Polymer-induced structural transitions in microemulsions

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Polymer-Induced Structural Transitions in Microemulsions

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We predict, qualitatively, the structural transitions in microemulsion systems induced by nonionic polymers, by virtue of their ability to associate with the surfactant assemblies. The predictions are made possible by linking (a) theoretical calculations of the domains of existence of oil-in-water (O/W) and water-in-oil (W/O) droplet microemulsions with (b) the experimental observation that on increasing the alcohol-to-surfactant ratio, an O/W droplet microemulsion phase inverts to a W/O droplet microemulsion, often via a bicontinuous microemulsion. We predict five distinct types of polymer-induced structural transitions: (I) an O/W droplet microemulsion remains an O/W droplet system but the amount of oil solubilized and the radius of the droplet are both reduced; (II) a bicontinuous microemulsion transforms into an O/W droplet microemulsion; (III) a W/O droplet microemulsion inverts to an O/W droplet microemulsion with the droplet radius either decreasing in size (IIIA) or increasing in size (IIIB); (IV) a W/O droplet microemulsion transforms into a bicontinuous microemulsion; (V) a W/O droplet microemulsion remains a W/O system but the droplet radius and the amount of water solubilized are both increased. We also predict that the addition of polymers cannot lead to the following types of transitions: (VI) an O/W droplet microemulsion cannot invert to a W/O droplet microemulsion; (VII) an O/W droplet microemulsion cannot transform into a bicontinuous microemulsion; (VIII) a bicontinuous microemulsion cannot transform into a W/O droplet microemulsion. From a practical point of view, the above predictions open up an effective approach to the manipulation of microemulsion structures using nonionic–polymer molecules as additives.

I. Introduction

In a recent paper, Lianos et al.[1] examined how water-in-oil (W/O) droplet microemulsions consisting of water, cyclohexane, 1-pentanol, and sodium dodecyl sulfate (SDS) are modified on the addition of a water-soluble uncharged polymer, poly(oxyethylene glycol). From dynamic light-scattering measurements, they found that the polymer induces a structural reorganization of the dispersed water phase such that the droplets grow in size and, correspondingly, their number density in the microemulsion phase decreases. Such a structural modification was shown to be consistent with the results from luminescence and conductivity measurements. The authors concluded that the polymer molecules associate with and become an integral part of the structure of the microemulsion droplets.

In this paper, we explore what other types of polymer-induced structural transitions can occur in microemulsion systems, when the polymer molecules associate with the surfactant microstructures. For this purpose, we employ a simple molecular model developed earlier[2] to describe the association of nonionic polymers with surfactant aggregates such as globular and rodlike micelles, vesicles, bilayers, and microemulsions.

The microemulsions being considered are schematically depicted in Figure 1. The Winsor 1 system refers to an O/W microemulsion coexisting with an excess oil phase. The Winsor 2 system is also a two-phase system where a W/O microemulsion coexists with an excess aqueous phase. In these two systems, the microemulsion is characterized by the presence of spherical droplets with a relatively narrow dispersion of sizes. The Winsor 3 system refers to a three-phase system wherein the microemulsion coexists with both excess aqueous and oil phases. In this case, the microemulsion is characterized by a random bicontinuous structure. Many experimental studies have shown that in systems containing surfactant, alcohol, oil, water, and electrolyte, one can achieve a transition from the Winsor
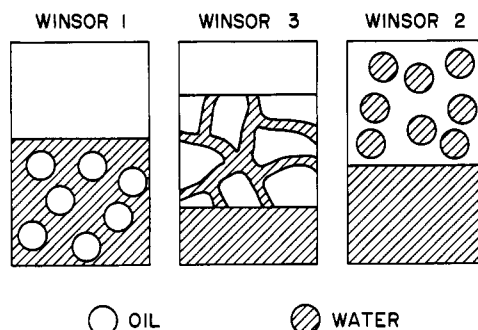
Figure 1. Schematic representation of Winsor 1, Winsor 2, and Winsor 3 microemulsion systems. Winsor 1 and Winsor 2 systems are characterized by spherical droplet microstructures and two coexisting phases. Winsor 3 system is characterized by bicontinuous microstructure and three coexisting phases.

1 to the Winsor 2 system via the Winsor 3 system by increasing either the electrolyte concentration, the ratio of alcohol to surfactant, or the hydrophobic chain length of the surfactant. An illustrative example showing the experimental conditions under which such transitions are realized can be found in ref 3 for the system consisting of SDS, 1-pentanol, water, cyclohexane, and NaCl. The experimental results imply that we can infer the domain of existence of the Winsor 3 system from knowledge of the domains of existence of Winsor 1 and Winsor 2 systems, when the alcohol-to-surfactant ratio is used as the variable to effect transitions from one type of system to another.

The molecular model used in our study has evolved from the thermodynamic treatment of micelles pioneered by Tanford.[4] It has been shown that such a molecular approach can be extended to the quantitative treatment of both O/W and W/O droplet microemulsions[5-7] as well. Here, we adapt such a molecular approach to account for the association of polymers with the microemulsion

(1) Lianos, P.; Modes, S.; Staikos, G.; Brown, W. *Langmuir* **1992**, *8*, 1054.

(2) Nagarajan, R. *J. Chem. Phys.* **1989**, *90*, 1980.

(3) de Bruyn, P. L.; Overbeek, J. Th. G.; Verhoeckx, G. J. *J. Colloid Interface Sci.* **1989**, *127*, 244.

(4) Tanford, C. *The Hydrophobic Effect*; Wiley: New York, 1973; *J. Phys. Chem.* **1974**, *24*, 2469.
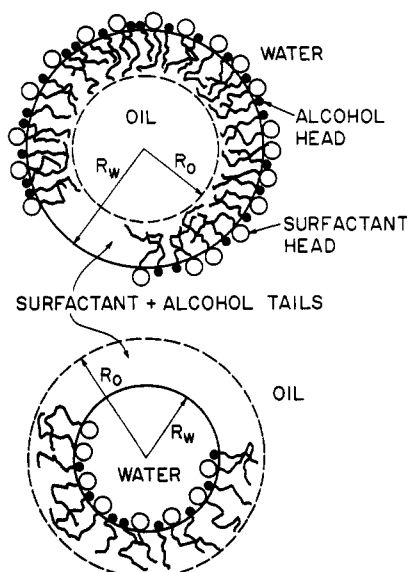
Figure 2. Microemulsion droplets of oil-in-water type and water-in-oil type indicating the different radii. The film region lies between the two radii.

droplets. One must note that the molecular model discussed in this paper and the calculations based on it focus only on dilute droplet microemulsions and not on the bicontinuous-type structures. Nevertheless, we are able to draw conclusions also about the bicontinuous microemulsion systems, as explained before, by simply exploiting the experimental observation[3] that in passing from the Winsor 1 system to the Winsor 2 system mediated by increasing alcohol-to-surfactant ratio, the Winsor 3 system often appears in between.

II. Model of Droplet Microemulsions

We consider microemulsions containing oil droplets in water and water droplets in oil, as shown in Figure 2. The dispersed phase in each droplet is separated from the continuous-phase by a layer of surfactant and alcohol molecules, and this region will be referred to as the film region. For simplicity, we assume that oil molecules are excluded from the film region. We also ignore the self-association of alcohol in the oil. Both these assumptions can be readily relaxed in order to obtain model predictions for quantitative comparison with experiments. We consider situations where the microemulsion coexists with an excess phase so that the O/W microemulsion is saturated in oil while the W/O microemulsion is saturated in water. The size distribution of droplets in the microemulsion phase is obtained from the condition of minimum Gibbs energy of the entire system[5-7] and is given by

$$X_g = X_{SW}{}^{g_{SI}} X_{AW}{}^{g_{AI}} \exp\left[-\left(\frac{g_{SI}\Delta\mu^\circ{}_{gI}}{kT}\right)\right],$$

$$\Delta\mu^\circ{}_{gI} = \frac{\mu^\circ{}_{gI}}{g_{SI}} - \mu^\circ{}_{SW} - \left(\frac{g_{AI}}{g_{SI}}\right)\mu^\circ{}_{AW} \quad (2.1)$$

Here, X_g is the mole fraction of droplets (treated as a distinct chemical species) in the continuous phase of the microemulsion, X_{SW} and X_{AW} are the mole fractions in water of the singly-dispersed surfactant and the singly-dispersed alcohol molecules, g_{SI} and g_{AI} are the numbers

(5) Oakenfull, D. *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 1875.
(6) Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 601.
(7) Ruckenstein, E. In *Progress in Microemulsions*; Martellucci, S., Chester, A. N., Eds.; Plenum Press: New York, 1989; p 41.

of surfactant and alcohol molecules in the film region of the droplet, $\mu^\circ{}_{SW}$ and $\mu^\circ{}_{AW}$ are the standard chemical potentials of the surfactant and the alcohol defined as those corresponding to their infinitely-dilute states in water, and $\mu^\circ{}_{gI}$ is the standard chemical potential of the film region defined as that of a film separating water and oil phases. The standard free energy difference term $\Delta\mu^\circ{}_{gI}$ is associated with the transfer of one surfactant molecule and (g_{AI}/g_{SI}) alcohol molecules from water to the film region of the droplet. In writing eq 2.1, we have neglected possible interactions between the droplets.

The size-distribution equation is the main thermodynamic result which allows one to calculate the properties of the microemulsion system. However, when the droplets are narrowly dispersed in size as is known to be the case with droplet microemulsions, it is not necessary to calculate the entire size distribution. One can assume a single droplet size and calculate the droplet characteristics by determining the conditions which maximize the droplet concentration X_g using eq 2.1. Alternately, one can visualize the droplet as a pseudophase and determine the equilibrium droplet characteristics from the condition of minimization of the standard free energy difference term $\Delta\mu^\circ{}_{gI}$. In general, when narrowly dispersed aggregates of large enough aggregation numbers are formed, the results obtained from the size-distribution equation, the results based on the maximization of the aggregate concentration X_g, and the results derived from the pseudophase approach are all close to one another. For the illustrative purposes of this paper and with the view of developing simple analytical results, we will adopt the pseudophase approach to calculate the droplet characteristics.

To proceed further, we need to formulate an expression for the standard free energy difference term, $\Delta\mu^\circ{}_{gI}$. Such an expression is developed by considering all the changes experienced by the surfactant and the alcohol molecules when transferred from the aqueous medium to the film region of the microemulsion droplet. The various free energy contributions to $\Delta\mu^\circ{}_{gI}$ have been discussed in detail in the treatments of micellization and solubilization.[8] Here, we will write a simple phenomenological expression that qualitatively accounts well for all the free energy contributions described in ref 8

$$\Delta\mu^\circ{}_{gI} = C + \frac{\sigma_{agg}(a - a_{oS} - \{g_{AI}/g_{SI}\}a_{oA})}{kT} -$$
$$\ln\left(1 - \frac{a_{pS} + \{g_{AI}/g_{SI}\}a_{pA}}{a}\right) + \frac{\phi}{a^2} \quad (2.2)$$

where C is a constant. The constant term contains the transfer free energy of the surfactant and the alcohol tails when removed from water to a liquid hydrocarbon; it also contains the free energy of mixing of the surfactant and the alcohol tails in the film region, since we will examine the equilibrium properties of the microemulsion systems holding the composition of the film region constant. The second term refers to the free energy of formation of an interface between the hydrophobic domain of the aggregate and water. Here, σ_{agg} is the macroscopic interfacial tension characteristic of this interface, a is the surface area of the interface per surfactant molecule that is in contact with water and a_{oS} and a_{oA} are the areas per molecule shielded from contact with water because of the presence of the polar heads of the surfactant and the alcohol, respectively. The third term provides an estimate of the steric interactions among the polar heads at the aggregate surface. It is written in a form analogous to that suggested by the

(8) Nagarajan, R.; Ruckenstein, E. *Langmuir* **1991**, *7*, 2934.

van der Waals equation of state. Here, a_{pS} and a_{pA} are the effective cross-sectional areas of the polar heads of the surfactant and the alcohol, respectively. The last term has a functional form consistent with the free energy of chain deformation due to the packing constraints on the surfactant tails.[8] The parameter ϕ has a magnitude of the order of 100 Å^4 when used to describe this free energy contribution. The last term can also be thought of as including the electrostatic repulsions between the polar heads, for zwitterionic or ionic surfactants. Expressions that are dependent on $(1/a)$, $(1/a^2)$, or $(1/a^3)$ have been suggested by Tanford[4] for this purpose. The parameter ϕ has a magnitude of the order of $(1-20) \times 10^3$ Å^4 when used to describe the electrostatic repulsions between the polar heads. Thus, the last term is quite important for ionic and zwitterionic surfactants, while for nonionic surfactants this term makes only a marginal contribution to the free energy when compared to the remaining terms.

For a given alcohol-to-surfactant ratio in the film region, the area a at equilibrium is found by minimizing the free energy difference $\Delta\mu^\circ_{gI}$ with respect to a. On the basis of such minimization, the equilibrium area of the droplet per surfactant molecule is given by the implicit relation

$$a = \left[\frac{(a_{pS} + \{g_{AI}/g_{SI}\}a_{pA})}{a - (a_{pS} + \{g_{AI}/g_{SI}\}a_{pA})} + \frac{2\phi}{a^2} \right]\left(\frac{\sigma_{agg}}{kT} \right)^{-1} \quad (2.3)$$

Once the area per molecule a is known, and given the alcohol-to-surfactant ratio in the film region, we can calculate various properties of the droplets using the geometrical relations given in the Appendix. Specifically, the radius of the droplet is calculated from eqs A.1 and A.5, the volume ratio of the amount of oil or water solubilized in the droplet to the volume of the surfactant from eq A.6 or A.7, and the number of surfactant molecules in the film region of the droplet from eq A.2.

III. Model of Polymer–Microemulsion Association

In the presence of nonionic polymer molecules, the expression for $\Delta\mu^\circ_{gI}$ will be modified since additional free energy contributions due to the association of the polymer with the microemulsion droplets should be considered. For this purpose, we visualize that the polymer molecules are located at the interface between the hydrophobic and hydrophilic domains such that the polymer segments shield a part of the hydrophobic domain from being in contact with water. The magnitude of the area of mutual contact between the polymer molecule and the hydrophobic domain of the aggregate is determined by the structural and physicochemical properties of the polymer molecule. This area of mutual contact, per surfactant molecule in the aggregate, is denoted by a_{pol}. The magnitude of a_{pol} for a given polymer molecule can be determined using a single experimental measurement, namely the polymer-induced change in the critical micelle concentration of any one surfactant. One can use this value of a_{pol} to predict the changes induced by this polymer, in the micellization, solubilization, and microemulsification behavior of other surfactant molecules.[9,10]

The polymer–aggregate association modifies the microenvironment of the polymer segments. Specifically, a part of the polymer molecule (i.e. the area a_{pol} per surfactant molecule) is removed from contact with water and brought into the proximity of the hydrophobic domain of the aggregate. The free energy contribution due to this effect depends on the hydrophobicity of the polymer

molecule. We choose, as a quantitative measure, the variable $\Delta\sigma_{pol}$, which is the difference between the macroscopic interfacial tensions of polymer–water and polymer–hydrocarbon interfaces. Both these interfacial tensions are experimentally accessible and can be independently determined. Thus, the two parameters a_{pol} and $\Delta\sigma_{pol}$ are used to describe how the presence of the polymer affects surfactant microstructures. An alternate approach to quantitatively describe the influence of the polymer via the interfacial properties at the aggregate–water interface has been proposed by Ruckenstein et al.[11]

On the basis of the visualization of polymer microemulsion association described above, we modify eq 2.2 to obtain

$$\Delta\mu^\circ_{gI} = C + \frac{\sigma_{agg}(a - a_{oS} - \{g_{AI}/g_{SI}\}a_{oA} - a_{pol})}{kT} -$$
$$\ln\left(1 - \frac{a_{pS} + \{g_{AI}/g_{SI}\}a_{pA} + a_{pol}}{a} \right) + \frac{\phi}{a^2} - \frac{\Delta\sigma_{pol}a_{pol}}{kT} \quad (3.1)$$

The first and the fourth terms are identical to those appearing in eq 2.2. The modified second term accounts for the enhanced shielding of the hydrophobic domain from water provided by the polymer. The modified third term accounts for the increase in the steric repulsions due to the presence of the polymer. The fifth term is new compared to eq 2.2 and represents the gain in hydrophobic free energy for the polymer molecule when its microenvironment is modified. Yet another term that should be considered but not included here relates to the entropic effects associated with the confinement of the polymer to the film–water interface when compared to the initial state of free polymer molecules present in the aqueous phase. This free energy contribution is not dependent on the aggregate area a per surfactant molecule and hence will not affect the equilibrium area calculations. However, this free energy contribution influences the magnitude of $\Delta\mu^\circ_{gI}$ and thus has an effect on whether the polymer-associated droplets will form or polymer-free droplets will form.

The equilibrium area per surfactant molecule of the aggregate in the presence of the polymer is found as before by minimizing $\Delta\mu^\circ_{gI}$ with respect to the area a. One gets in place of eq 2.3, the following implicit expression

$$a = \left[\frac{a_{pS} + \{g_{AI}/g_{SI}\}a_{pA} + a_{pol}}{a - (a_{pS} + \{g_{AI}/g_{SI}\}a_{pA} + a_{pol})} + \frac{2\phi}{a^2} \right]\left(\frac{\sigma_{agg}}{kT} \right)^{-1} \quad (3.2)$$

As mentioned before, once the equilibrium area a is known and given the alcohol-to-surfactant ratio in the film region, we can use the geometrical relations given in the Appendix to calculate the droplet radius, the extent of solubilization of oil or water within the droplets, and the number of surfactant molecules in the film region of the droplets.

To summarize, in order to conclude that the polymer molecules associate with the droplets, the free energy of formation of polymer-bound droplets, eq 3.1, must be lower than the free energy of formation of the polymer-free droplets, eq 2.2. One can calculate the properties of these droplets by eqs 3.2 and 2.3, respectively, in conjunction with the geometrical relations given in the Appendix. One may note that no explicit reference to the concentration of the polymer added has been made in the model. This is because the model assumes that enough polymer molecules are available to occupy the film–water interface at the rate of an area a_{pol} per surfactant molecule. If the amount of polymer added is inadequate to maintain the

(9) Nagarajan, R. *Colloids Surf.* **1985**, *13*, 1.
(10) Nagarajan, R. *Adv. Colloid Interface Sci.* **1986**, *26*, 205.

(11) Ruckenstein, E.; Huber, G.; Hoffmann, H. *Langmuir* **1987**, *3*, 382.
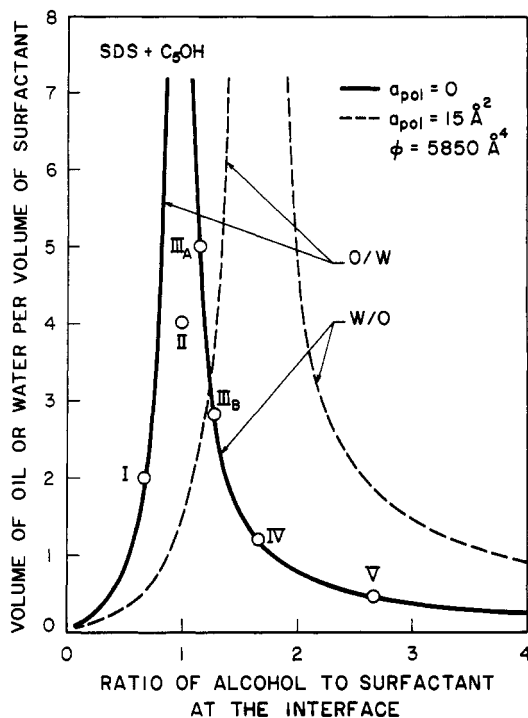
Figure 3. Volume ratio of the dispersed phase (oil or water) in the microemulsion droplet to the surfactant in the film region of the droplet. Continuous lines refer to the polymer-free droplets while the dotted lines refer to the polymer-bound droplets. See text for a discussion of the five points indicated in the figure which correspond to the five types of allowed structural transitions.

above condition, then both polymer-associated and polymer-free droplets will coexist and the experimentally determined properties would be the appropriate averages of the two kinds of droplets.

IV. Prediction of Polymer-Induced Transitions

For a quantitative calculation of the droplet characteristics, we need to specify a number of molecular constants. These are estimated from knowledge of the molecular properties of the surfactant, the alcohol, and the oil. The estimated molecular constants have already been employed in model calculations of micellization, mixed-micellization, solubilization, and droplet micro-emulsions.[5-8] For SDS, the molecular constants at 25 °C are $v_S = 351$ Å^3, $l_S = 16.7$ Å, $a_{pS} = 17$ Å^2, $a_{oS} = 17$ Å^2, and $v_{pS} = 56$ Å^3. For 1-pentanol (designated as C$_5$OH in the figures), $v_A = 162$ Å^3, $l_A = 7.9$ Å, $a_{pA} = 8$ Å^2, $a_{oA} = 8$ Å^2, and $v_{pA} = 18$ Å^3. (See Nomenclature for the definitions of the variables listed here.) Further, because of the anionic nature of the surfactant, electrostatic interactions among the polar heads are present. We have found from earlier calculations[2] that the micellization properties of SDS in the absence of any added electrolyte are well reproduced when ϕ is taken to be 11 700 Å^4. Here, for the illustrative calculations, ϕ is taken equal to 5850 Å^4. The use of a lower value of ϕ implies that some electrolyte is present in the system and it decreases the magnitude of the electrostatic repulsions. The parameter σ_{agg} is taken to be 50 dyn/cm corresponding to an interface between water and aliphatic hydrocarbon tails of the surfactant and the alcohol. This parameter would have to be modified somewhat if we consider that oil can penetrate the film region. In such a situation, σ_{agg} would be influenced by the magnitude of the oil–water interfacial tension and the extent of oil penetration into the film region. If the oil is
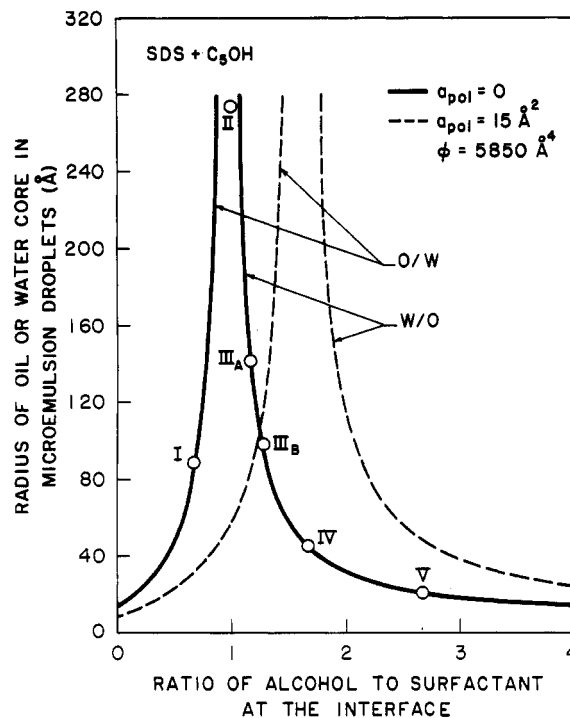

Figure 4. Radii of the film–water and film–oil intefaces in microemulsion droplets. Continuous line refers to the polymer-free droplets while the dotted line refers to the polymer-bound droplets. The system is identical to that in Figure 3 and the five points marked here correspond to those in Figure 3.

a saturated hydrocarbon such as cyclohexane considered in the experimental study of Lianos et al.,[1] then the present estimate for σ_{agg} remains valid even when oil is present in the film region. The only parameter related to the polymer needed for the calculations is a_{pol}, since the other parameter $\Delta\sigma_{pol}$ determines whether polymer-associated structures form but not the microscopic characteristics of these associated structures. We present in this paper, the model predictions for an assumed value of $a_{pol} = 15$ Å^2 which is taken to represent poly(oxyethylene).[2]

The calculated results are shown in Figures 3–5 for the system SDS, 1-pentanol, water, oil, and electrolyte, both in the absence of polymers and when nonionic polymer molecules are present. Figure 3 presents the volume of oil or water solubilized in a droplet per unit volume of the surfactant in the film region of the droplet. The radii of the oil core of the O/W droplets and of water core of the W/O droplets are shown in Figure 4. Figure 5 shows the number of surfactant molecules in the film region of a microemulsion droplet for the same conditions as in the previous two figures. In all three figures, the calculated droplet characteristics are presented as functions of the molar ratio of alcohol-to-surfactant in the film region. This ratio will be different from the overall ratio of alcohol-to-surfactant in the system because of the presence of alcohol also in the oil phase, as mentioned earlier.

From all three figures we observe that at low alcohol-to-surfactant ratios, O/W droplet microemulsions are formed. With increasing ratio of alcohol to surfactant, a phase inversion to the W/O droplet microemulsion occurs. As mentioned earlier, our model and hence the calculations are limited to droplet microemulsions. However, based on the experimental studies in the literature such as ref 3, we know that for intermediate ranges of alcohol-to-surfactant ratios, bicontinuous microemulsions are generated. In this manner, we are able to identify the alcohol-to-surfactant ratios for which either droplet or bicontinuous microemulsions are formed, in both polymer-free and
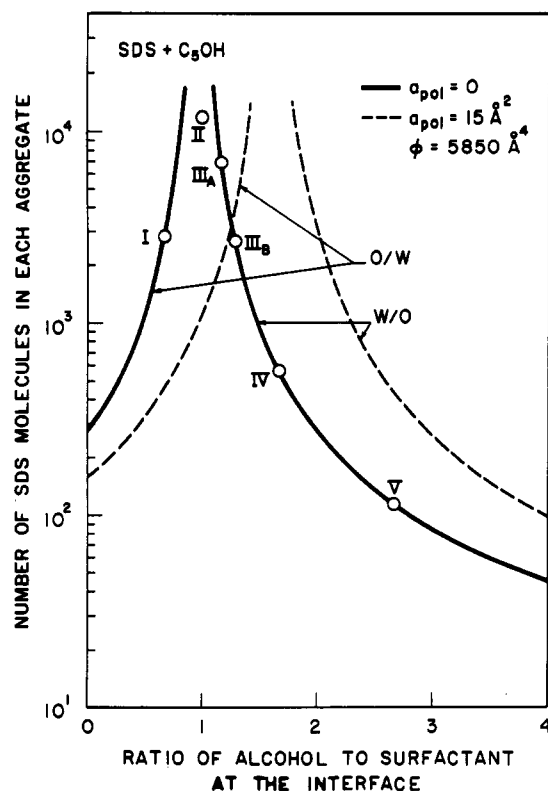
Figure 5. Number of surfactant molecules contained within the film region of the microemulsion droplet. Continuous lines refer to the polymer-free droplets while the dotted lines refer to the polymer-bound droplets. The system is identical to that in Figure 3 and the five points marked here correspond to those in Figure 3.

polymer-containing systems, using the model applicable only to droplet microemulsions. Thus, for a given alcohol-to-surfactant ratio, these calculated results allow us to identify the polymer-induced structural transitions in the microemulsion systems.

Figures 3–5 show that the presence of the polymer essentially shifts the solubilization curves to the right. However, the qualitative trends of increasing oil solubilization with increasing amount of alcohol in the O/W microemulsion and of decreasing water solubilization with increasing amount of alcohol in the W/O microemulsion are displayed by both the polymer-free system as well as the polymer-containing systems.

Variations in the chain length of alcohol, the parameter a_{pol} characteristic of the polymer, and the parameter ϕ which depends on the electrolyte concentration, all produce qualitatively the same types of solubilization curves as shown in Figures 3–5. The solubilization curves are displaced further to the right when a_{pol} is increased, alcohol chain length is decreased, or ϕ is increased. Thus, qualitative conclusions arrived at in this paper are general and valid for other surfactants, alcohols, and electrolyte concentrations.

Various transitions in microemulsion structures are revealed by the calculated results. The five types of transitions that are induced by the presence of the polymer are identified through the composition points marked I to V, Figures 3–5. The points identified on the continuous lines correspond to various types of microemulsions that exist in the absence of the polymer. The new microemulsion structures that will come into existence on the addition of the polymer can be found by projecting the points (that is keeping the alcohol-to-surfactant ratio constant) to the dotted lines shown in the figures.

Point I corresponds to an O/W droplet microemulsion. In the presence of the polymer and at this alcohol-to-surfactant ratio, the calculations show that O/W droplet microemulsions are formed. Thus, on the addition of the polymer, the type of the microemulsion remains unaffected, but the maximum amount of oil solubilized per unit surfactant volume is decreased substantially (Figure 3), the radius of the oil core is decreased (Figure 4), and the number of surfactant molecules in the film region of the droplet is also significantly diminished (Figure 5). Correspondingly, for a given total concentration of the surfactant, the number density of the droplets is increased. One may further infer that if we had started with a single-phase O/W microemulsion, the addition of the polymer would cause an excess-oil-phase to be separated. If we had a two-phase (Winsor I) system to begin with, the volume of the excess oil phase is going to be increased.

Point II corresponds to a bicontinuous microemulsion. In locating this point in Figures 3–5, only the alcohol-to-surfactant ratio on the horizontal axis should be taken as a relevant parameter; the values on the vertical axes have no significance since we do not carry out any direct analysis of the characteristics of the bicontinuous microemulsion. In the presence of the polymer and at this alcohol-to-surfactant ratio, the calculations show that O/W droplet microemulsions will be generated whose microscopic features are described by the values on the vertical axes of Figures 3–5. Thus, the bicontinuous-microemulsion system II transforms into an O/W droplet-microemulsion system on the addition of the polymer.

Points IIIA and IIIB refer to W/O droplet microemulsions. In the presence of the polymer and at these alcohol-to-surfactant ratios, the calculations show that O/W droplet microemulsions are formed. Thus, on the addition of the polymer, the W/O droplet microemulsions phase invert to O/W droplet microemulsions. System IIIA contains more solubilized water than system IIIB. When phase-inversion occurs, the polymer-associated system IIIA has less oil solubilized compared to the polymer-associated system IIIB. Correspondingly, the droplet radius and the number of surfactant molecules in the film region of a droplet both decrease for IIIA and increase for IIIB when compared to the polymer-free IIIA and IIIB microemulsions.

Point IV denotes a W/O droplet microemulsion system. In the presence of the polymer and at this alcohol-to-surfactant ratio, the calculations show that droplet microemulsions are excluded and we infer that a bicontinuous microemulsion is generated. Thus, a W/O droplet microemulsion at IV transforms into a bicontinuous microemulsion system, on the addition of the polymer. As mentioned before, the values on the vertical axes have no significance for the bicontinuous systems since we do not carry out any direct analysis of the characteristics of the bicontinuous microemulsion.

Point V corresponds to a W/O droplet microemulsion. In the presence of the polymer and at this alcohol-to-surfactant ratio, the calculations show the formation of a W/O droplet microemulsion. Thus, on the addition of the polymer, the type of the microemulsion remains unaltered but the amount of water solubilized per unit volume of the surfactant (Figure 3), the radius of the water core of the droplet (Figure 4), and the number of surfactant molecules in the film region of a droplet (Figure 5) all appreciably increase. Point V qualitatively corresponds to the type of microemulsion systems investigated by Lianos et al.[1] It is obvious that if the total amount of surfactant is fixed, the addition of the polymer will cause

the number density of droplets to diminish, since the polymer-associated droplet is larger than that in the polymer-free system.

The transitions in the microemulsion structures described above arise from the rightward shift of the solubilization curves on the addition of the polymer. Consequently, other transitions that require a leftward shift in the solubilization curves are disallowed. Specifically, an O/W droplet microemulsion cannot invert to a W/O droplet microemulsion system (type VI) or transform into a bicontinuous microemulsion (type VII). Also, a bicontinuous-microemulsion system cannot transform into a W/O droplet microemulsion system (type VIII).

The influence of the polymer on structural transitions in microemulsion systems discussed above can be understood via simple geometric arguments. At any alcohol-to-surfactant ratio, the association of the polymer with the microemulsion droplet causes an increase in the equilibrium area per surfactant molecule (eq 3.2) when compared to that in the polymer-free droplet (eq 2.3). Consequently, in view of the geometrical relations characterizing the droplets (see Appendix), the ratio R_O/R_W always decreases on the addition of the polymer (eq A.5), thus rationalizing the allowed as well as the disallowed transitions among microemulsions. The predictions of this simple model, except that corresponding to point V, remain to be experimentally tested.

V. Conclusions

A simple molecular model of droplet microemulsions is used to explore how the microemulsion structures are altered by the addition of nonionic polymer molecules that associate with the aggregates. In arriving at our predictions, we also exploit the experimental observation that when the alcohol-to-surfactant ratio is increased, the inversion from the Winsor 1 to the Winsor 2 system often occurs via the Winsor 3 system. Illustrative calculations are presented for a system consisting of SDS, 1-pentanol, oil, water, and electrolyte. The model predicts that five types of transitions between Winsor 1, Winsor 2, and Winsor 3 microemulsions can be induced by the polymer molecules while three types of transitions are disallowed. The results are qualitative because of the simplifications employed but have generality for microemulsions formulated with nonionic, zwitterionic, or ionic surfactants. Most importantly, the model predictions suggest a novel approach to manipulating microemulsion structures via the addition of polymer molecules that are able to associate with surfactant microstructures.

Nomenclature

a	surface area of the aggregate–water interface per molecule of the surfactant
a_{oS}	area per molecule of the aggregate–water interface that is shielded from contact with water because of the presence of the polar head of the surfactant
a_{oA}	area per molecule of the aggregate–water interface that is shielded from contact with water because of the presence of the polar head of the alcohol
a_{pS}	cross-sectional area of the polar head of the surfactant
a_{pA}	cross-sectional area of the polar head of the alcohol
a_{pol}	contact area between the polymer and the hydrophobic surface of the aggregate per molecule of the surfactant

g_{SI}	number of surfactant molecules in the film region of the aggregate
g_{AI}	number of alcohol molecules in the film region of the aggregate
k	Boltzmann constant
l_S	extended length of the hydrophobic tail of the surfactant
l_A	extended length of the hydrophobic tail of the alcohol
R_O	radius of the film–oil interface in a microemulsion droplet
R_W	radius of the film–water interface in a microemulsion droplet
T	absolute temperature of the solution
v_S	molecular volume of the hydrophobic tail of the surfactant
v_A	molecular volume of the hydrophobic tail of the alcohol
v_{pS}	molecular volume of the polar head of the surfactant
v_{pA}	molecular volume of the polar head of the alcohol
μ°_{SW}	standard chemical potential of the singly dispersed surfactant
μ°_{AW}	standard chemical potential of the singly dispersed alcohol
μ°_{gI}	standard chemical potential of the film region of an aggregate containing surfactant and alcohol molecules
σ_{agg}	macroscopic interfacial tension between water and the hydrophobic domain of the aggregate
$\Delta\sigma_{pol}$	difference between the macroscopic polymer–water interfacial tension and polymer–hydrocarbon interfacial tension
ϕ	parameter describing (a) electrostatic repulsions between surfactant polar heads at the aggregate surface and (b) the deformation free energy of the surfactant tails in the aggregate due to molecular packing restrictions

Appendix: Geometrical Characteristics of Droplets

The properties of the microemulsion droplets can be estimated from the alcohol-to-surfactant ratio in the film region, the molecular characteristics of the surfactant and the alcohol, and the equilibrium area a determined from free energy considerations. Considering the droplets depicted in Figure 2, let the surfaces of the film region have radii of R_W and R_O, respectively, depending upon whether they are in contact with the water or the oil domains. One may note that when $R_O/R_W < 1$, the microemulsion is of the oil-in-water type. For $R_O/R_W > 1$, one obtains the water-in-oil microemulsions. As suggested in the work of Oakenfull[5], the thickness of the film region is taken to be the composition-averaged-length of the extended tails of the surfactant and the alcohol. Therefore

$$|R_W - R_O| = \frac{g_{SI}l_S + g_{AI}l_A}{g_{SI} + g_{AI}} = l_S \frac{\left(1 + \dfrac{g_{AI}l_A}{g_{SI}l_S}\right)}{\left(1 + \dfrac{g_{AI}}{g_{SI}}\right)} \quad \text{(A.1)}$$

Here, g_{SI} and g_{AI} are the numbers of surfactant and alcohol molecules in the film region of the droplet and l_S and l_A are the extended lengths of their respective hydrophobic tails. The total volume V of the film region and its surface area A in contact with water are given by

$$V = g_{SI}v_S + g_{AI}v_A = \frac{4\pi|R_W^3 - R_O^3|}{3},$$

$$A = g_{SI}a = 4\pi R_W^2 \quad (A.2)$$

where v_S and v_A refer to the volumes of the hydrophobic tails of the surfactant and the alcohol, respectively, while a denotes the area per surfactant molecule of the film surface in contact with water. From eqs A.1 and A.2, one obtains

$$1 + \left(\frac{R_O}{R_W}\right) + \left(\frac{R_O}{R_W}\right)^2 = \frac{\left(\frac{3v_S}{al_S}\right)\left(1 + \frac{g_{AI}v_A}{g_{SI}v_S}\right)\left(1 + \frac{g_{AI}}{g_{SI}}\right)}{\left(1 + \frac{g_{AI}l_A}{g_{SI}l_S}\right)}$$

$$(A.3)$$

Since the hydrophobic parts of the surfactant and the alcohol are taken to be aliphatic chains, one can write

$$\frac{v_A}{v_S} \approx \frac{l_A}{l_S} \quad (A.4)$$

The ratio between the radii of the two interfaces of the film region is obtained from eqs A.3 and A.4 to be

$$\frac{R_O}{R_W} = \left[\left(\frac{3v_S}{al_S}\right)\left(1 + \frac{g_{AI}}{g_{SI}}\right) - \frac{3}{4}\right]^{1/2} - \frac{1}{2} \quad (A.5)$$

The radii R_W and R_O can be calculated explicitly using eqs A.1 and A.5. Given these two radii, the volume of the oil solubilized per unit volume of the surfactant molecule in an O/W microemulsion can be estimated using the relation

$$\frac{V_{oil}}{V_{surf}} = \left(\frac{R_O^3}{R_W^3 - R_O^3}\right)\left(1 + \frac{g_{AI}v_A}{g_{SI}v_S}\right)\left(\frac{v_S}{v_S + v_{pS}}\right),$$

$$\frac{R_O}{R_W} \leq 1 \quad (A.6)$$

Note that the volume of the surfactant molecule includes that of the hydrophobic part denoted by v_S as well as that of the polar head denoted by v_{pS}. Similarly, the volume of water solubilized per unit volume of surfactant molecule in a W/O droplet is given by the expression

$$\frac{V_{water}}{V_{surf}} = \left(\frac{R_W^3}{R_O^3 - R_W^3}\right)\left(1 + \frac{g_{AI}v_A}{g_{SI}v_S}\right)\left(\frac{v_S}{v_S + v_{pS}}\right) -$$

$$\left(1 + \frac{g_{AI}v_{pA}}{g_{SI}v_{pS}}\right)\left(\frac{v_{pS}}{v_S + v_{pS}}\right), \quad \frac{R_O}{R_W} \geq 1 \quad (A.7)$$

Here, v_{pA} refers to the volume of the polar head of the alcohol molecule. One may observe that in calculating the amount of water solubilized, the above equation takes into account the volumes of the polar heads of the surfactant and the alcohol that are present along with water molecules in the core of the water-in-oil droplets. All the necessary geometrical relations are now available to calculate the structural features of the microemulsion droplets. For a given alcohol-to-surfactant ratio (g_{AI}/g_{SI}) in the film region, the only unknown is the equilibrium are a per molecule of the surfactant appearing in eq A.5. This equilibrium area is calculated knowing the free energy of formation of the microemulsion droplet.