LBL-24266
Preprint c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JAN 8 1988

LIBRARY AND
DOCUMENTS SECTION

Submitted to the AIChE Journal

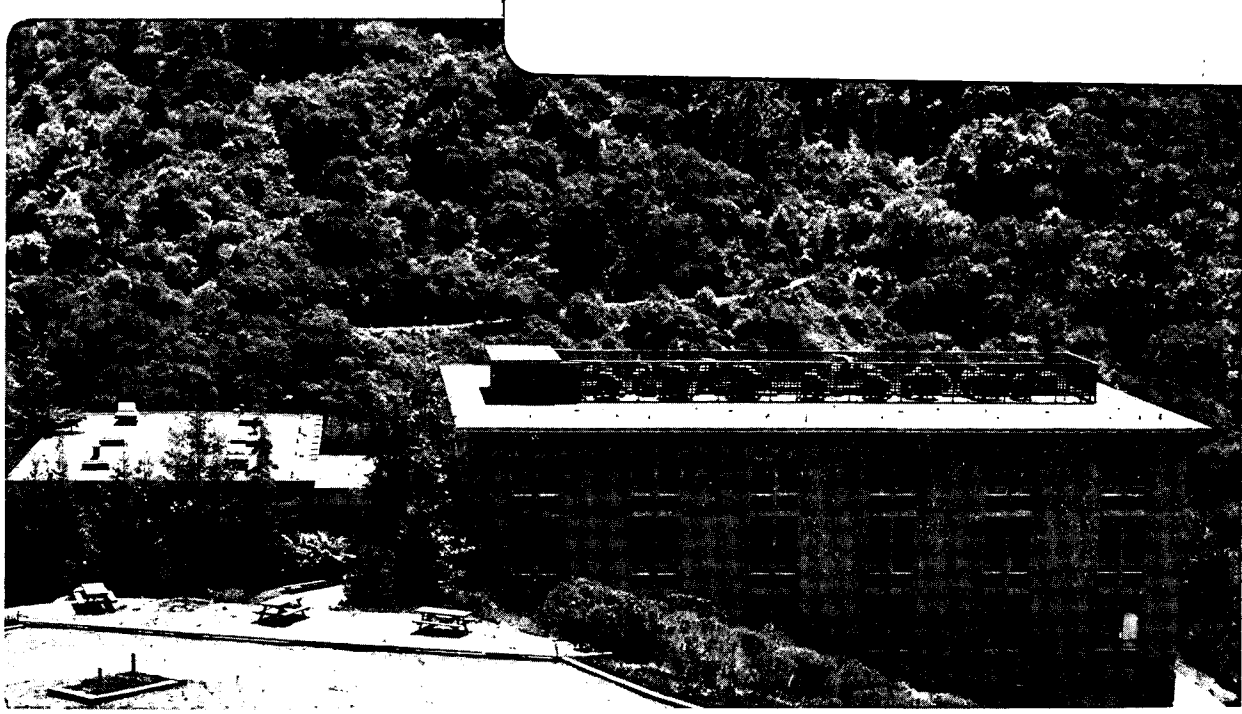
Molecular Thermodynamics of Partially-Ordered Fluids: Phase Behavior of Microemulsions

Y. Hu and J.M. Prausnitz

November 1987

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.



LBL-24266 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Molecular Thermodynamics of Partially-Ordered Fluids: Phase Behavior of Microemulsions

*Ying Hu * and John M. Prausnitz*

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
and
Chemical Engineering Department
University of California, Berkeley
Berkeley, California 94720

ABSTRACT

Mixtures of water, oil and surfactant often form microemulsions where tiny drops of oil (or water) are dispersed in a matrix of water (or oil). A microemulsion is a partially-ordered fluid where the surfactant molecules exist in an oriented layer at the boundary between the continuous phase and the discontinuous phase. This work proposes a molecular-thermodynamic model which is useful for calculating a variety of phase diagrams observed in microemulsion-forming systems.

The model is based on a revised form of Widom's abstract representation of a microemulsion; that representation provides a procedure for calculating essential contributions to the configurational entropy. In Widom's representation, all molecules are difunctional dumbells such that all the hydrophilic ends are situated together in some lattice sites and all the lipophilic ends are situated together in other sites. A form of Guggenheim's quasichemical theory is used to evaluate the combinatorial contributions which correspond to Widom's picture. Chemical association of surfactant molecules and physical interactions are also taken into account. Minimization of the Gibbs energy yields a distribution function for representing micelle sizes.

Calculated ternary phase diagrams are in good agreement with experimental results. Different types of diagrams can be obtained upon changing physically-significant model parameters. A study of how these parameters affect phase behavior provides insight on microemulsion stability.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

*East China Institute of Chemical Technology, Shanghai 201107, China

September 1987

Molecular Thermodynamics of Partially-Ordered Fluids: Phase Behavior of Microemulsions

*Ying Hu * and John M. Prausnitz*

Materials and Chemical Sciences Division,
Lawrence Berkeley Laboratory
and
Chemical Engineering Department,
University of California, Berkeley
Berkeley, CA 94720, USA

Introduction

Microemulsions are omnipresent in nature, including fluids essential for plant and animal life. Further, microemulsions are of much use in chemical technology (e.g. paints, coatings, detergents) and pharmaceutics. Chemical processes are sometimes carried out in emulsions (e.g. emulsion polymerization, tertiary oil recovery) as discussed, for example, by Langevin (1984). Recently, Olien (1987) has called attention to the role of microemulsions in biotechnology, including the use of reverse micelles for enzymatic reactions (Shield et al, 1986). Toward better understanding of the equilibrium properties of microemulsions, it is desirable to construct a quantitative molecular-thermodynamic model. This work provides a reasonable first-order version of such a model.

A microemulsion is a clear, transparent and stable fluid consisting essentially of oil-in-water (or water-in-oil) droplets with typical dimensions in the range 10-60nm or of laminar structures, as indicated in Figure 1. General behavior of microemulsions has been discussed in a series of reviews (Winsor,1968; Ekwall,1975; Tiddy,1980; Luisi and Straub,1984).

Efforts to describe the structure of a microemulsion can be traced back at least 50 years. To explain the formation of clear isotropic solutions when benzene and water are mixed in the presence of potassium oleate, Schulman (Hoar and Schulman,1943), a pioneer in this field, suggested that the aqueous droplet in oil is an aqueous sphere surrounded by a surfactant membrane. This drop with a membrane surface is called a micelle. Using simple geometry, we can evaluate the average radius of a micelle on the basis of Schulman's picture. More recently, Israelachivilli, Mitchell and Ninham (Israelachivilli et al, 1976; Mitchell et al, 1981) have discussed the conditions required for the formation of spherical, rodlike, bilayer or other-shaped aggregates. Upon constructing a theory for chemical potentials, they could estimate the size distribution of micelles. Using similar ideas, Robins (1977) showed that observed limits in a phase diagram are related to the structure of the surfactant molecules.

Various improvements in the theory of microemulsions have been developed along different directions. One of them is based on the idea of chemical equilibria (mass-action theory) which has long existed in the field of aqueous surfactant solutions. For example, Mazer, Benedek and Carey (1980), and Stecker and Benedek (1984) applied chemical-equilibrium theory to multicomponent micelles and microemulsions with the use of an empirical function to describe micelle size distribution. Ben-Shaul et al (1986) considered cosurfactants; they assumed that the cosurfactant is a "spacer" that dilutes the charge density at the interface. Blankschtein et al (1986; Thurston et al, 1986) extended the mass-action theory by incorporating interactions between the micelles; their theory describes phase separation in binary surfactant solutions. Other theories, emphasizing the role of interfacial tension, have been put forward by Ruckenstein et al (1978,1980; Nagarajan and Ruckenstein, 1979). Considering a microemulsion to contain monodisperse spherical droplets, the radius of

*East China Institute of Chemical Technology, Shanghai 201107, China

a droplet can be determined by minimizing the free energy. The most important terms in this theory reflect the effect of interfacial tension and entropy of mixing. Finally, Rosen et al (1982) have presented a model based on the Flory-Huggins equation and Kilpatrick et al (1985) have applied this model to a quaternary system containing brines.

Talmon and Prager (1978) modeled a microemulsion as a random geometry of interspersed domains generated by Voronoi polyhedrons with the surfactant adsorbed at the boundary. Larson, Scriven and Davis (1985) studied a two-dimensional microemulsion using Monte-Carlo simulation. De Gennes and Taupin (1982), and Widom (1984), inspired by the model of Talmon and Prager, proposed a simplified version in which the domains are cubes packed in a regular array, and the entropy of the folded film is estimated as the entropy of random mixing of the components. Finally, Widom (Wheeler and Widom, 1968; Widom, 1984a,1986) has modeled a microemulsion as a mixture of difunctional groups and he has mapped this picture onto an Ising model. These more sophisticated theories can describe phase separation in microemulsion systems. However, they are too abstract and cumbersome for practical use at this time.

The aim of the present work is to develop a molecular-thermodynamic model for microemulsions which is able to describe phase behavior in a manner that is on the one hand realistic, yet on the other, sufficiently simple for engineering purposes.

Molecular-Thermodynamic Framework

The thermodynamics of liquid solutions has been dominated by the ideal-solution concept as exemplified by Raoult's law. Typical molecular-thermodynamic models for liquid mixtures offer first-order corrections to Raoult's law or else to Flory's expression for athermal solutions of chain molecules. Nearly all engineering-oriented models present variations on a theme where the liquid solution is considered to be an assembly of more-or-less randomly mixed molecules. For associated solutions (e.g. alcohols in hydrocarbons), some ordering is introduced by incorporating chemical equilibria into the model; however, for such solutions, it is then assumed that the various molecular species (monomers, dimers, etc) form a more-or-less random mixture.

To describe the equilibrium properties of a microemulsion, we cannot use conventional expressions for the entropy of mixing because a microemulsion is not even approximately a random mixture. In a microemulsion, not only are water and oil immiscible components but, more important, the surfactant molecules are not free to position themselves anywhere; they must be at the water-oil interface. In a microemulsion, we do not have a liquid that is homogeneous on a molecular scale but instead, we have a heterogeneous medium with microphases or domains. Therefore, conventional expressions yield an entropy of mixing which is too large. To describe the equilibrium properties of a microemulsion, we require a molecular-thermodynamic theory for a partially-ordered fluid.

We consider a ternary mixture of water, oil and surfactant. We seek an expression for the Gibbs energy G as a function of temperature, pressure and number of molecules N_W, N_O and N_S (water, oil, surfactant). Initially, all components are in their standard states designated by superscript o: pure liquid water, pure liquid oil, and surfactant monomer at infinite dilution in water, all at system temperature and pressure. The Gibbs energy of the microemulsion is given by

$$G = G^o + \Delta G_I + \Delta G_{II} + \Delta G_{III} \tag{1}$$

where G^o is the Gibbs energy of the system when each component is in its standard state; ΔG_I is the Gibbs energy change due to formation of oligomers (chemical association) of the surfactant; ΔG_{II} and ΔG_{III} are, respectively, combinatorial and physical-interaction contributions due to mixing. Upon minimizing the Gibbs energy with respect to the concentration of the oligomers, we obtain the size distribution of the micelles. Upon differentiation with respect to nominal composition, we obtain chemical potentials and phase equilibia.

G^o : Gibbs energy of the standard state

The Gibbs energy of the standard state G^o is given by

$$G^o = N_W\mu_W^o + N_O\mu_O^o + N_S\mu_{S1(W)}^o \tag{2}$$

where μ_i^o is the chemical potential of component i in the standard state; subscript (W) indicates aqueous phase.

ΔG_I : *Gibbs energy change due to chemical association of the surfactant*

Monomer S_1 associates to form an oligomer S_j where j is an integer between j_m and ∞,

$$j(S_1) \rightarrow S_j \qquad j=j_m \rightarrow \infty$$

Here j_m is the smallest allowed aggregation number. The Gibbs energy change due to association is given by

$$\Delta G_I = \sum_{j=j_m}^{j=\infty} N_{Sj}(\mu_{Sj}^o - j\mu_{S1(W)}^o) \tag{3}$$

where N_{Sj} is the number of molecules of surfactant j-mer and μ_{Sj}^o is the corresponding standard-state chemical potential. For μ_{Sj}^o, the standard state is a hypothetical, infinite dilute solution of S_j such that the hydrophilic end of S_j is in water while its hydrophobic lipophilic end is in oil. For estimating μ_{Sj}^o, we use an expression based on the theory of Lennard-Jones, Devonshire and Prigogine (Prigogine, 1957):

$$\mu_{Sj}^o = \varepsilon_{Sj}^o - Ts_{Sj}^o = \varepsilon_{Sj}^o - kTln v_{f,Sj} \tag{4}$$

where ε_{Sj}^o is the internal energy (more strictly, the enthalpy), s_{Sj}^o is the entropy, and $v_{f,Sj}$ is the free volume of oligomer S_j in its standard state, as defined above.

We assume that ε_{Sj}^o is a linear function of the aggregation number j,

$$\varepsilon_{Sj}^o = j\varepsilon_{S1}^o - D_o(j_m-1) - D(j-j_m) \ . \tag{5}$$

Here D_o is the association energy (per pair of monomers) for associated surfactant of the smallest micelles which have the greatest curvature and which contain neither oil nor water at their centers; D is the average value of the association energy (per pair of monomers) for associated surfactant of those micelles which have oil or water at their centers; these larger micelles have smaller curvature. The energy of monomer ε_{S1}^o depends on the oil-water ratio. We make the reasonable assumption

$$\varepsilon_{S1}^o = \varepsilon_{S1(W)}^o + \varepsilon_{S1(O-W)}^o \Phi_O/(\Phi_O+\Phi_W) \ . \tag{6}$$

Here $\varepsilon_{S1(O-W)}^o$ is a characteristic constant determined by the binaries S-O and S-W. If the free volume of monomer is independent of its environment,

$$\varepsilon_{S1(O-W)}^o = \mu_{S1(O)}^o - \mu_{S1(W)}^o \tag{7}$$

where subscript (O) indicates organic phase. Φ_O and Φ_W are the volume fractions of oil and water:

$$\Phi_O = N_O r_O/N_r, \quad \Phi_W = N_W r_W/N_r \tag{8}$$

$$N_r = N_W r_W + N_O r_O + N_S r_S \tag{9}$$

where r is a molecular size parameter. The free volume of associated surfactant is assumed to be additive:

$$v_{f,Sj} = jv_{f,S1} \tag{10}$$

Eqn.(10) is advantageous for calculating the size distribution, as shown in Appendix I.

ΔG_{II} : Gibbs energy change due to mixing water, oil and associated surfactant. Combinatorial contribution

The combinatorial part of the Gibbs energy change is obtained from the athermal entropy of mixing water, oil and surfactant. However, this entropy cannot be calculated from conventional expressions used in classical theories of solution because a microemulsion is not a random mixture where molecules mix in an essentially disordered, statistical manner; instead, it is a partially-ordered mixture. To take into account that nearly all of the surfactant oligomers are situated in an orderly fashion between the oil and water molecules, we derive here an expression for the entropy of mixing based on Widom's abstract lattice representation (Wheeler and Widom, 1968, Widom, 1984a, 1986). In that representation, all monomer molecules are considered to be difunctional species. Consistent with its amphiphilic nature, a surfactant is represented by a dumbell where one end is a dot and the other a circle. Water and oil molecules are represented as dumbells containing, respectively, two circles and two dots. Forming a lattice, all the difunctional species are arranged in such a way that all the dots are situated in some sites and all the circles are situated in other sites, as shown in Figure 2. To allow for the rare existence of monomers in this lattice, the bond between dot and circle can be unoccupied as a vacancy bond.

It is important to note that, in Figure 2, lattice sites are not molecule sites as in typical lattice theories of fluids. Instead, lattice sites here are points where the ends of selected dumbells congregate. In the two-dimentional view shown in Figure 2, each lattice point can accomodate a maximum of four dumbell ends.

In the next paragraphs we apply statistical and material-balance arguments which utilize the number of lattice sites as defined above. In these arguments we also use the number of bonds which link the nearest sites.

We designate with letter A those sites filled with dots, and with letter B those filled with circles. The numbers of such sites are given by N_A and N_B respectively. Material balances give

$$N_A = (2N_W + N_S + N_V)/z_A \tag{11}$$

$$N_B = (2N_O + N_S + N_V)/z_B \tag{12}$$

where z_A and z_B are coordination numbers for site A and site B respectively. N_V is the number of vacancy bonds; this is a very small number whose precise value has no effect on the final results of our calculations. However, we do not set N_V equal to zero because of a necessary boundary condition, as discussed in Appendix II.

Coordination numbers z_A and z_B need not be identical. Their values need not be specified because, as shown below, the combinatorial entropy of interest here does not use N_A and N_B. Instead, the combinatorial entropy depends on the number of bonds.

To calculate the combinatorial entropy, we introduce the number of A-A, A-B, B-A and B-B bonds designated by $N_{AA}, N_{AB(S)}, N_{AB(V)}, N_{BA(S)}, N_{BA(V)}$ and N_{BB}. Here subscripts (S) and (V) indicate surfactant and vacancy, respectively. They are given by material balances:

$$N_{AA} = N_W, \quad N_{BB} = N_O \tag{13}$$

$$N_{AB(S)} = N_{BA(S)} = N_S/2, \quad N_{AB(V)} = N_{BA(V)} = N_V/2 \tag{14}$$

The combinatorial contribution to the Gibbs energy change is the sum of two parts. The first follows from the configurational change of the system as a result of mixing. The second accounts for size distribution caused by chemical association.

$$\Delta G_{II} = \Delta G_{II}' + \Delta G_{II}'' \tag{15}$$

First, we consider $\Delta G_{II}'$. Following the classical quasichemical procedure of Guggenheim (1952), the number of configurations in the lattice is given by

$$\Omega = \frac{(N_{AA}+N_{AB(S)}+N_{AB(V)}+N_{BA(S)}+N_{BA(V)}+N_{BB})!}{N_{AA}!N_{AB(S)}!N_{AB(V)}!N_{BA(S)}!N_{BA(V)}!N_{BB}!}$$

$$= \frac{(N_W + N_O + N_S + N_V)!}{N_W!N_O![(N_S/2)!]^2[(N_V/2)!]^2} \tag{16}$$

However, Equation (16) does not meet the necessary boundary condition that, when N_S goes to zero, Ω must approach unity, because oil and water are here considered totally immiscible. Therefore, we propose a more realistic formula for Ω . We distinquish between two kinds of bonds, those which are congregated at site A and those which are congregated at site B , and we treat them as independent from each other. This distinction suggests the following expression

$$\Omega = \frac{(N_W+N_S/2+N_V/2)!(N_O+N_S/2+N_V/2)!}{N_W!N_O![(N_S/2)!]^2[(N_V/2)!]^2} \tag{17}$$

The two factorials in the numerator reflect, respectively, the contributions of the bonds congregated at site A and those congregated at site B. Neglecting the minor volume change of mixing, the configurational Gibbs energy change for the mixing step is

$$\Delta G_{II}' = -kTln\frac{\Omega}{\Omega_W\Omega_O\Omega_S} \tag{18}$$

where $\Omega_W=\Omega_O=1$. Because of symmetry, each surfactant molecule has two choices: "dot to circle" and "circle to dot" ; therefore, $\Omega_S=2^{N_S}$. Upon substituting Eqn.(16) into Eqn.(17), we have

$$\begin{aligned}\Delta G_{II}' = {} & N_W kTln\frac{N_W}{N_W+N_S/2+N_V/2}+N_O kTln\frac{N_O}{N_O+N_S/2+N_V/2} \\ & +N_S kTln\frac{N_S}{(N_W+N_S/2+N_V/2)^{1/2}(N_O+N_S/2+N_V/2)^{1/2}} \\ & +N_V kTln\frac{N_V/2}{(N_W+N_S/2+N_V/2)^{1/2}(N_O+N_S/2+N_V/2)^{1/2}}\end{aligned} \tag{19}$$

We now consider $\Delta G_{II}''$. Equation (17) neglects the contribution to ΔG_{II} due to association of surfactant molecules. To correct for this neglect, we introduce a Flory-Huggins term to take into account the surfactant-size distribution caused by chemical association,

$$\Delta G_{II}'' = kT\sum_{j=1}^{j=\infty} N_{Sj}\ln\Phi_{Sj} - kTN_S\ln\Phi_S \tag{20}$$

where

$$\Phi_{Sj} = N_{Sj}r_{Sj}/N_r \tag{21}$$

and

$$r_{Sj} = jr_S \tag{22}$$

The combinatorial contribution ΔG_{II} is the sum of Eqns.(19) and (20), as indicated by Eqn(15).

ΔG_{III} : Gibbs energy change due to mixing water, oil and associated surfactant. Contribution from physical interactions

We have six kinds of interactions; they are S-S, W-W, O-O, S-W, S-O and W-O. However, interactions W-W and O-O are included in the standard states while interactions S-W and S-O are included in chemical association energies D_o and D. Therefore, only the remaining interactions S-S and W-O require attention here. For surfactant interactions, Huang (1985) has made extensive studies using a light-scattering technique. He found that the experimental results could be analyzed in terms of a Carnahan-Starling equation modified by a two-body attractive term. It is therefore reasonable in our model to choose a simple attractive van der Waals expression to account for these interactions:

$$\Delta G_{III} = -(N_S^2 a_{SS} + N_W N_O a_{WO})/V \quad . \tag{23}$$

Here a_{SS} is a function of temperature and of the oil-to-water ratio. We assume

$$a_{SS} = a_{SS(W)} + a_{SS(O-W)}\Phi_O/(\Phi_O+\Phi_W) \tag{24}$$

where $a_{SS(O-W)}=a_{SS(O)}-a_{SS(W)}$ and where subscripts (W) and (O) designate aqueous and organic phase, respectively. Because the surfactant molecules are always situated between the oil and water molecules, parameter a_{WO} depends on the properties of the surfactant in the microemulsions; therefore, it is a characteristic constant of the ternary system.

Substitution into Eqn.(1) gives the Gibbs energy for a microemulsion.

Size Distribution of Micelles

To calculate the size distribution of the micelles, we first minimize the Gibbs energy with respect to N_{Sj}. As shown in Appendix I, from Eqn.(1), we can obtain an expression for the volume fraction of oligomer S_j :

$$\Phi_{Sj} = \frac{K_o^{jm-1}}{K^{jm}} j\Phi_{S1}^j K^j \tag{25}$$

where

$$K_o = exp\,[(D_o/kT)-lnv_{f,S1}+1] \tag{26}$$

and

$$K = exp\,[(D/kT)-lnv_{f,S1}+1] \tag{27}$$

Eqns.(26) and (27) define chemical equilibrium constants.

For convenience, we also define a generalized (relative) equilibrium constant

$$K_R = K/K_o \tag{28}$$

and we define a generalized volume fraction

$$\Phi_{Sj}^* = \Phi_{Sj}K \quad . \tag{29}$$

Substitution gives a generalized distribution,

$$\Phi_{Sj}^* = K_R^{1-jm} j\Phi_{S1}^{*j} \tag{30}$$

and

$$\Phi_S^* = \Phi_S K = \sum_{j=1}^{j=\infty}\Phi_{Sj}^* = \Phi_{S1}^* + K_R^{-jm}\Phi_{S1}^{*jm}\left[\frac{j_m}{1-\Phi_{S1}^*} + \frac{\Phi_{S1}^*}{(1-\Phi_{S1}^*)^2}\right] \tag{31}$$

Eqns.(25) and (31) give the size distribution of surfactant. When the oil-to-water ratio is very small or very large, and when the concentration of surfactant is sufficiently large, we can distinguish between an oil-in-water microemulsion and a water-in-oil microemulsion. (The latter corresponds to what is called reverse micelle.) For both cases, we can estimate the size distribution of the micelles as follows:

· For a micelle with surfactant aggregation number j , the volume of the surfactant is proportional to j; the maximum volume for oil or water in the micelle is correspondingly proportional to $j^{3/2}$. Therefore, for an oil-in-water microemulsion,

$$\Phi_{Oj} \propto j^{1/2}\Phi_{Sj} \quad . \tag{32}$$

Substitution of Eqns.(29) and (30) yields

$$\Phi_{Oj} = \Phi_O \frac{j^{3/2}\Phi_{S1}^{*j}}{\sum_{j=j_m}^{j=\infty} j^{3/2}\Phi_{S1}^{*j}} \tag{33}$$

where Φ_{Oj} is the volume fraction of oil in those micelles whose surfactant aggregation number is j. The denominator of Eqn.(33) is calculated numerically, e.g., by using the Gaussian-quadrature method.

Since the volume of the micelle is the sum of the volumes of surfactant and oil in it, the total size distribution of micelles is given by

$$\Phi_{Mj} = \Phi_{Sj} + \Phi_{Oj} \tag{34}$$

which is the sum of Eqn(27) and (33). Φ_{Mj} is the volume fraction of micelles with aggregation number j of the surfactant.

We define the moment of distribution of order k by

$$M_{(k)} = \sum_{j=1}^{j=\infty} j^k \Phi_{Sj}^* \tag{35}$$

We can then obtain the following relations:

$$M_{(0)} = \Phi_S^* \tag{36}$$

$$M_{(1)} = \sum_{j=1}^{j=\infty} j\Phi_{Sj}^* = <j>_{(S)} M_{(0)} \tag{37}$$

$$M_{(2)} = \sum_{j=1}^{j=\infty} j^2\Phi_{Sj}^* = <j^2>_{(S)} M_{(0)} \tag{38}$$

$$\sigma_j^2 = <j^2>_{(S)} - <j>_{(S)}^2 = \frac{M_{(2)}}{M_{(0)}} - (\frac{M_{(1)}}{M_{(0)}})^2 \tag{39}$$

where $<j>_{(S)}$ is the average aggregation number of surfactant averaged with respect to the distribution of the surfactant and where σ_j^2 is the variance of the distribution. Similarly, we can define another average aggregation number of surfactant $<j>_{(O)}$ by

$$<j>_{(O)} = \sum_{j=j_m}^{j=\infty} j\Phi_{Oj}/\Phi_O \tag{40}$$

which is averaged with respect to the distribution of oil in the micelles.

The average aggregation number of surfactant (averaged with respect to the distribution of all micelles) then can be calculated from

$$<j>_{(M)} = <j>_{(S)} \frac{\Phi_S}{\Phi_O + \Phi_S} + <j>_{(O)} \frac{\Phi_O}{\Phi_O + \Phi_S} \tag{41}$$

Figure 3 shows a series of typical distribution curves for Φ_{Sj} and Φ_{Mj} for different concentrations of surfactant. As the concentration of surfactant increases, the distribution becomes wider and shifts toward the high aggregation-number region. At a fixed value of surfactant concentration, the distribution of micelles favors the high aggregation-number region more strongly than that of surfactant.

Chemical Potentials

Chemical potentials are obtained from Eqn.(1) by classical thermodynamics. They are given in Appendix II.

Parameters characteristic for the system are :

$\varepsilon_{(O-W)}/kT$. If we consider the critical micelle concentration (c.m.c.) as a solution property similar to the saturated concentration, this parameter can be evaluated approximately by taking the logarithm of the ratio of the c.m.c. of the surfactant in binary O-S to that in binary W-S,

K_o and K, are best obtained from size-distribution data such as $<j>$ and σ_j by Eqns.(30),(37) and (39).

$\frac{a_{SS(W)}}{v_S kT}, \frac{a_{SS(O)}}{v_S kT}, a_{SS(O-W)}=a_{SS(O)}-a_{SS(W)}$, can be estimated by fitting binary phase-separation data.

$\frac{a_{WO} v_S}{v_W v_O kT}$, must be estimated from ternary phase equilibria data.

r_O/r_W and r_S/r_W, are estimated from pure-component molecular-size data.

Strictly speaking, K varies with the changing environment. However, as a good approximation for the systems considered here, under isothermal conditions it can be considered to be a constant because it depends only on the chemical association of the surfactant molecules and on the physical interactions of the surfactant with water and with oil; all of these do not change significantly over the entire composition range. It is evident that our approximate model is limited to relatively simple microemulsions. Extensive modifications are required for applicability to systems containing electrolytes and/or liquid-crystalline mesophases.

Phase Diagrams

Surfactant-containing systems exhibit a wide variety of phase behavior as indicated in the compilation of phase diagrams by Ekwall (1975). The molecular-thermodynamic model developed here allows us to calculate phase behavior for several of these systems. We present some results for simple ternary systems containing water, oil and surfactant.

A ternary homogeneous liquid phase separates into two liquid phases (phase-splitting) if the criterion for instability is satisfied. That criterion is

$$\frac{\partial^2 G}{\partial x_S^2}\frac{\partial^2 G}{\partial x_O^2}-\left(\frac{\partial^2 G}{\partial x_S \partial x_O}\right)^2 \leq 0 \tag{42}$$

Equation (42) gives the spinodal of the ternary mixture. However, to calculate the compositions of two (or more) phases at equilibrium, we require the binodal curve and the tie lines, as discussed elsewhere (e.g. Prausnitz et al, 1980). Figures 4-7 show four types of calculated phase diagrams; when mole fraction $x_i < 0.1$, the ordinates are on a logarithmic scale to show more clearly the phase behavior in the dilute region. For comparison, the upper left shows the corresponding triangular phase diagram. Binodals, spinodals and tie lines are indicated.

Figure 4 shows only one two-phase region due to immiscibility of water and oil; an example is provided by the ternary hexaoxyethylene-glycol- monohexyl ether/octan-1-ol/water (Mulley and Metcalf, 1964).

Figure 5 has three two-phase regions arising from three partially immiscible binaries.

In Figure 6, two of the two-phase regions have merged, forming a folding-fan type region; two examples are provided by the ternaries sodium cholate/decan-1-ol/water and sodium desoxycholate/decan-1-ol/water (Fontell, 1969).

In Figure 7, there is a three-phase region, indicated by a triangle; an example is provided by the ternary Aerosol OT/decan-1-ol/water (Ekwall et al, 1970).

Phase-diagram calculations require parameters which are shown on the figures. The position and magnitude of any two-phase region can be changed by adjusting these parameters. For example, as a_{WO} becomes increasingly negative, a higher binodal curve appears in Figure 4. As a_{SS} and K rise, there is an increase in the size of the two-phase regions from the binaries containing surfactant.

Provided that K_R is in the vicinity of unity, it has virtually no effect on the phase diagram.

Stability of a Microemulsion

Many authors have concerned themselves with the well-known observation that when sufficient surfactant is added to an immiscible mixture of oil and water, a stable microemulsion is formed spontaneously.

Ruckenstein and coworkers (1978,1980) have concluded that the thermodynamic stability of microemulsions is due first, to a decrease in interfacial tension, and second, to a dilution effect which gives rise to a positive entropy of dispersion of the globules; these negative contributions to the Gibbs energy overcome that due to the small positive contribution from interfacial tension. Ruckenstein's view is no doubt correct. However, to construct a quantitative, predictive model, we have to consider in more detail the Gibbs energy of a microemulsion, as we have attempted to do here.

First, we consider the entropy of mixing. The common method for calculating the entropy of mixing is based on equations similar to that of Carnahan-Starling or that of Flory-Huggins. However, these equations are for random mixtures. As pointed out by Luisi (1984), microemulsions represent a form of self-organization of matter; they can be considered as a primitive step toward forming bio-substances. The entropy of mixing must reflect this semi-organization. In our model, we assure that nearly all surfactant molecules exist between the water and oil molecules. This partial ordering intuitively causes a decrease in the entropy of mixing.

For partially-ordered systems, another shortcoming of the Flory-Huggins equation becomes clear when the surfactant concentration approaches zero; in that case, the number of possible configurations should return to a small value close to unity, corresponding to immiscible water and oil. However, if we use the Flory-Huggins random mixing approach, we overestimate the entropy.

Second, we consider the energy effect. Ruckenstein emphasizes that low interfacial tension gives a low Gibbs energy. However, in thermodynamically stable microemulsions, there is no well-defined surface. We cannot determine the interfacial tension experimentally. In our model, the contribution of the so-called interfacial tension is represented by parameter a_{WO} , which provides a measure of the interaction between water and oil at the interface.

Figure 8 shows the variation of spinodals with a_{WO}. The more negative a_{WO} , the larger the binodal envelope, i.e., the more unstable the microemulsion. If the so-called interfacial tension equals zero, a_{WO} also approches zero. In that event, a stable microemulsion always occurs in the entire range of oil-to-water ratios. For real systems, however, in most cases, there is a finite phase-separation region, indicating that there is no surface layer in the classical sense. Water and oil molecules more or less permeate or penetrate into the boundary and increase the instability of the system. While not considered quantitatively in this work, the role of a cosurfactant lies mainly in lowering the absolute value of a_{WO} , leading to increased stability.

Other properties, in addition to the interfacial tension (or a_{WO}) have much influence on stability. One of them is a_{SS} which is usually positive and represents the interaction between the micelles whose boundaries are composed of surfactant. Figure 9 shows the variation of spinodals with respect to a_{SS} . As interaction becomes stronger, i.e., as a_{SS} increases, the immiscibility gap becomes wider, i.e., more unstable. The value of a_{SS} primarily changes the higher surfactant- concentration boundary; it has only a minor effect on the lower surfactant-concentration boundary, consistent with our expectation. In the lower boundary, the concentration of surfactant is usually very small; therefore, a change in a_{SS} may not exert an important influence as in the upper boundary where the surfactant concentration is large. When the surfactant is an electrolyte, the function of a salt is to change the electric double layer outside or inside the micelle, therefore changing interaction parameter a_{SS} and affecting stability.

Another important factor is association constant K . Figure 10 shows the variation of spinodals with respect to K. Similar to a_{SS}, the larger K, the wider the immiscibility gap. However, contrary to a_{SS}, K primarily influences the lower surfactant-concentration boundary. The higher concentration

boundary is essentially unaffected because the association constant mainly determines the concentration of monomer. As K becomes very small, the concentration of monomer approaches the total concentration of surfactant. In that event, the upper gap in Figure 10 disappears.

Finally, the stability of a microemulsion is influenced by sizes of the molecules of oil and surfactant. Figures 11 and 12 show these effects, respectively. Generally speaking, the larger the size of the oil molecule, the wider the spinodals for the oil-surfactant binary and the corresponding ternary two-phase region. By contrast, the larger the size of the surfactant molecule, the greater the stability.

The bottom of Fig. 12 shows that as r_O/r_W rises, the spinodals become more unsymmetric.

Conclusion

In this work we have presented a molecular-thermodynamic model for microemulsions which reasonably describes the stability of these systems. Our equation for the Gibbs energy contains several parameters with clear physical meaning. These parameters make the equation flexible enough to reproduce a variety of different kinds of phase diagrams. While the present model is limited to relatively simple ternary systems containing water, oil and surfactant, it comprises the essentials of a molecular-thermodynamic framework suitable for further development.

Ackowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional support was supplied by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Appendix I : Derivation of the size distribution

For minimizing the Gibbs energy, we calculate the total differential from Eqn.(1):

$$dG = \sum_{j=1}^{j=\infty} \frac{\partial G}{\partial N_{Sj}} dN_{Sj} = 0 \tag{I-1}$$

$$\frac{\partial G}{\partial N_{Sj}} = \frac{\partial G^o}{\partial N_{Sj}} + \frac{\partial \Delta G_I}{\partial N_{Sj}} + \frac{\partial \Delta G_{II}}{\partial N_{Sj}} + \frac{\partial \Delta G_{III}}{\partial N_{Sj}} \tag{I-2}$$

Substituting Eqns.(3,15,23) into Eqn.(I-2) yields

$$\frac{\partial G}{\partial N_{Sj}} = \mu_{Sj}^o + kT(ln\Phi_{Sj} + 1 + jC) \tag{I-3}$$

where

$$C = \ln \frac{x_S}{(x_W + x_S/2 + N_V/2N_T)^{1/2}(x_O + x_S/2 + N_V/2N_T)^{1/2}}$$

$$-ln\Phi_S - 1 - r_S \frac{N_{T,mic} - N_S}{N_r} - \frac{2N_S a_{SS}}{VkT} + v_S \frac{N_S^2 a_{SS} + N_W N_O a_{WO}}{V^2 kT} \tag{I-4}$$

$N_{T,mic} = \sum N_{Sj}$, is the total number of micelles and v_S is the molecular volume of the surfactant monomer.

We minimize the Gibbs energy subject to the constraint of mass conservation. We use Lagrange's method by introducing an undetermined multiplier α ,

$$N_S = \sum_{j=1}^{j=\infty} jN_{Sj} \tag{I-5}$$

$$\sum_{j=1}^{j=\infty} \alpha j dN_{Sj} = 0 \ . \tag{I-6}$$

We obtain

$$\ln\Phi_{Sj} = -\frac{\mu_{Sj}^o}{kT} - 1 - jC + j\frac{\alpha}{kT} \tag{I-7}$$

$$\Phi_{Sj} = \Phi_{S1}^j exp - \frac{\mu_{Sj}^o - j\mu_{S1}^o}{kT} exp(j-1) \tag{I-8}$$

From Eqns.(4,5,10), we have

$$\mu_{Sj}^o - j\mu_{S1}^o = -D_o(jm-1) - D(j-jm) + kTlnj - (j-1)kTlnv_{f,S1} \ . \tag{I-9}$$

Substitution into Eqn.(I-8) yields Eqn.(25).

Appendix II : Equations for chemical potentials

The relation between chemical potential and Gibbs energy is given by

$$\mu_i = (\frac{\partial G}{\partial N_i})_{T,P;N_{j\neq i}} \tag{II-1}$$

For an associated system, the chemical potential of the associated component S equals the chemical potential of monomer S_1 (Prigogine and Defay,1954):

$$\mu_S = \mu_{S1} \ . \tag{II-2}$$

For a microemulsion, the chemical potentials are derived from Eqn.(1) as follows:

$$\frac{\mu_S}{kT} = \frac{\mu_{S1}}{kT} = \frac{1}{kT}\frac{\partial G}{\partial N_{S1}} = \frac{\mu_{S1(W)}^o}{kT} + \frac{\varepsilon_{(O-W)}\Phi_O}{kT(1-\Phi_S)} + ln\Phi_{S1} - ln\Phi_S - \frac{N_{T,mic}r_S}{N_r} + \Phi_S$$
$$+ \ln\frac{x_S}{(x_W+x_S/2+N_V/2N_T)^{1/2}(x_O+x_S/2+N_V/2N_T)^{1/2}} + ln(\frac{N_V}{2N_T})^{1/2}$$
$$+ \frac{a_{SS(W)}}{v_S kT}(-2\Phi_S+\Phi_S^2) + \frac{a_{SS(O-W)}}{v_S kT}(-2\Phi_S+\Phi_S^2)\frac{\Phi_O}{1-\Phi_S} + \frac{a_{WO}v_S}{v_W v_O kT}\Phi_W\Phi_O \tag{II-3}$$

$$\frac{\mu_W}{kT} = \frac{1}{kT}\frac{\partial G}{\partial N_W} = \frac{\mu_W^o}{kT} - \frac{\varepsilon_{(O-W)}}{kT}\frac{r_W\Phi_S\Phi_O}{r_S(1-\Phi_S)^2} - \frac{N_{T,mic}r_W}{N_r} + \Phi_S\frac{r_W}{r_S} + ln\frac{x_W}{x_W+x_S/2+N_V/2N_T}$$
$$+ \frac{a_{SS(W)}}{v_S kT}\Phi_S^2\frac{r_W}{r_S} + \frac{a_{SS(O-W)}}{v_S kT}\frac{r_W}{r_S}\frac{\Phi_S^2(2-\Phi_S)\Phi_O}{(1-\Phi_S)^2} + \frac{a_{WO}v_S}{v_W v_O kT}\frac{r_W}{r_S}(-\Phi_O+\Phi_W\Phi_O) \tag{II-4}$$

$$\frac{\mu_O}{kT} = \frac{1}{kT}\frac{\partial G}{\partial N_O} = \frac{\mu_O^0}{kT} - \frac{\varepsilon_{(O-W)}}{kT}\frac{r_O\Phi_S\Phi_W}{r_S(1-\Phi_S)^2} - \frac{N_{T,mic}r_O}{N_r} + \Phi_S\frac{r_O}{r_S} + ln\frac{x_O}{x_O+x_S/2+N_V/2N_T}$$
$$+ \frac{a_{SS(W)}}{v_S kT}\Phi_S^2\frac{r_O}{r_S} + \frac{a_{SS(O-W)}}{v_S kT}\frac{r_O}{r_S}\frac{\Phi_S^2}{(1-\Phi_S)^2}(-1+\Phi_S+2\Phi_O-\Phi_O\Phi_S) + \frac{a_{WO}v_S}{v_W v_O kT}\frac{r_O}{r_S}(-\Phi_W+\Phi_W\Phi_O) \tag{II-5}$$

where v_W and v_O are volumes of water molecule and oil molecule, respectively. The term $ln(N_V/2N_T)^{1/2}$ in Eqn.(II-3) is necessary to conform with the standard state of surfactant which should satisfy the boundary condition for a binary that, when mole fraction x_S=0, activity coefficient

(unsymmetric convention) of surfactant $\gamma_S=1$. The value of N_V/N_T can be arbitrarily small, e.g. 10^{-9} ; its exact value has virtually no influence on the final results of phase equilibrium calculations. In Eqns.(II-4) and (II-5), as $x_W=1$ or $x_O=1$, we have a very small residual term $ln(1+N_V/2N_T)$. For consistency, it can be considered as absorbed by the standard-state chemical potential corresponding to pure water or pure oil.

In these equations, Φ_{S1} for surfactant monomer is calculated from chemical-association equilibria , mainly Eqn.(31).

Notation

a = attractive parameter

D = association energy

G = Gibbs energy

j = aggregation number

j_m = smallest allowed aggregation number

k = Boltzmann constant

K = equilibrium constant

M = moment of distribution

N = number of molecules, sites or bonds

r = size parameter

T = temperature

s = entropy

v = molecular volume

V = volume

x = mole fraction

z = coordination number

<-> = average

Greek letters

ε = potential energy

γ = activity coefficient

μ = chemical potential

Ω = number of configurations

Φ = volume fraction

σ^2 = variance

subscripts

f = free volume

k = order of the moment of distribution

M = micelle

o = smallest micelle

O = oil

r = segment

S = surfactant

T = total number of molecules

T,mic = total number of micelles

W = water

V = vacancy

superscripts

o = standard state

* = generalized function

Literature Cited

Ben-Shaul, A., D. H. Rorman, G. V. Hartland, W. M. Gelbart, "Size Distribution of Mixed Micelles: Rodlike Surfactant- Alcohol Aggregates", *J. Phys. Chem.*, **90** 5277 (1986).

Blankschtein, D., G. M. Thurston, G. B. Benedek, "Phenomenological Theory of Equilibrium Thermodynamic Properties and Phase Separation of Micellar Solutions", *J. Chem. Phys.*, **85** 7268 (1986).

De Gennes, P.G. and C. Taupin, "Microemulsions and the Flexibility of Oil/Water Interfaces", *J. Phys. Chem.*, **86** 2294 (1982).

Ekwall, P., in *Adv. in Liquid Crystals*, ed. G. H. Brown, Academic Press, 1975.

Ekwall, P., L. Mandell, K. Fontell, "Some Observations on Binary and Ternary Aerosol OT Systems", *J. Colloid Interface Science*, **33** 215 (1970).

Fontell, K., "Micellar Structures in Bile Salt Solutions Containing Decanol", *Proc. Int. Congr. Surface Active Substances,5th, 1968*, Vol 2, 1033 (1969).

Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford, 1952.

Hoar, T. P. and J. H. Schulman, *Nature* **152** 102 (1943).

Huang, J. S., "Surfactant Interactions in Oil Continuous Microemulsions", *J. Chem. Phys.*, **82** 1 (1985).

Israelachivili, J. N., D. J. Mitchell. B. W. Ninham, "Theory of Self-Assembly of Hydrocarbon Amphiphiles into Micelles and Bilayers", *J. Chem. Soc. Fara. Trans. 2*, **72** 1525 (1976).

Kilpatrick, P. K., L. E. Scriven, H. T. Davis,"Thermodynamic Modeling of Quaternary Systems: Oil/Brine/Surfactant/ Alcohol", *Soc. Pet. Eng. J.*, 330 (1985).

Langevin, D., in *Reverse Micelles*, ed. P.L. Luisi and B. E. Straub, Plenum Press, 1984.

Larson, R. G., L. E. Scriven and H. T. Davis, "Monte Carlo Simulation of Model Amphiphile-Oil-Water Systems", *J. Chem. Phys.*, **83** 2411 (1985).

Luisi, P. L. and B. E. Straub, *Reverse Micelles*, Plenum Press, 1984.

Mazer N. A., G. B. Benedek, M. C. Carey, "Quasielastic Light Scattering Studies of Aqueous Binary Lipid Systems. Size, Shape, and Thermodynamics of Bile Salt Micelles", *Biochemistry*, **19** 601 (1980).

Mitchell D. J. and B. W. Ninham, "Micelles, Vescicles and Microemulsions", *J. Chem. Soc. Fara. Trans. 2* **77** 601 (1981).

Mulley, B. A. and A. D. Metcalf, "Nonionic Surface- Active Agents, Part 4" *J. Colloid Science*, **19** 501 (1964).

Nagarajan, R. and E. Ruckenstein, "Aggregation of Amphiphiles as Micelles or Vescicles in Aqueous Media", *J. Colloid Interface Science*, **71** 580 (1979).

Olien, N. A., "Thermodynamic Properties for Bioprocess Engineering", *Chem. Eng. Progress*, in press (1987).

Prausnitz, J., T. Anderson, E. Grens, C. Eckert, R. Hsieh, J. O'Connell, *Computer Calculation for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*, Prentice Hall, 1980.

Prigogine, I., *The Molecular Theory of Solutions*, Amsterdam, North-Holland Publishing Company, 1957.

Prigogine, I. and R. Defay, *Chemical Thermodynamics*, Longmans, Green & Co., 1954.

Robbins, M. L., in *Micellization, Solubilization and Microemulsions*, Vol 2 , ed. K. L. Mittal, Plenum Press, 1977.

Rosen, W. R., R. G. Brown, H. T. Davis, S. Prager, L. E. Scriven, "Thermodynamic Modelling of Pseudoternary Phase Behavior", *Soc. Pet. Eng. J.*, 945 (1982).

Ruckenstein, E., "The Origin of Thermodynamic Stability of Microemulsions", *Chem. Phys. Letters*, **57** 517 (1978).

Ruckenstein, E. and R. Krishnan, "The Equilibrium Radius and the Domain of Existence of Microemulsions", *J. Colloid Interface Science*, **76** 188 (1980).

Shield, J. W., H. D. Ferguson, A. S. Bommarius, T. A. Hatton, "Enzymes in Reversed Micelles as Catalysts for Organic-Phase Synthesis Reactions", *Ind. Eng. Chem. Fundam.*, **25** 603 (1986).

Stecker, M. M. and G. B. Benedek, "Theory of Multicomponent Micelles and Microemulsions", *J. Phys. Chem.*, **88** 6519 (1984).

Talmon, Y. and S. Prager, "Statistical Thermodynamics of Phase Equilibria in Microemulsions" *J. Chem. Phys.*, **69** 2984 (1978).

Thurston, G. M., D. Blankschtein, M. R. Fisch, G. B. Benedek, "Theory of Thermodynamic Properties and Phase Separation of Micellar Solutions with Lower Consolute Points", *J. Chem. Phys.*, **84** 4558 (1986).

Tiddy, G. J. T., "Surfactant-Water Liquid Crystal Phases", *Phys. Reports*, **57** 1 (1980).

Wheeler, J. C. and B. Widom, "Phase Transitions and Critical Points in a Model Three-Component System", *J. Am. Chem. Soc.*, **90** 3064 (1968).

Widom, B., "A Model Microemulsion", *J. Chem. Phys.*, **81** 1030 (1984).

Widom, B., "Lattice-Gas Model of Amphiphiles and of Their Orientation at Interfaces", *J. Phys. Chem.*, **88** 6508 (1984a).

Widom, B., "Lattice Model of Microemulsions", *J. Chem. Phys.*, **84** 6943 (1986).

Winsor, P. A., "Binary and Multicomponent Solutions of Amphiphilic Compounds. Solubilization and the Formation, Structure, and Theoretical Significance of Liquid Crystalline Solutions", *Chem. Rev.*, **68** 1 (1968).

Figure Captions

Fig. 1 Schematic illustration of typical structures in microemulsions

Fig. 2 A lattice model for microemulsions. a--micelle with neither oil nor water in center; b,c,d--micelle with oil in center; e--surfactant monomer

Fig. 3 Size distribution of micelles

Fig. 4 Calculated phase diagram with one two-phase region

Fig. 5 Calculated phase diagram with three two-phase regions

Fig. 6 Calculated phase diagram with a folding-fan type two-phase region

Fig. 7 Calculated phase diagram with a three-phase region

Fig. 8 Influence of a_{WO} on spinodals

Fig. 9 Influence of a_{SS} on spinodals

Fig. 10 Influence of K on spinodals

Fig. 11 Influence of r_O/r_W on spinodals

Fig. 12 Influence of r_S/r_W on spinodals

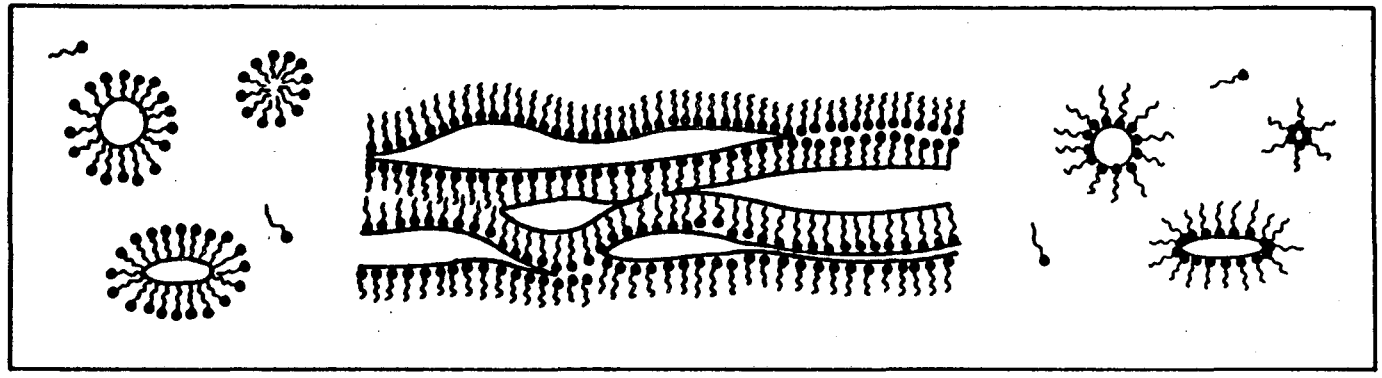


Fig. 1 Schematic illustration of typical structures in microemulsions

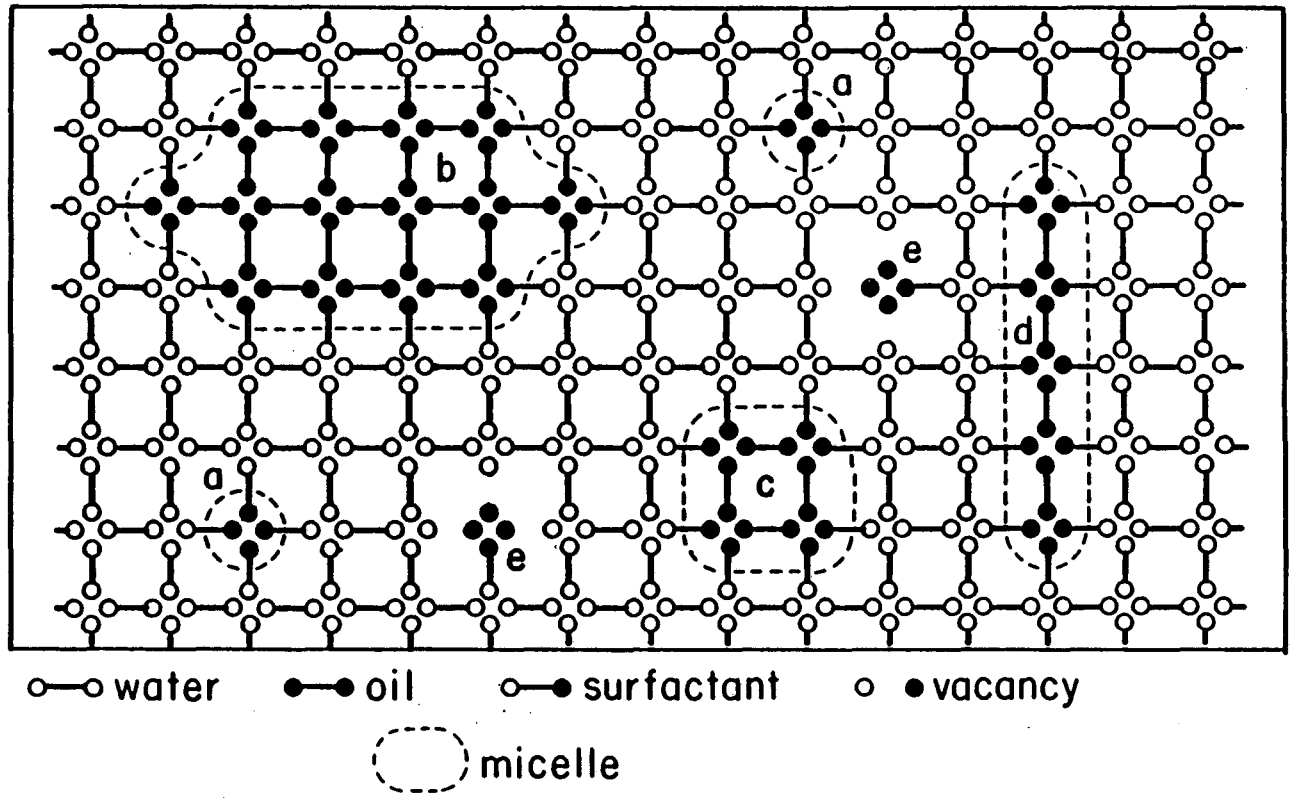
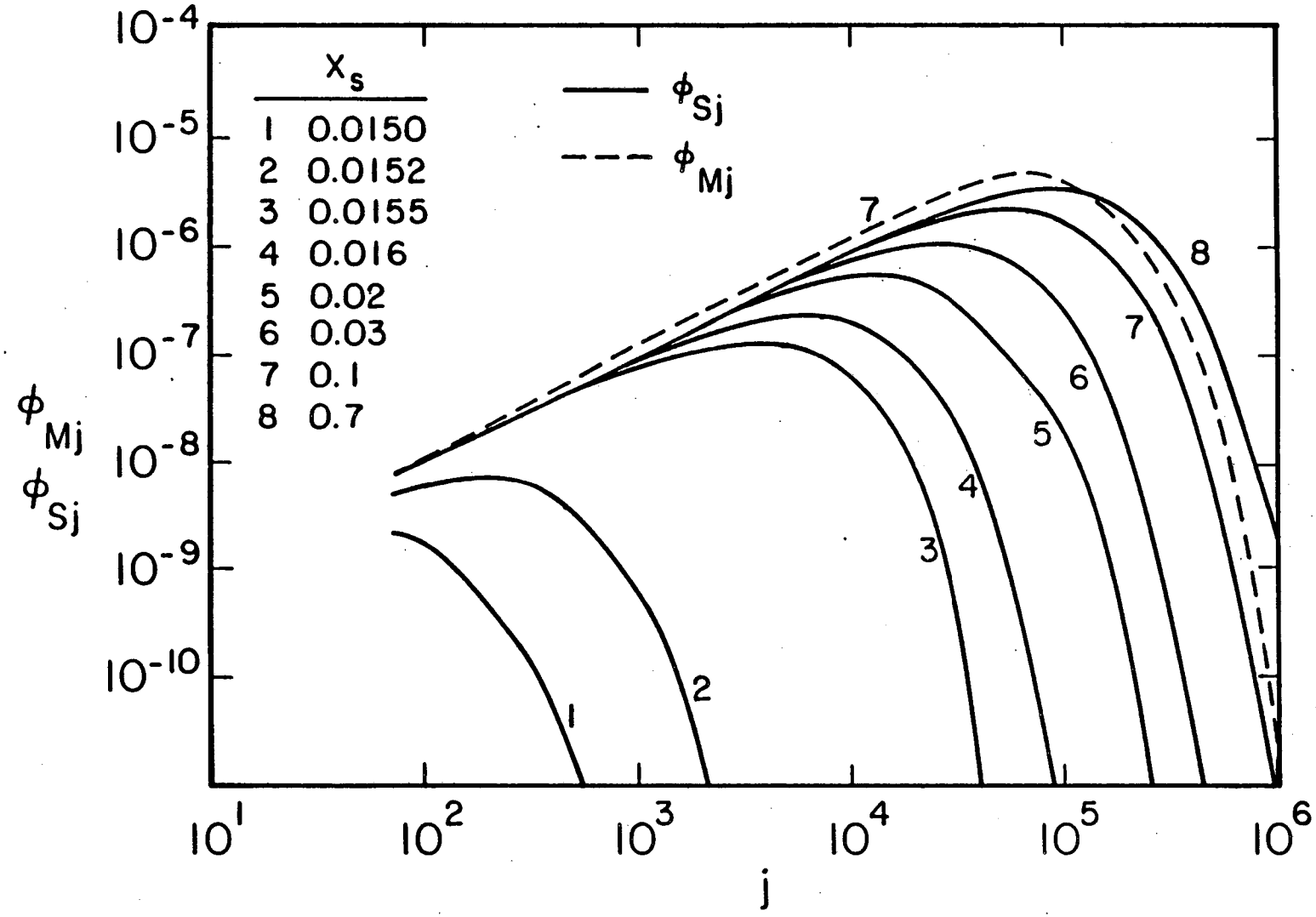
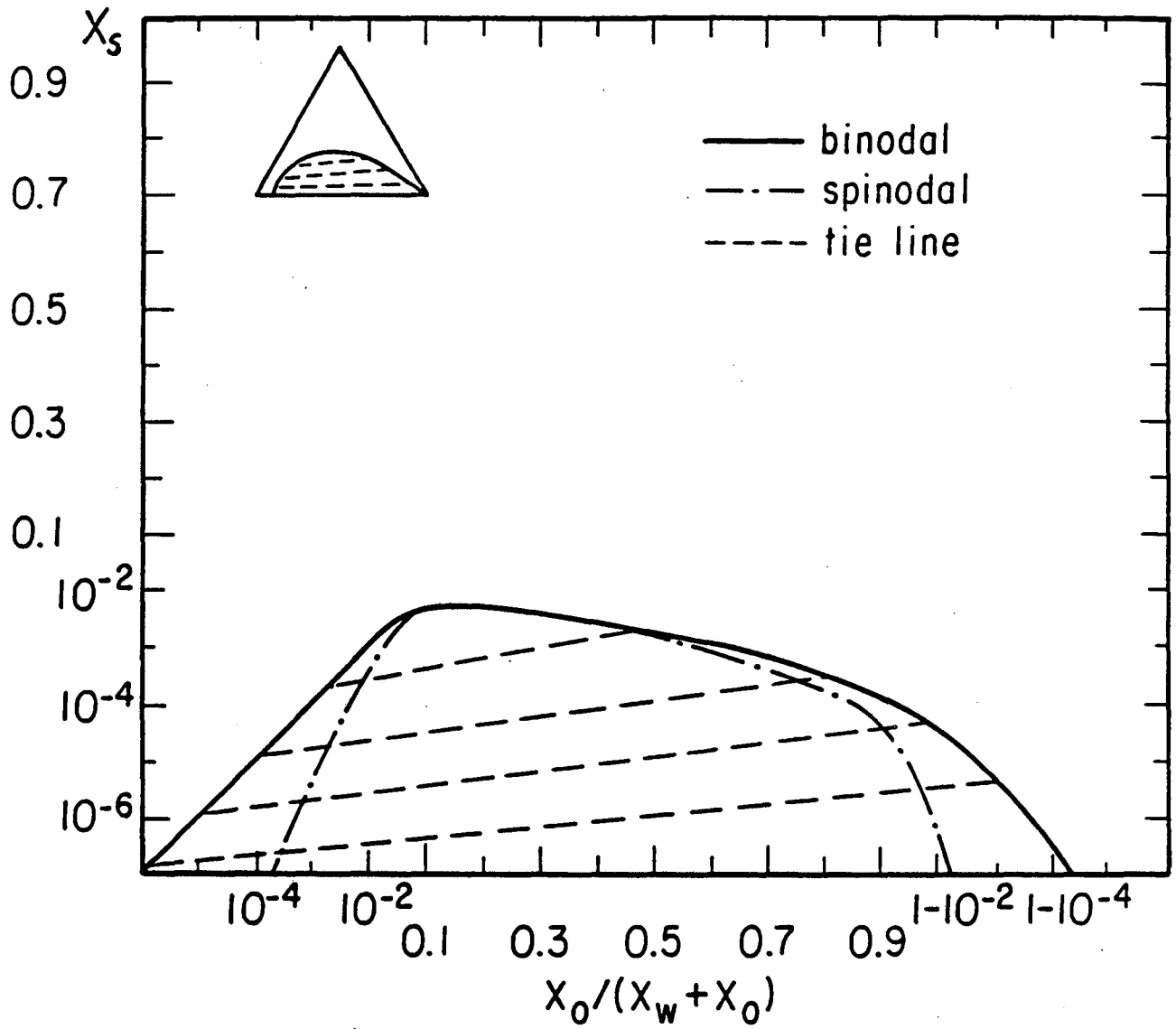


Fig. 2 A lattice model for microemulsions. a--micelle with neither oil nor water in center; b,c,d--micelle with oil in center; e--surfactant monomer.



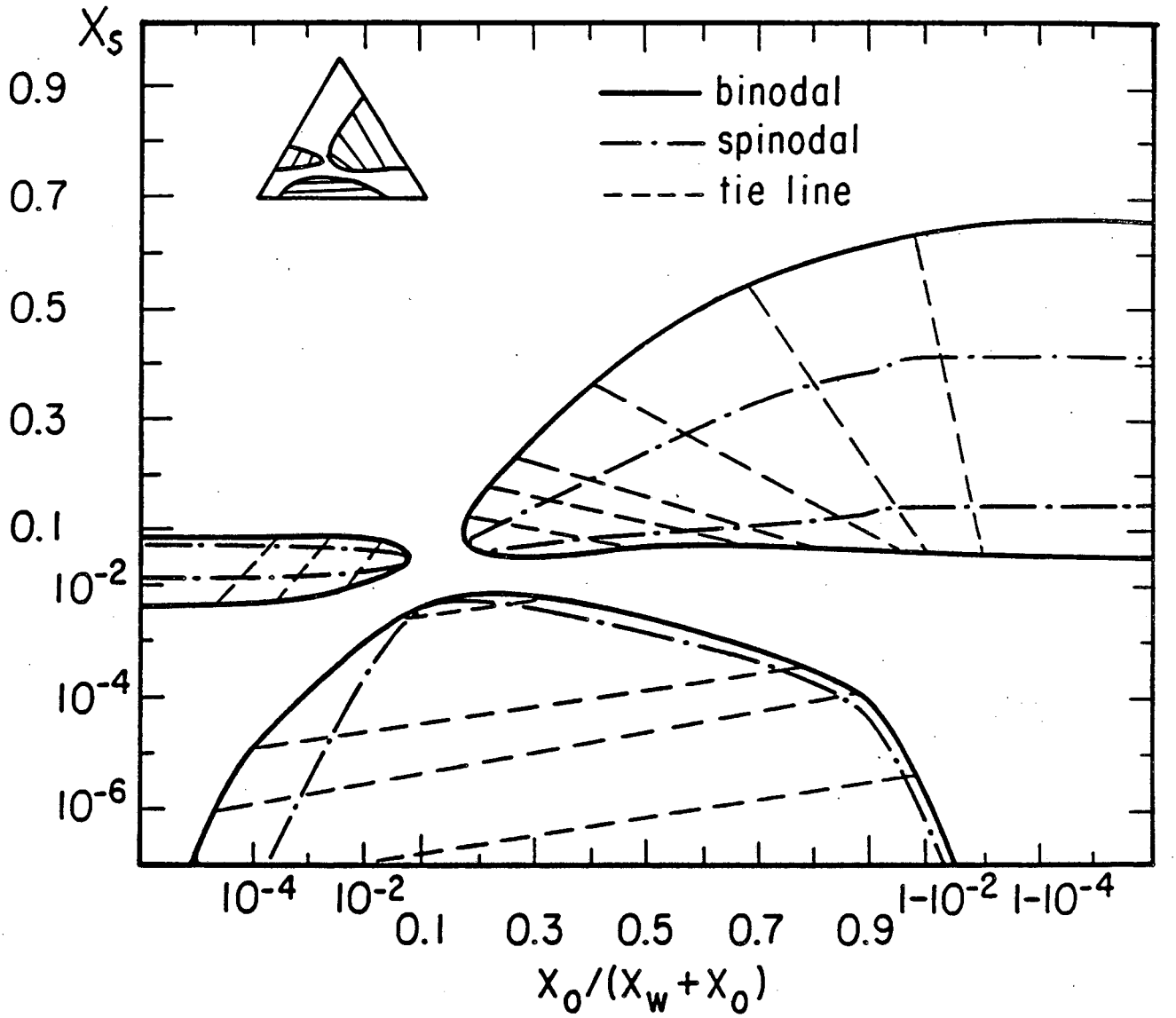
$X_0/(X_0+X_w) = 0.2$; $r_s/r_w = 20.17$; $r_0/r_w = 10.08$; $K_R^{-1} = 0.7038$; $K = 0.1 \times 10^2$.

Fig. 3 Size distribution of micelles



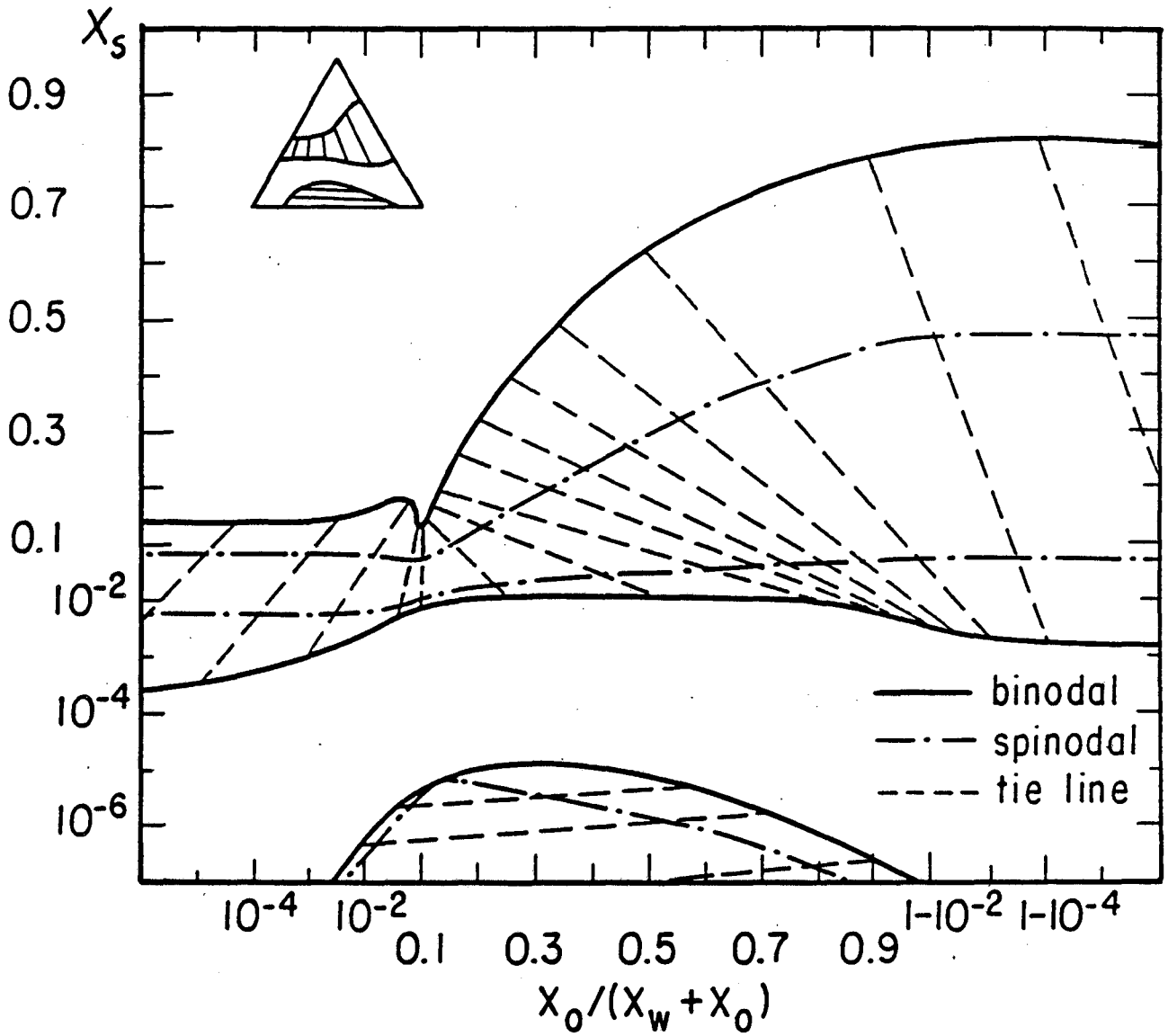
$r_s/r_w = 20.17$; $r_0/r_w = 10.08$; $j_m = 60$; $\epsilon_{(0-w)}/kT = 0.1$;
$a_{ss(w)}/v_s kT = 1.0$; $a_{ss(0-w)}/v_s kT = 0.2$; $a_{wo} v_s / v_w v_0 kT = -0.1$;
$K_R^{-1} = 0.7038$; $K = 0.1 \times 10$.

Fig. 4 Calculated phase diagram with one two-phase region



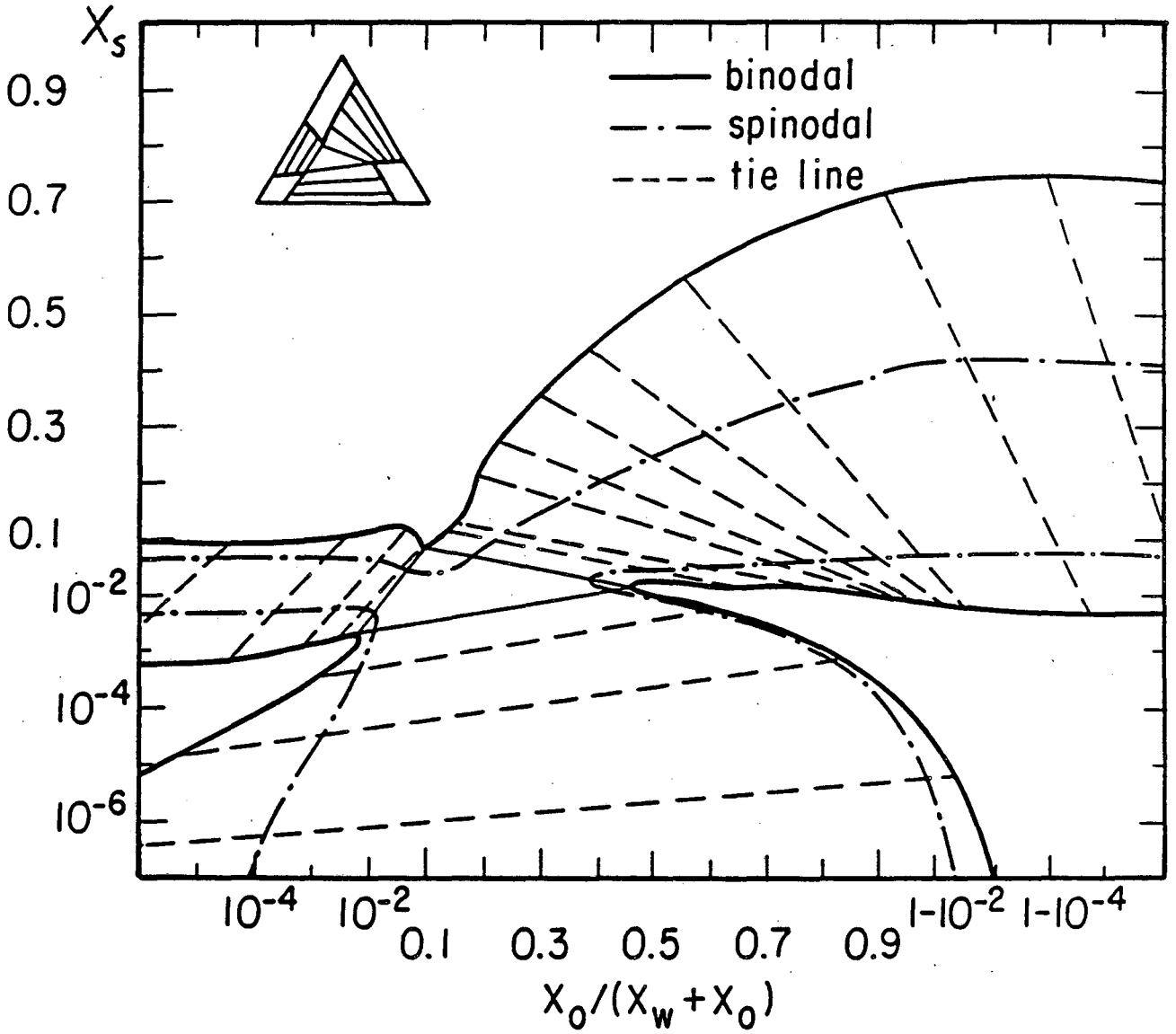
$r_s/r_w = 20.17$; $r_0/r_w = 10.08$; $j_m = 60$; $a_{ss(w)}/v_s kT = 1.0$; $a_{ss(0-w)}/v_s kT = 0.2$; $\epsilon_{(0-w)}/kT = 0.1$; $a_{w0} v_s / v_w v_0 kT = -0.1$; $K_R^{-1} = 0.7038$; $K = 0.4 \times 10$.

Fig. 5 Calculated phase diagram with three two-phase regions



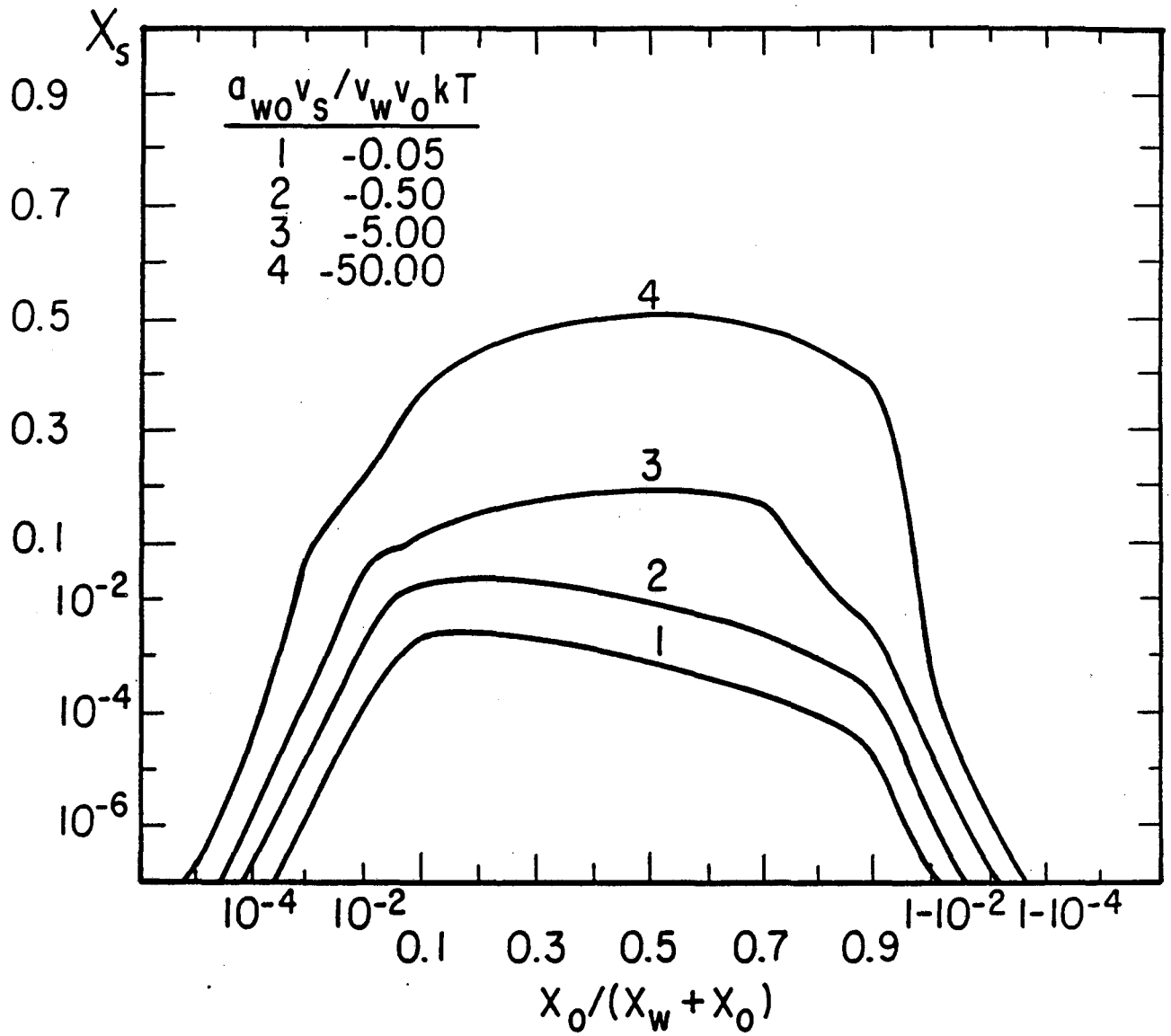
$r_s/r_w = 20.17$; $r_0/r_w = 10.08$; $j_m = 60$; $a_{ss(w)}/v_s kT = 1.5$; $a_{ss(0-w)}/v_s kT = 0.4$; $\epsilon_{(0-w)}/kT = 0.1$; $a_{wo} v_s / v_w v_o kT = -0.1 \times 10^{-3}$; $K_R^{-1} = 0.7038$; $K = 0.1 \times 10^2$.

Fig. 6 Calculated phase diagram with a folding-fan type two-phase region



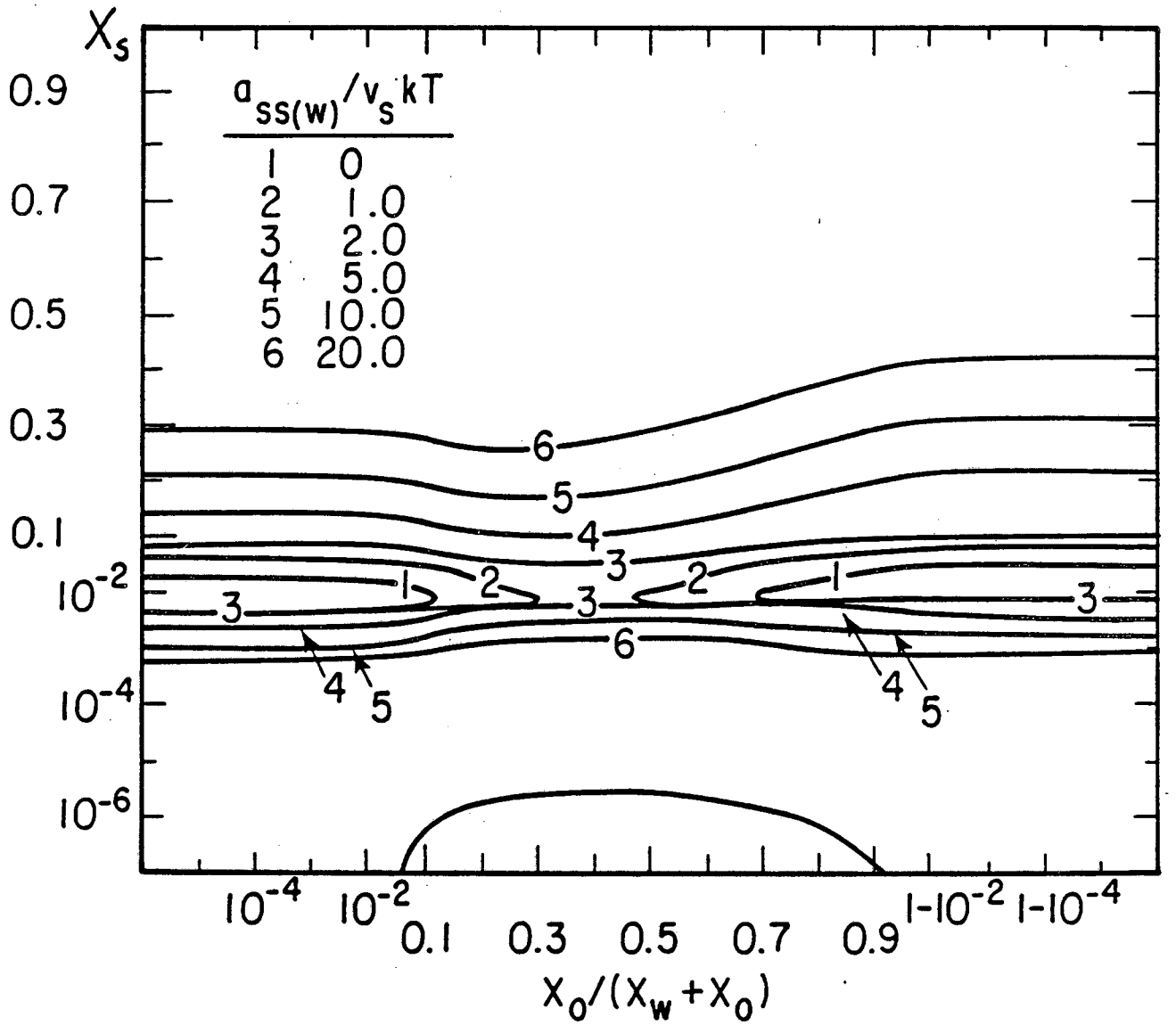
$r_s/r_w = 20.17$; $r_o/r_w = 10.08$; $j_m = 60$; $a_{ss(w)}/v_s kT = 1.0$; $a_{ss(o-w)}/v_s kT = 0.4$; $\epsilon_{(o-w)}/kT = 0.1$; $a_{wo} v_s / v_w v_o kT = -0.5$; $K_R^{-1} = 0.7038$; $K = 0.1 \times 10^2$.

Fig. 7 Calculated phase diagram with a three-phase region



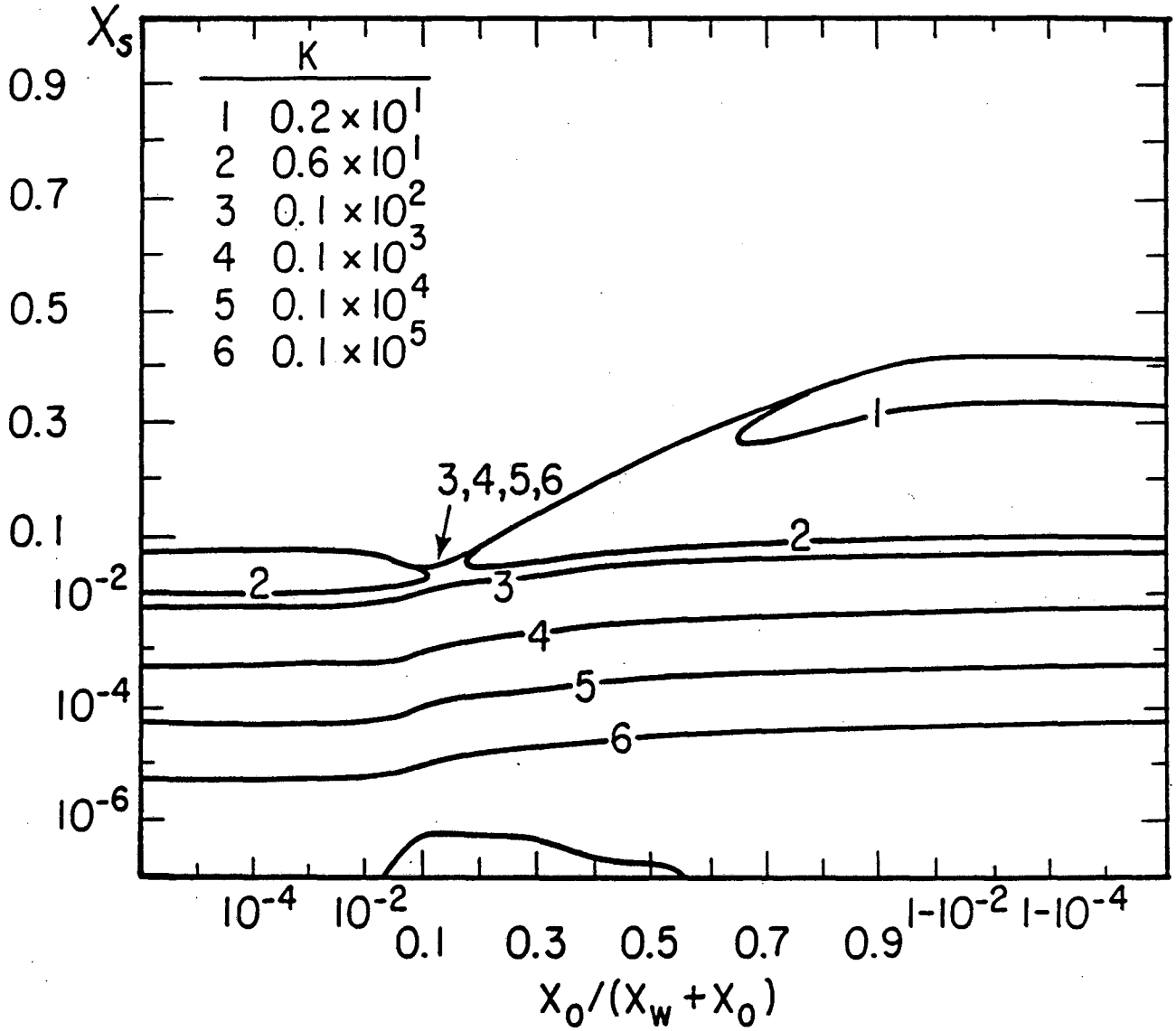
$r_s/r_w = 20.17$; $r_o/r_w = 10.08$; $j_m = 60$; $a_{ss(w)}/v_s kT = 1.0$; $a_{ss(o-w)}/v_s kT = 0.2$; $\epsilon_{(o-w)}/kT = 0.1$; $K_R^{-1} = 0.7038$; $K = 0.1 \times 10$.

Fig. 8 Influence of a_{wo} on spinodals



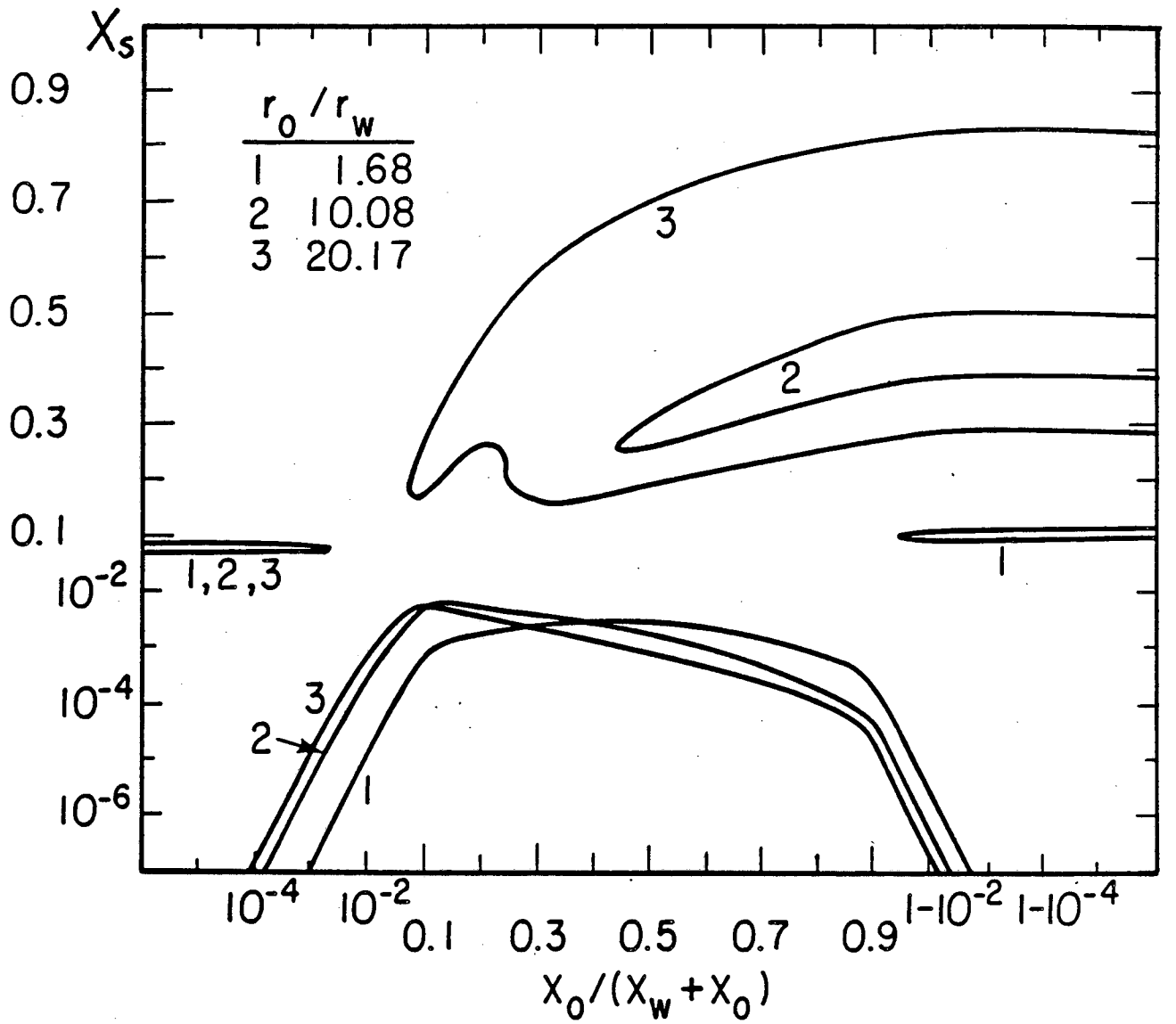
$r_s/r_w = 20.17$; $r_o/r_w = 1.68$; $j_m = 60$; $\epsilon_{(o-w)}/kT = 0$; $a_{ss(o-w)}/v_s kT = 0$; $a_{wo}v_s/v_w v_o kT = -0.0001$; $K_R^{-1} = 0.7038$; $K = 0.1 \times 10^2$.

Fig. 9 Influence of a_{ss} on spinodals



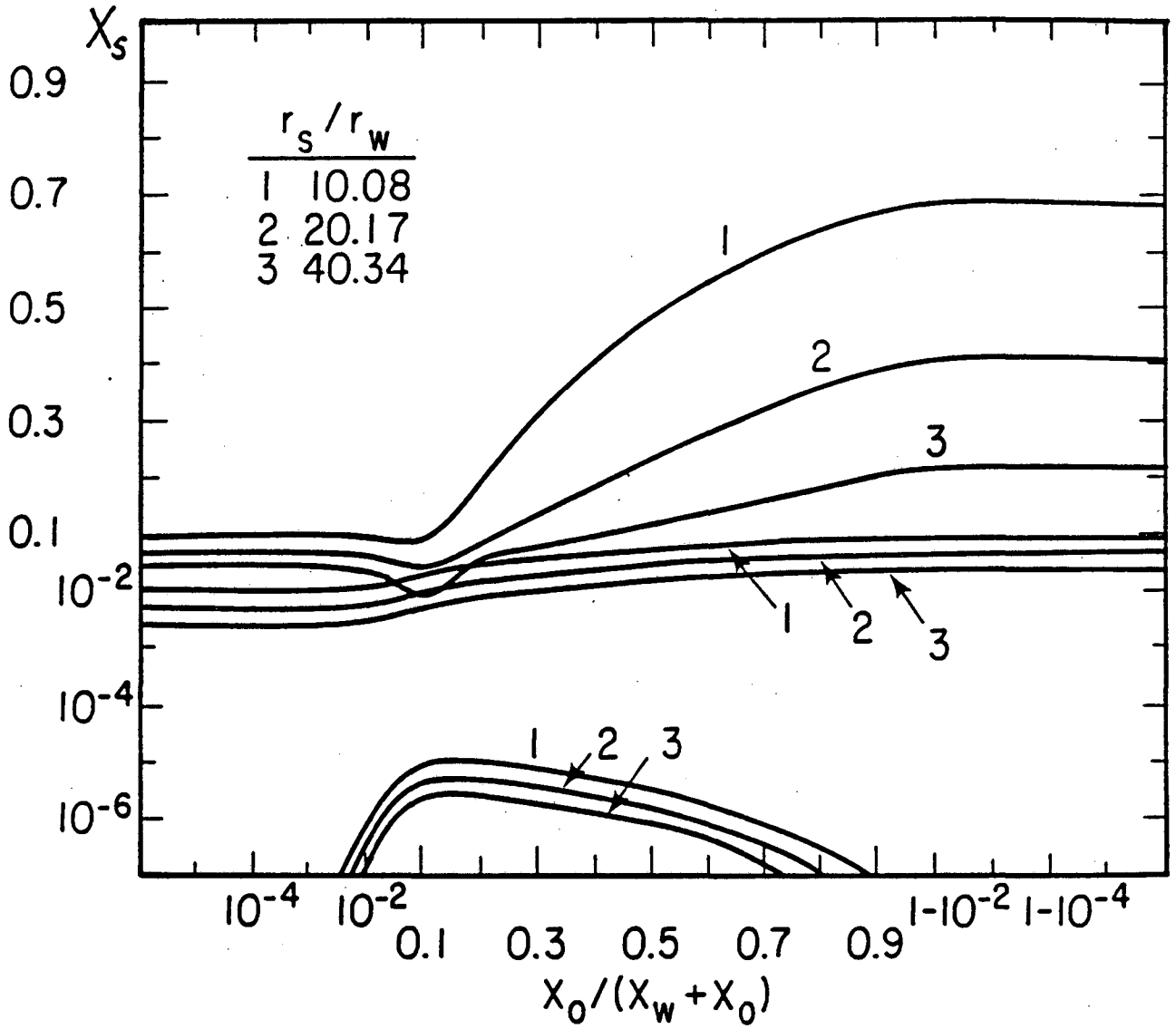
$r_s/r_w = 20.17$; $r_0/r_w = 10.08$; $j_m = 60$; $a_{ss(w)}/v_s kT = 1.0$;
$a_{ss(0-w)}/v\ kT = 0.4$; $a_{w0}v_s/v_w v_0 kT = -0.1\times10^{-4}$;
$\epsilon_{(0-w)}/kT = 0.1$; $K_R^{-1} = 0.7038$.

Fig. 10 Influence of K on spinodals.



$r_s/r_w = 20.17$; $j_m = 60$; $\epsilon_{(0-w)}/kT = 0$; $a_{ss(w)}/v_s kT = 1.5$; $a_{ss(0-w)}/v_s kT = 0$; $a_{wo} v_s / v_w v_o kT = -0.1$; $K_R^{-1} = 0.7038$; $K = 0.18 \times 10$.

Fig. 11 Influence of r_0/r_w on spinodals



$r_0/r_w = 10.08$; $j_m = 60$; $\epsilon_{(0-w)}/kT = 0.1$; $a_{ss(w)}/v_s kT = 1.0$; $a_{ss(0-w)}/v_s kT = 0.4$; $a_{wo} v_s / v_w v_o kT = -0.0001$; $K_R^{-1} = 0.7038$; $K = 0.1 \times 10^2$.

Fig. 12 Influence of r_s/r_w on spinodals.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720