed the slope of the phase boundaries indicates that for this system addition of one mole of Ca^{+2} is equivalent to addition of some 11.5 moles of Na^+.

Figure 7 shows the phase behavior observed when these solutions are equilibrated with equal volumes of dodecane. Addition of either Na^+ or Ca^{+2} makes the surfactant more oil-soluble and acts to induce transformation from a lower to a middle or from a middle to an upper phase microemulsion. The optimum salinity line is also shown on Figure 6 for comparison with the aqueous solution phase boundaries. It occurs in the (S+L) region and has about the same slope as the nearby phase boundaries of Figure 6. As Figure 7 indicates, the boundaries of the middle phase region are also of the same slope. Hence, the equivalence of 11.5 moles of Na^+ to one mole of Ca^{+2} exists for both the aqueous solutions and the microemulsions.

It should be noted that small particles of precipitate were observed in both the aqueous surfactant solutions and in the microemulsions or excess oil or brine phases when Ca^{+2} was present. Figure 8 shows a lamellar (L) phase as viewed by optical microscopy. It is interesting that the particles of precipitate concentrate along the defects in the liquid crystalline structure.

Viscosity of the aqueous solutions was measured using the cone-and-plate technique. Figure 9 shows viscosity as a function of salinity and time in the absence of divalent ions, while Figure 10 is a similar plot with a three-to-one ratio of NaCl to $CaCl_2$ by weight. Behavior in the two cases is similar. The viscosity of solutions with S structures is initially high but decreases with time, whereas solutions with L structures begin with a low viscosity and exhibit and increase in viscosity with time. The highest viscosity after 30 minutes of shearing is about 40 cp in both cases and occurs for a structure which initially is of the (S+L) type. As we have reported previously, a viscosity maximum in the (S+L) region is characteristic of anionic surfactant solutions. Note that the sample with the highest salinity in Figure 4 is the "C" phase, which is isotropic but with some streaming birefringence. Its viscosity is low and does not change with time.

III. EFFECT OF DISPERSION ON MICROEMULSION DROP SIZE
(S. Mukherjee)

In our previous Annual Report(3) we outlined a theory of drop size in microemulsions which included an improved model of the surfactant films at the drop surfaces. The model included bending effects by considering the interface between the surfactant film and water to contain hard disks representing surfactant and alcohol polar groups and by using a lattice treatment to account for oil penetration into the hydrocarbon chain region of the film. Various predictions of the "natural" radius of curvature of a drop were given, i.e., excluding the effects of drop dispersion and interaction. These predictions were in general agreement with experimental observation.

The model has now been extended to include the effects of drop dispersion. The Percus-Yevick-Carnahan-Starling equation for hard spheres(5) was used. Results are shown in Figure 11 for calculations with Texas-1 as surfactant, n-propanol as co-surfactant, and n-decane as oil. Both with (curve 2) and without (curve 1) dispersion, addition of the water-soluble alcohol, i.e., a decrease in surfactant-to-cosurfactant ratio, causes inversion of an oil-continuous system to a water-continuous system. But drop size is always smaller when dispersion is considered. The reason is that the decrease in system free energy due to dispersion is greater for many small drops than for a few large drops when a given amount of surfactant is present. This effect exceeds the increase in energy required to bend the film from its natural radius to a smaller size.

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2. Benton, W.J., J. Natoli, S. Qutubuddin, S. Mukherjee, C.A. Miller, and T. Fort, Jr., "Phase Behavior of Two Model Surfactant Systems," Soc. Pet. Eng. J. 22, 53 (1982).

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PRESENTATIONS AND PUBLICATIONS

Presentations by C.A. Miller

a. "Interfacial Phenomena in Enhanced Oil Recovery Processes," Rice University, February, 1981.

b. "Microemulsions and Liquid Crystals in Enhanced Oil Recovery," AIChE National Meeting, Houston, April, 1981.

c. "Microemulsions in Systems Containing Fatty Acids," DOE Contractors' Meeting, Fountainhead Resort, Oklahoma, August, 1981.

d. "Theory of Drop Size in Microemulsions," AIChE Annual Meeting, New Orleans, November, 1981.

Presentations by W.J. Benton

a. "Phase Behavior and Structures in Quaternary Systems of Anionic Surfactants, Cosurfactants, Electrolyte, and Water. "Fourth International Conference on Surface and Colloid Science, Jerusalem, June, 1981.

b. "Phase Behavior and Structures of Dilute Anionic Surfactant, Alcohol, Brine Systems." Technion, Haifa, Israel, July, 1981.

Presentations by S. Mukherjee

a. "Theory of Drop Size in Microemulsions -- Bending Effects," Union Carbide Corporation, Charleston, W. Va., May, 1981.

b. "Theory of Drop Size in Microemulsions -- Bending Effects," Gordon Research Conference on Fluids in Permeable Media, Tilton, N.H., August, 1981.

Presentations by S. Qutubuddin

a. "Phase Behavior of pH-Dependent Microemulsions with Low Interfacial Tensions," Fourth International Conference on Surface and Colloid Science, Jeruselem, June, 1981.

b. "A Proposed Mechanism for Polymer - Surfactant Interactions in Enhanced Oil Recovery," ACS National Meeting, New York, August, 1981.

c. "Phase Behavior of Microemulsions Exhibiting Ultralow Interfacial Tensions," Carnegie-Mellon University Graduate Student Symposium, October, 1981.

d. "Phase Behavior of Microemulsions Exhibiting Ultralow Interfacial Tensions," Rice University Graduate Student Symposium, November, 1981.

Presentation by J. Natoli (former Ph.D. student with group)

"Phase Behavior and Structure of Anionic Surfactant, Alcohol, Brine Systems." AIChE Annual Meeting, New Orleans, November, 1981.

Publications

Benton, W.J., J. Natoli, S. Qutubuddin, S. Mukherjee, C.A. Miller, and T. Fort, Jr., "Phase Behavior Studies of Two Model Surfactant Systems," Soc. Pet. Eng. J. 22, 53 (1982).

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Legend for Figures 1 through 6

T	=	Turbid phase
I_1 or Iso_1	=	Isotropic brine-rich phase
I_2 or Iso_2	=	Isotropic alcohol-rich phase
S	=	Dispersion of Spherulites
L	=	Homogeneous lamellar phase
C	=	Cubic or Viscous Isotropic phase

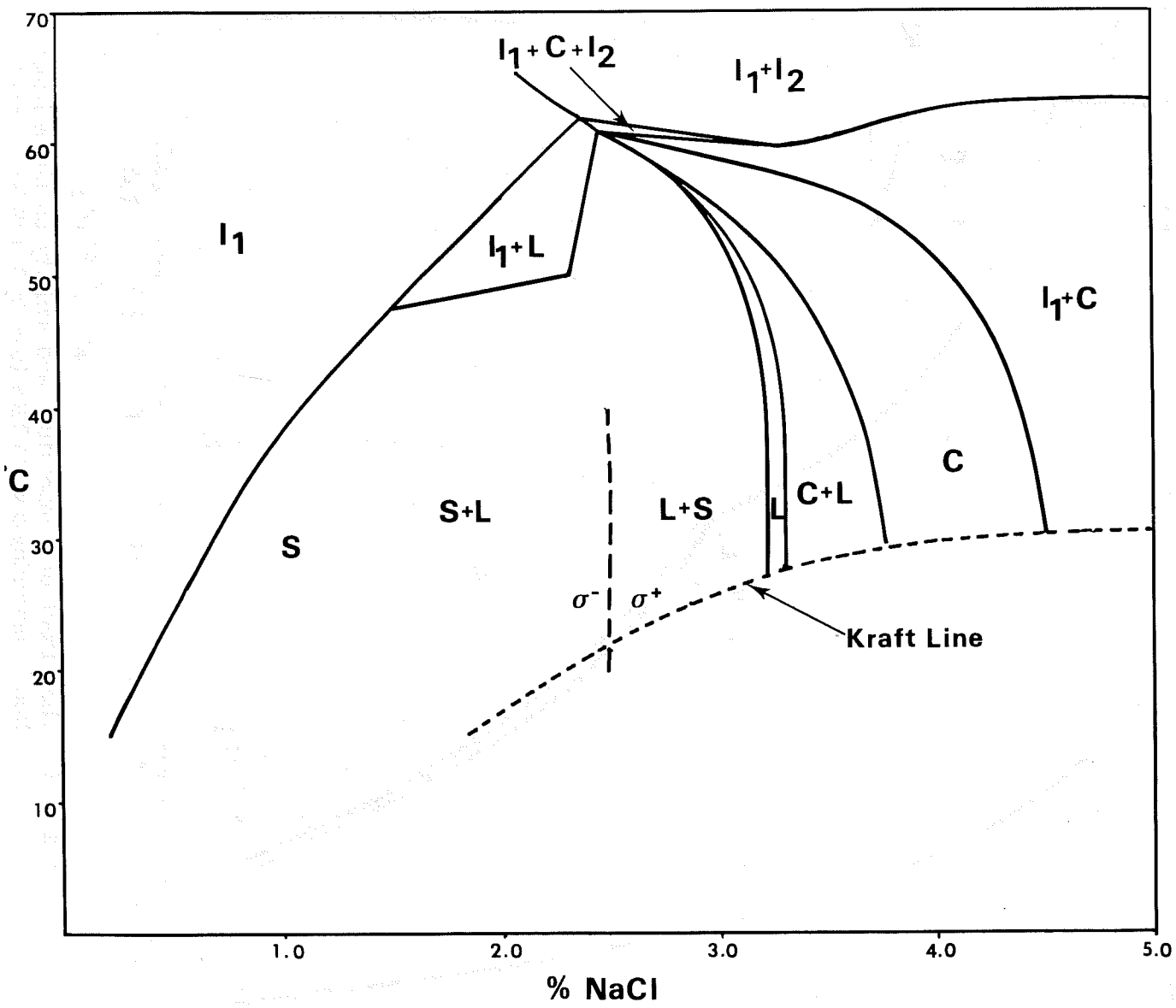

Figure 1 The effect of temperature and salinity on phase behavior of aqueous "solutions" containing 1.5 wt.% Texas 1, 10 wt.% n-propanol.

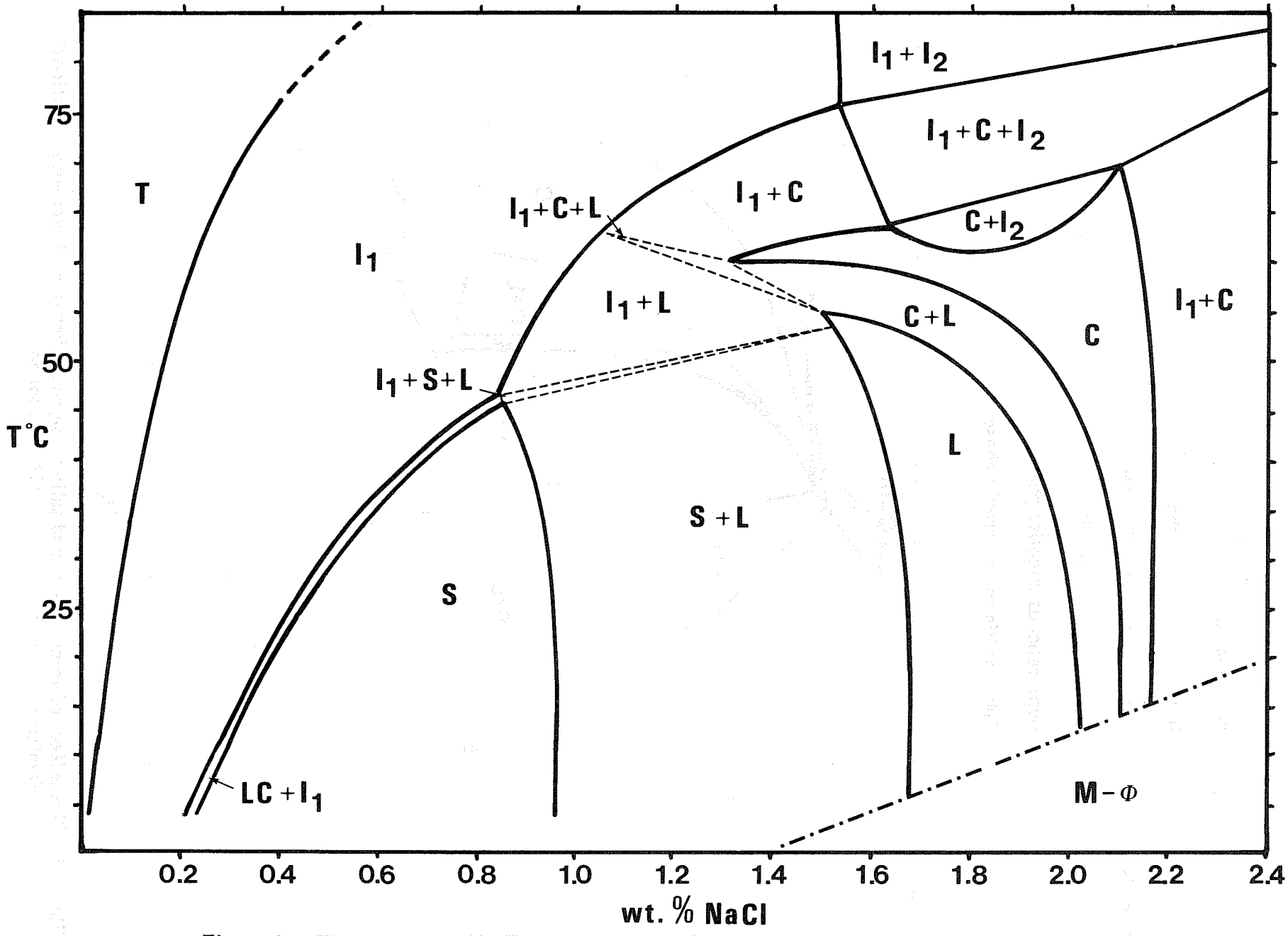

Figure 2 The effect of temperature and salinity on phase behavior of aqueous "solutions" containing 5 wt.% TRS 10-410, 3wt.% iso-butanol.

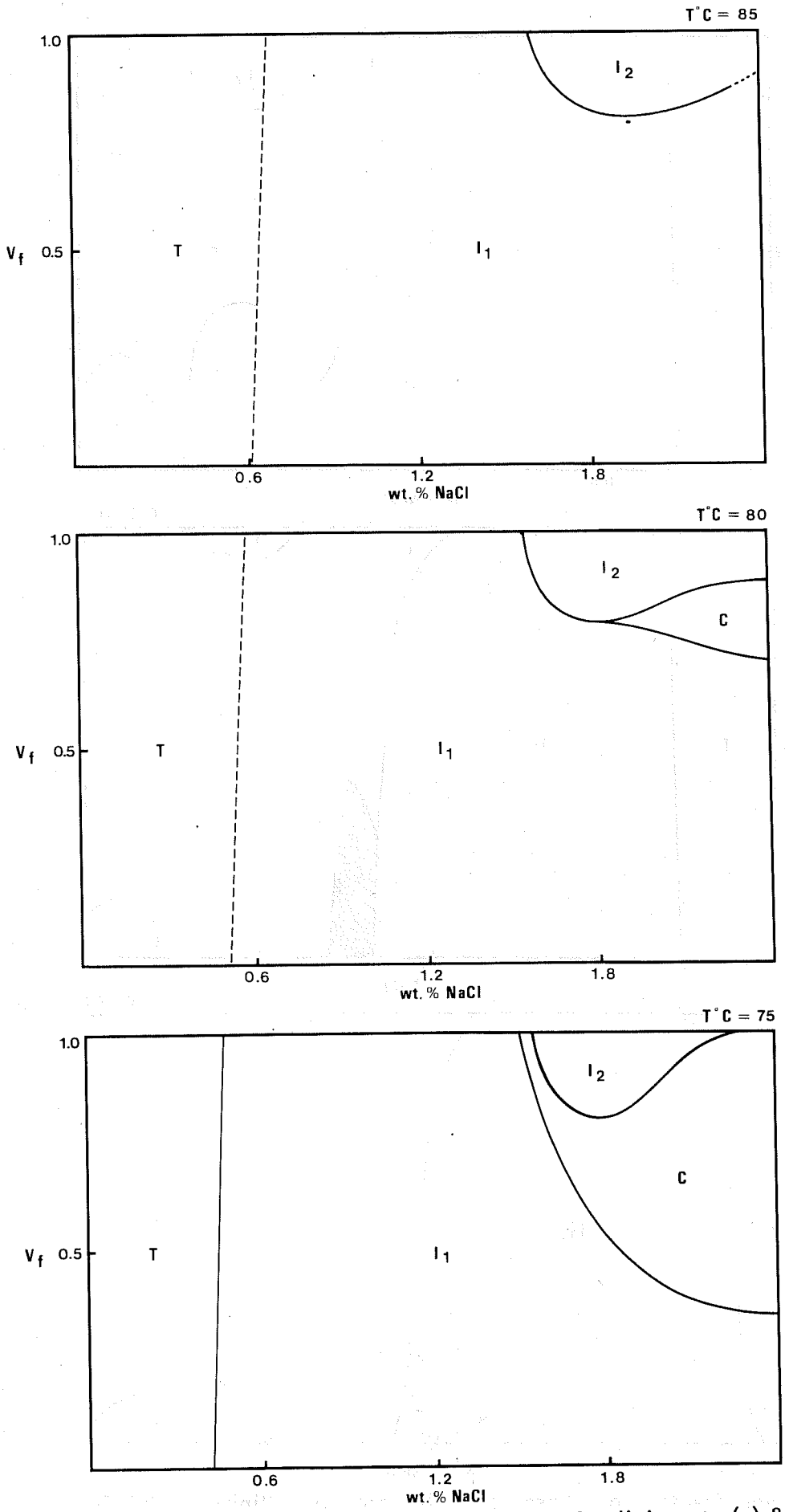

Figure 3 Volume fraction of phases as a function of salinity at (a) 85 (b) 80 and (c) 75°C for 5 wt.% TRS 10-410, 3 wt.% iso-butanol.

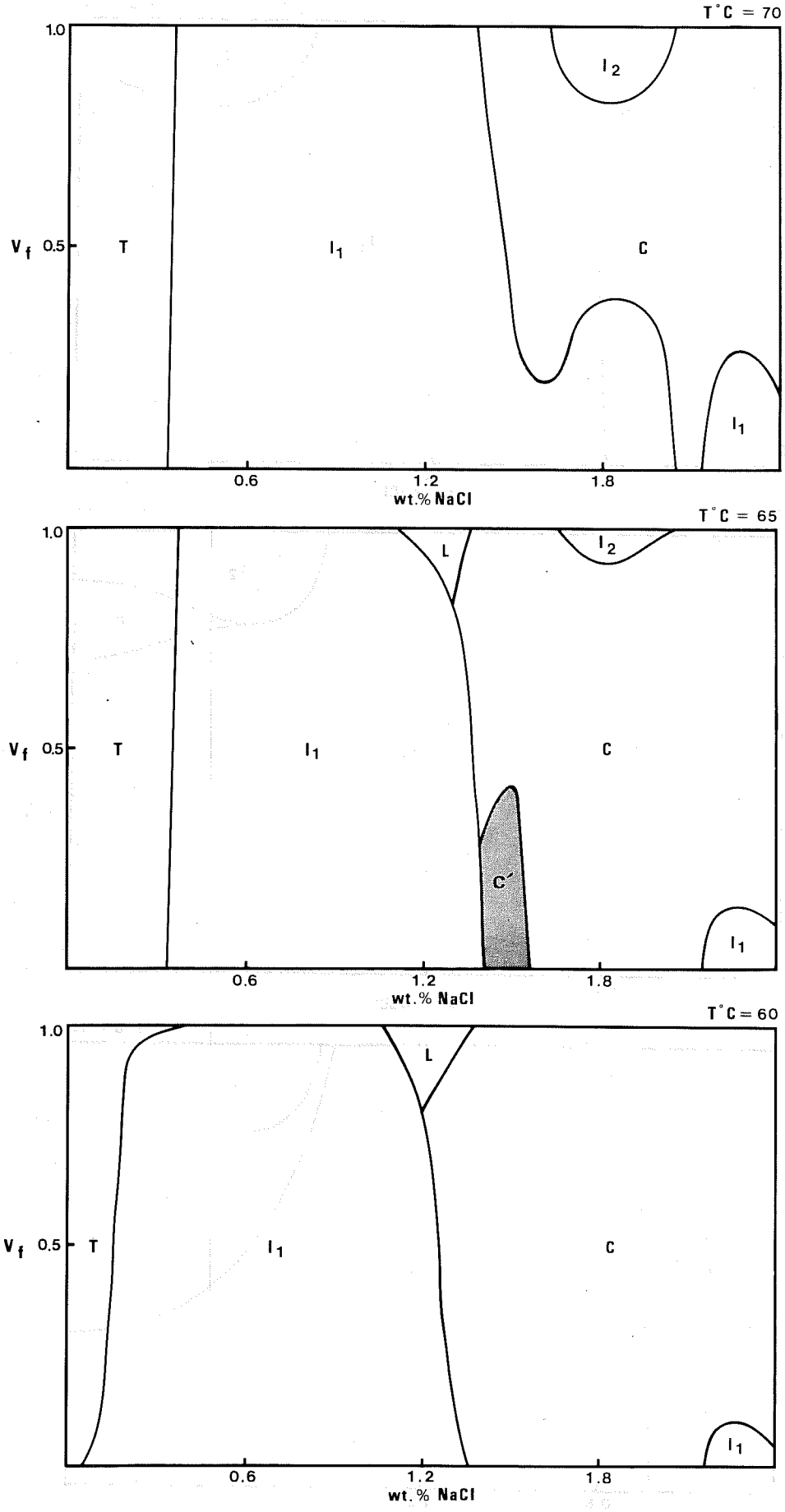

Figure 4 Volume fraction of phases as a function of salinity at (a) 70. (b) 65 and (c)60°C for 5 wt.% TRS 10-410. 3 wt.% iso-butanol.

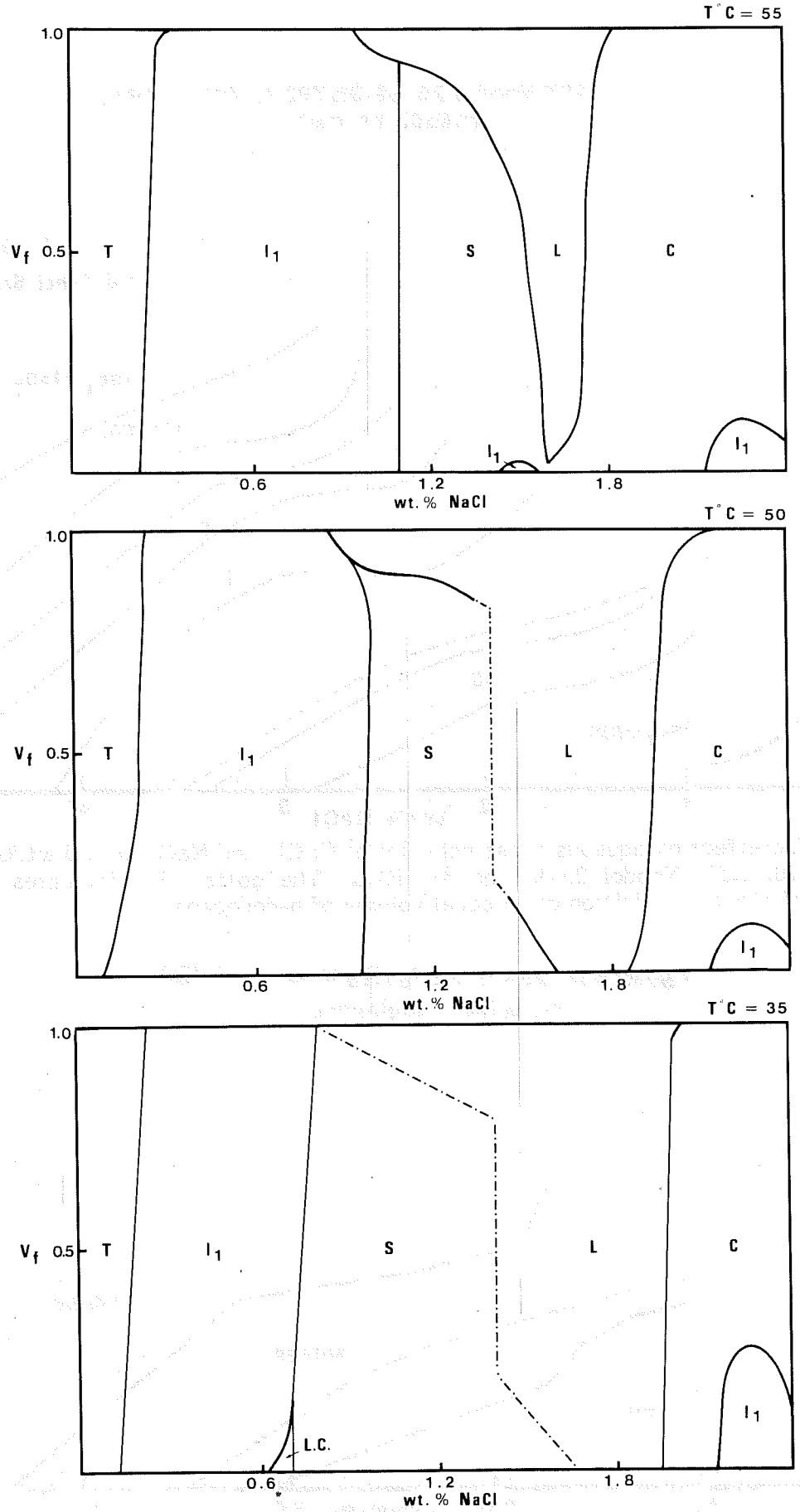

Figure 5 Volume fraction of phases as a function of salinity at (a) 55, (b) 50 and (c) 35°C for 5 wt.% TRS 10-410, 3 wt.% iso-butanol.

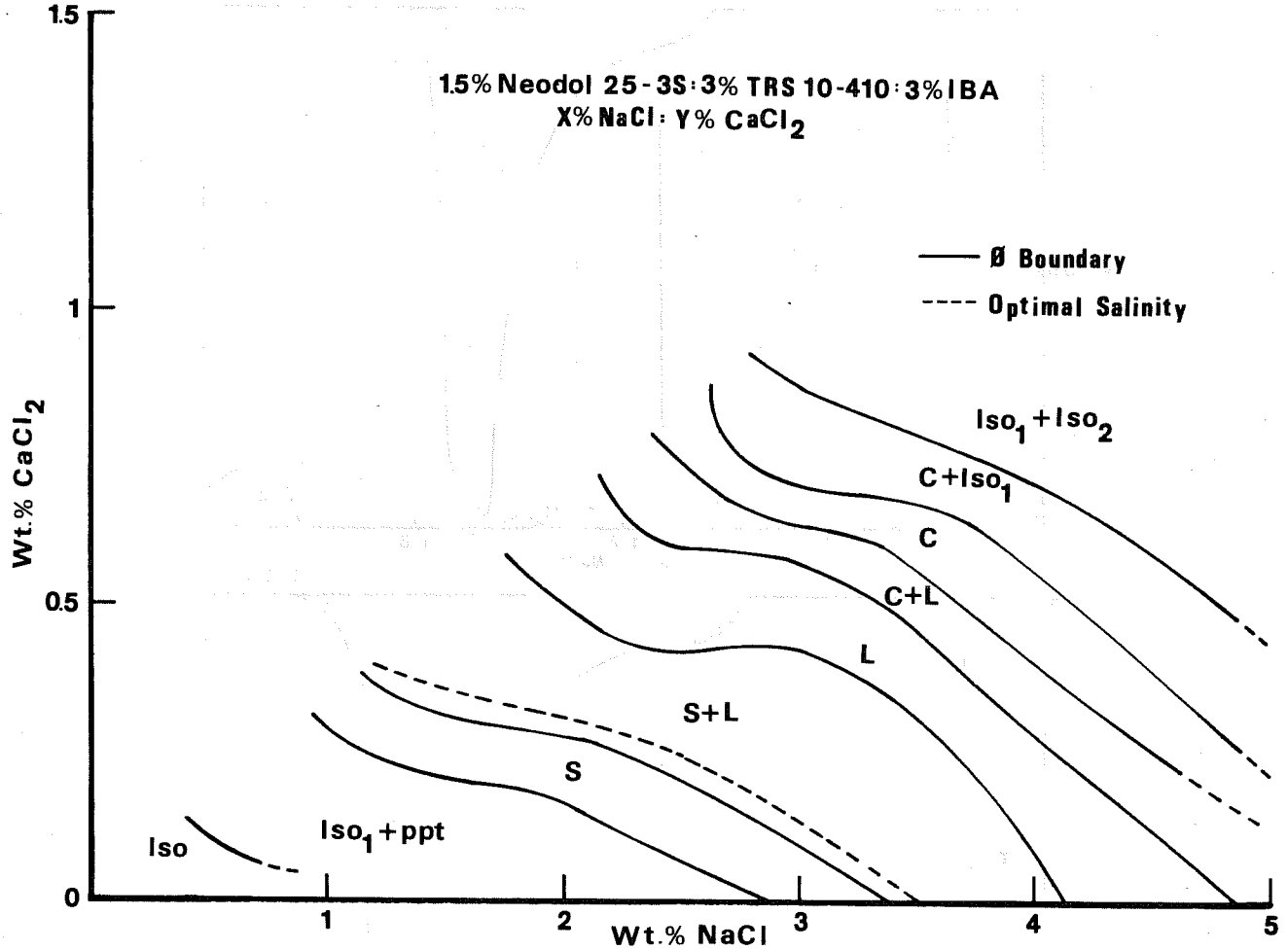

Figure 6 The effect on aqueous phase behavior of $CaCl_2$ and NaCl for 3.5 wt.% TRS 10-410, 1.5% Neodol 25-3S and 3% IBA. The dotted line indicates optimum salinity upon addition of an equal volume of n-dodecane.

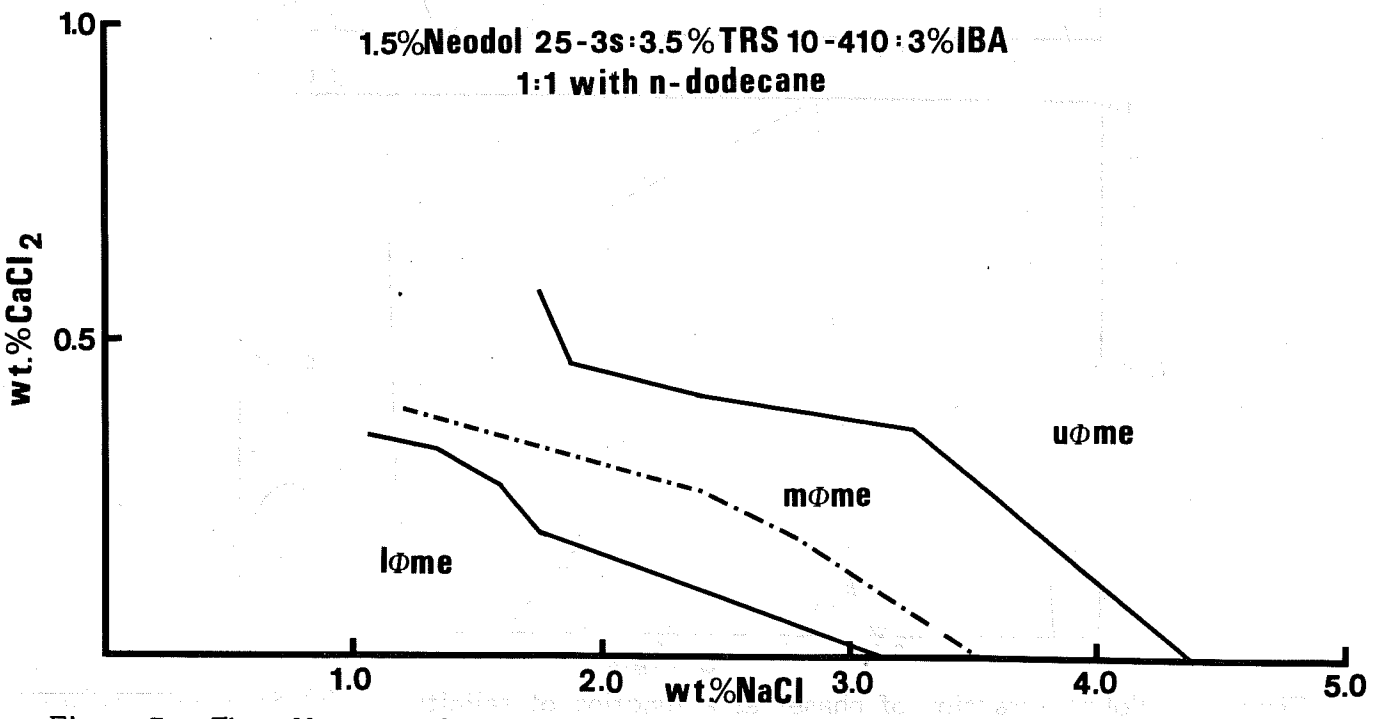

Figure 7 The effect on microemulsion phase behavior of $CaCl_2$ and NaCl for 3.5 % TRS 10-410, 1.5% Neodol 25-3S, 3% IBA. The oil is n-dodecane and the ratio of surfactant solution to oil is 1:1.

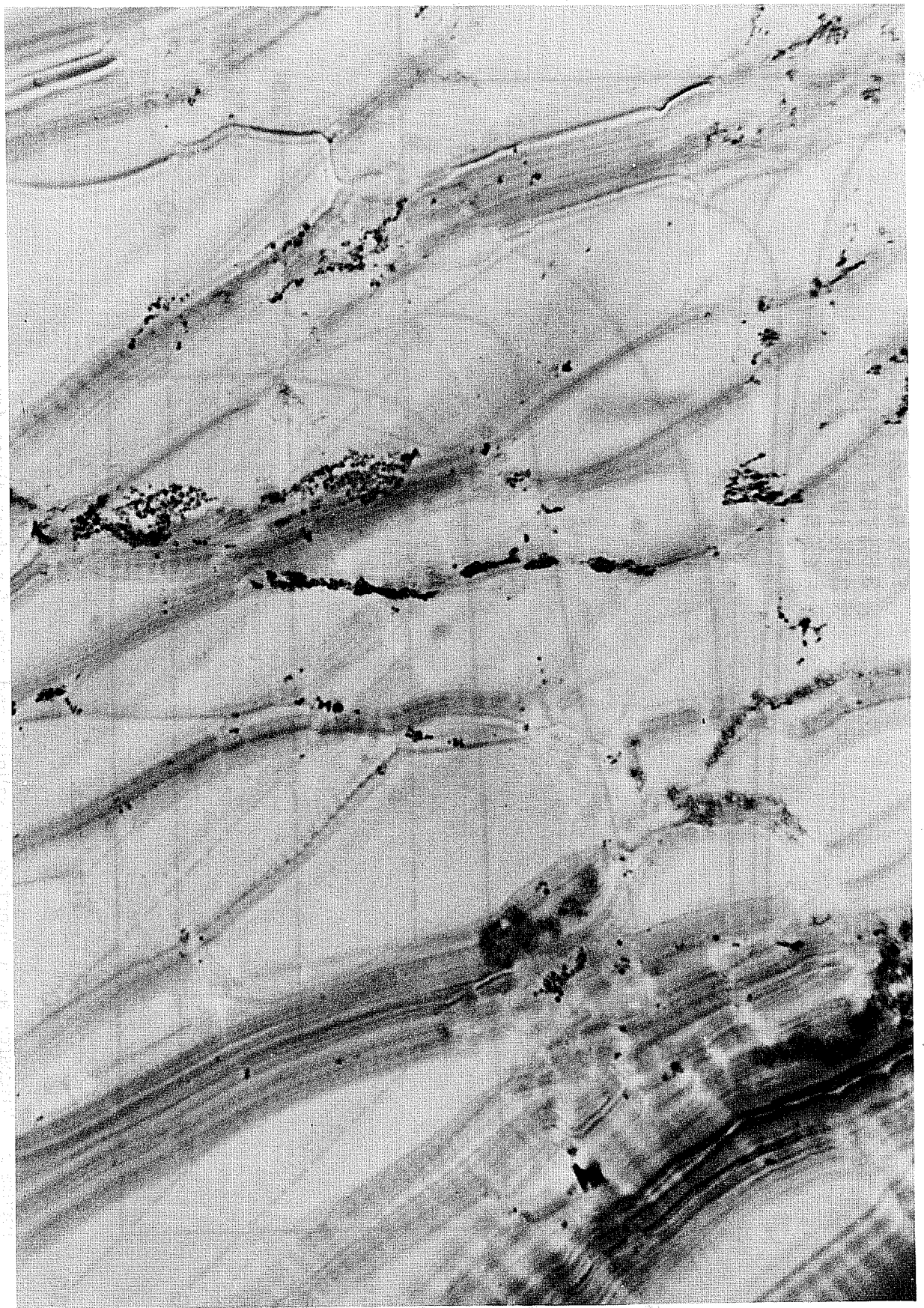

Figure 8 Photomicrograph in polarized light + ¼ λ plate of 3.5% TRS 10-410, 1.5% Neodol 25-3S, 3% IBA 0.67% $CaCl_2$ and 2.0% NaCl showing precipitate particles along "oily streak" defect-lines in L phase.

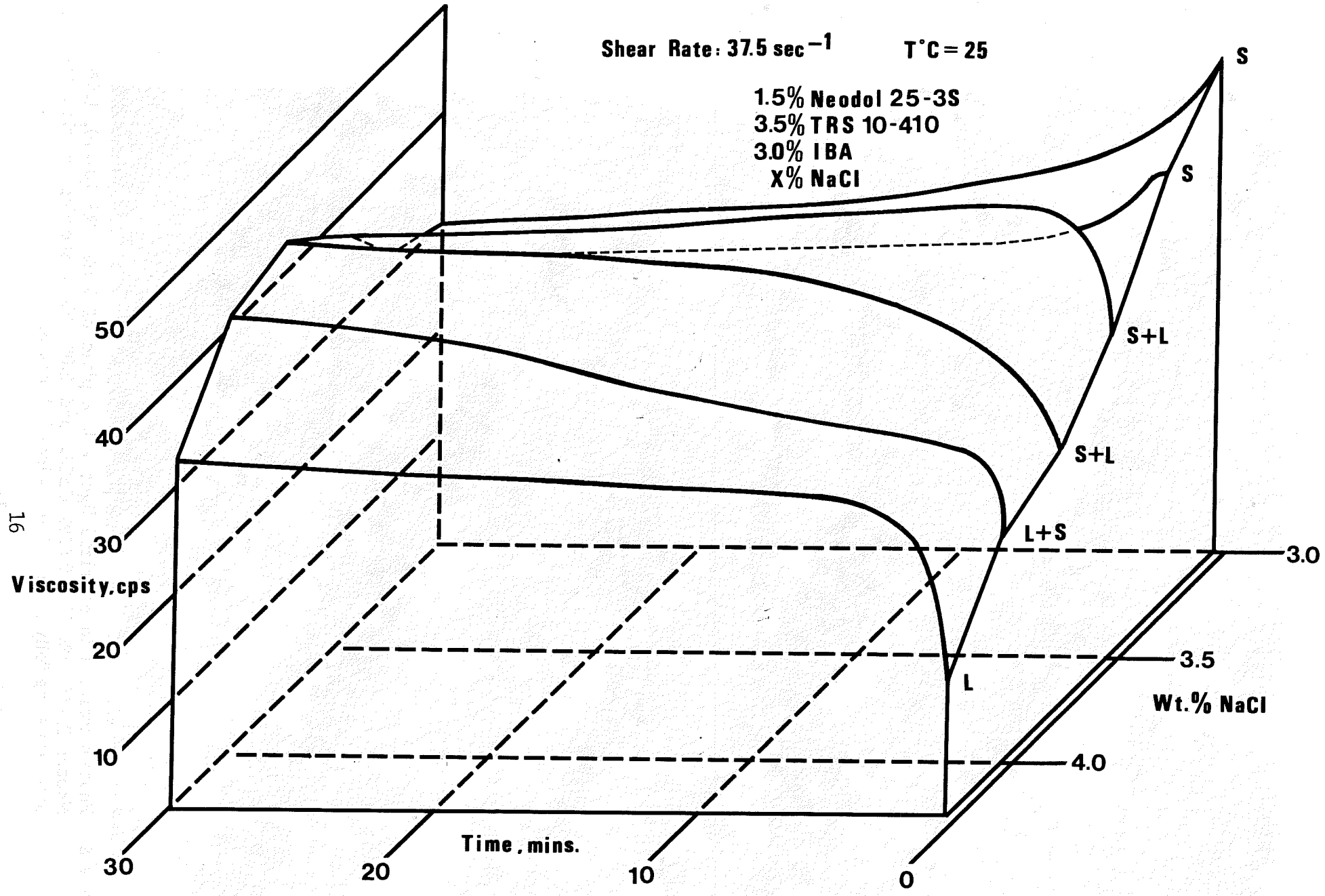

Figure 9 Viscosity as a function of salinity and time for short times for aqueous solutions containing 3.5 % TRS 10-410, 1.5% Neodol 25-3S. 3% IBA without $CaCl_2$.

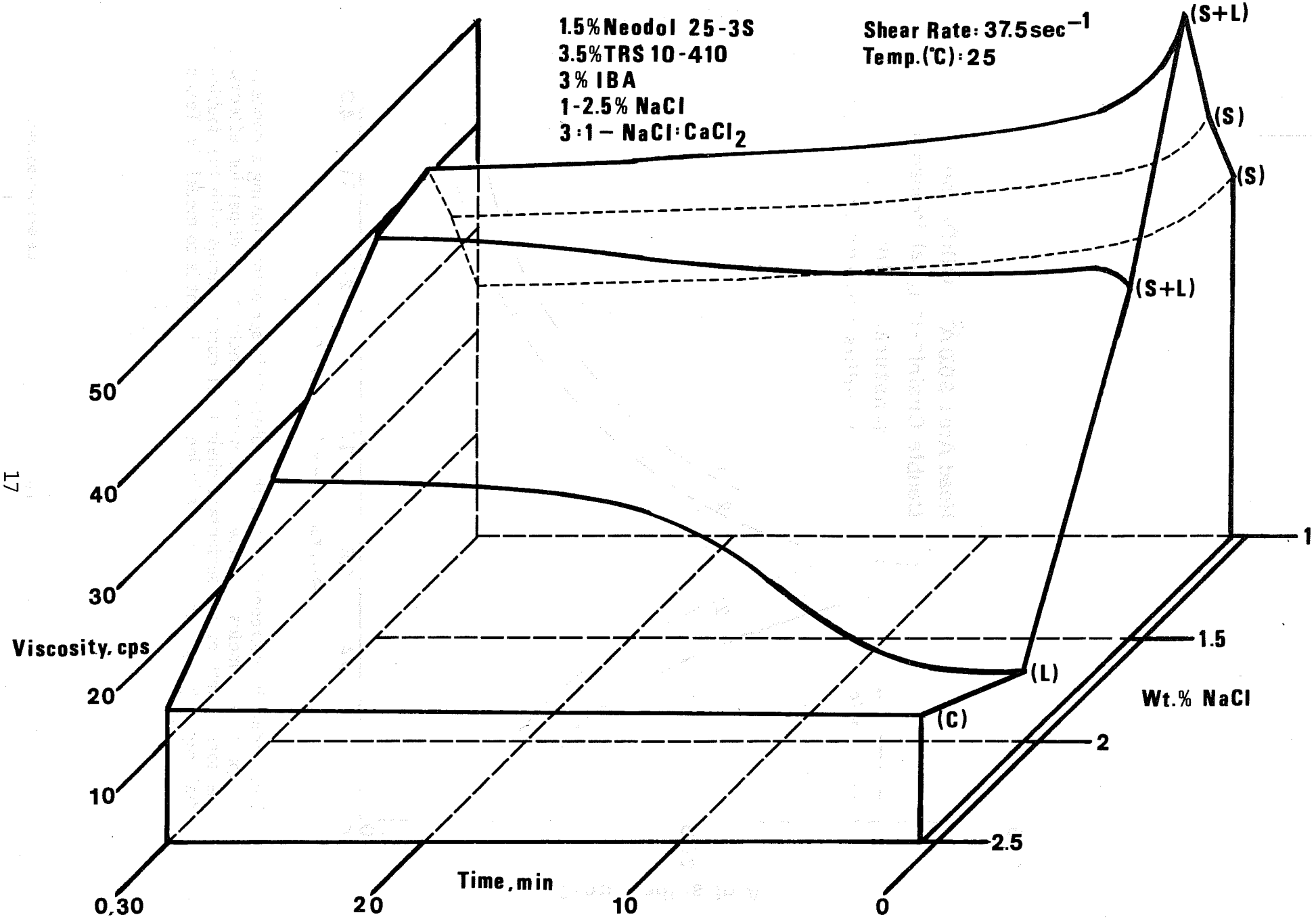

Figure 10 Viscosity as a function of salinity and time for short times for aqueous solutions containing 3.5% TRS 10-410, 1.5% Neodol 25-3S. 3% IBA with 3:1 - NaCl: $CaCl_2$

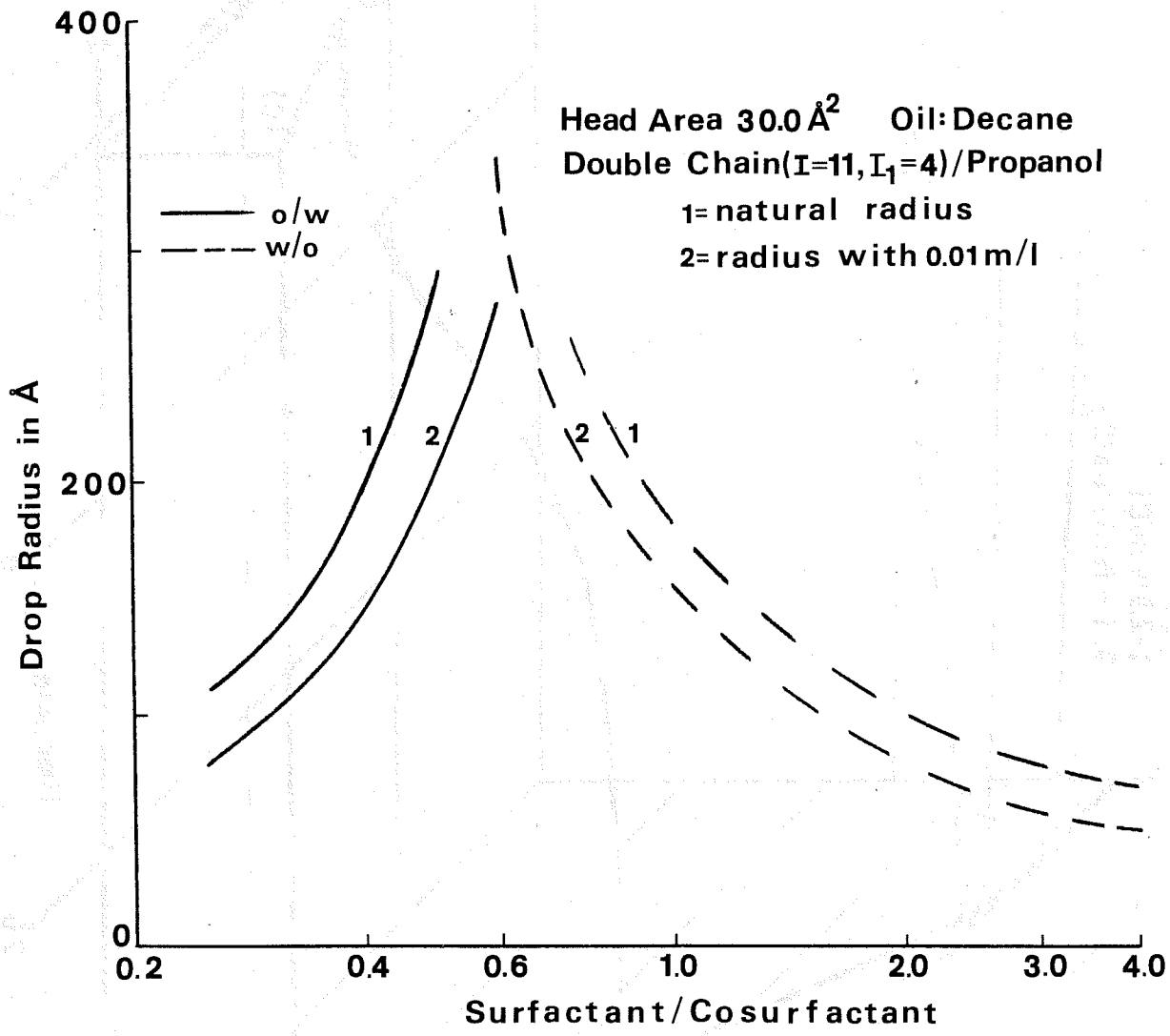

Figure 11 Drop radius in microemulsions with double-chain surfactant having a concentration of 0.01 moles/l both with and without inclusion of dispersion effects. The total length of the surfactant chain is 11 carbon atoms with the double-chain region being 7 carbon atoms in length. The intent is to model the Texas 1 molecule.

☆ U.S. GPO: 1982 - 569-028/25