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Conductivity measurements on this system are interpreted in terms of the percolation and effective medium theories. From this interpretation, the ratio of hexylamine to sodium dodecyl sulfate in the microemulsion droplet surfaces can be deduced. Following that determination it is possible to obtain approximate values for the radius of the water pools and the number and surface area of droplets per unit volume of the microemulsion system. © 1987 Academic Press, Inc.

INTRODUCTION

The common microemulsion systems containing intermediate chain length alcohols as cosurfactants usually reach a maximum water solubilization at about 60% with concentrations of surfactant higher than 15% and of cosurfactant around 25% (1). In a previous study (2), we reported a novel microemulsion system consisting of sodium dodecyl sulfate (SDS), hexylamine, heptane, and water. The system exhibited some unusual properties, such as very high water solubilization at a very low surfactant concentration. The system could reach a maximum water solubilization higher than 90%, while the surfactant concentration was as low as about 1.5% and the cosurfactant concentration was less than 7% starting with a hydrocarbon–cosurfactant mixture that was 25% heptane–75% hexylamine.

Since the discovery of microemulsions, many different techniques have been used to investigate their structures. Among these, conductivity measurement provides a particularly convenient and useful tool for investigation of structure and phase inversion phenomena in microemulsions (3–5). Our microemulsion system is characterized by a continuous solubility region from high hydrocarbon levels to high water content. It appears reasonable to expect structure inversion.

It has been shown that, for some microemulsion systems, conductivity behavior can be described in terms of percolation and effective medium theories (3, 6, 7). In the present study we propose a simple model for our systems and find that the conductivity data can be fitted nicely by the effective medium formula. Moreover, the ratio of the cosurfactant (hexylamine) to surfactant (SDS) molecules in the interfacial film can be evaluated using this approach. With this ratio known, we are able to calculate the approximate droplet size and the number of droplets per unit volume of microemulsion based on the assumption that the droplets or aggregates are monodisperse.

MATERIALS AND METHODS

Materials. Hexylamine was purchased from Eastman–Kodak (Cat. No. 117, 7559, 99%) and used as received. Heptane was from Fisher (Cat. No. 03008) and used without further purification. Sodium dodecyl sulfate (SDS) was purchased from BDH and recrystallized twice with absolute ethanol. Water was triple distilled.

Methods. Conductivity was measured by using a Kent EIL 5007 conductivity meter op-

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erating at 70 Hz or 1 kHz and temperature compensated to 25°C. Each experiment was done while keeping the ratio of SDS to hexylamine constant. Water was added to the sample until the composition of the system was close to the boundary of the microemulsion region where turbidity due to phase separation is observed.

Phase diagrams were determined at 25 ± 0.05°C by the titration method, as described elsewhere (2).

RESULTS

Figure 1a shows the tertiary phase diagram for the system consisting of SDS, hexylamine (Ha), and water. Figures 1b, 1c, and 1d show the pseudotertiary phase diagrams of the systems containing different amounts of heptane (Hp). From these diagrams it is seen that water is soluble in pure hexylamine up to around 63%. However, addition of heptane to the hexylamine progressively reduces this water solubility. It is interesting to note that a linear relation exists between water solubility and the weight ratio of heptane to heptane plus hexylamine when no surfactant is present, as

shown by curve (1) in Fig. 2. It is noticeable that the maximum content of solubilized water in these microemulsion systems is very high even when the oil level is high and the surfactant concentration is very low. Curve (2) in Fig. 2 shows the variation of the maximum water solubilization into the microemulsion with the heptane content as determined from the four phase diagrams of Fig. 1. This water solubilization first increases and reaches a maximum at a hydrocarbon level about 25%, then decreases to about 60% when the ratio of Hp/(Ha + Hp) is equal to 75%.

Figures 3 to 8 show some typical conductivity data from the present microemulsions. Detailed discussion about these data will be given in the following section.

DISCUSSION

Conductivity behaviors of emulsions and microemulsions have been studied by investigators using various models (3, 8, 9). It is expected that microemulsions must have conductivity properties different from those of emulsions since the structures of microemulsions and emulsions are very different. As in-
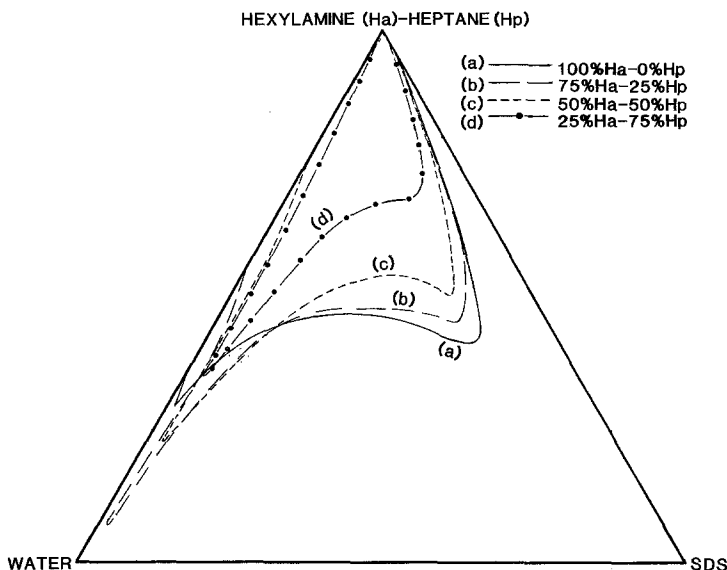

FIG. 1. Partial pseudotertiary phase diagram of the system composed of sodium dodecyl sulfate (SDS), hexylamine (Ha), heptane (Hp), and water.
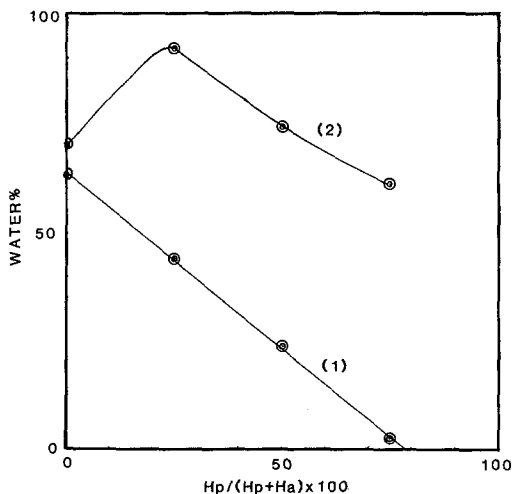
FIG. 2. Solubility of water as represented on the phase diagrams of Fig. 1. (1) Solubility of water in the mixture of hexylamine and heptane with no surfactant present. (2) Maximum water solubilization into the microemulsions when surfactant is present.

dicated by some authors (10), water continuous (O/W) type microemulsions show much more complicated conductivity behavior than do the oil continuous (W/O) types. In the present systems it is believed that the microemulsions are W/O type at lower water concentrations. We find that the percolation and effective medium theories, which were developed for semiconductor–metal transitions observed in inhomogeneous systems and for transport properties in amorphous solids (11), can be used to explain the observed conductivity behavior. According to Clausse and co-workers (7), the present microemulsions should belong to the U-type system which is characterized by a phase diagram in which the W/O and O/W areas merge into each other and form a unique domain and the conductivity behavior of such U-type microemulsions can be described by percolation and effective medium theories. Our results agree with such an interpretation as will be shown in the following sections.

It is well known that a microemulsion is a transparent liquid dispersion system of two immiscible liquids (12), such as oil and water,

containing amphiphilic molecules as a third and/or fourth component. In applying the percolation and effective medium theories to such a system, let us first consider the low water concentration region. When water concentration is low, the microemulsion can be oil continuous. Thus the disperse phase consists of water droplets surrounded by amphiphilic molecules. These droplets behave as the electrical conducting constituent in the system. If the volume fraction (ϕ_d) of the disperse phase (water droplets) is below a critical value called the percolation threshold and designated ϕ_p, then the conductive droplets are isolated from each other and contribute little to conductance. However, when the volume fraction of the disperse phase reaches and exceeds the percolation threshold, some of these conductive droplets begin to contact each other and form clusters with many conductive paths. Conductivity therefore begins to increase rapidly from an almost zero value to some much higher level. This phenomenon can be seen from Figs. 4 to 7.

Lagourette et al. (3) state that in the vicinity of the percolation threshold the relation of conductivity, σ, to volume fraction, ϕ, can be described by the scaling equation

$$\sigma \alpha (\phi - \phi_p)^t, \qquad [1]$$

where t is usually equal to $\frac{8}{5}$ (3, 6). Our results are in agreement with this equation, as shown in Fig. 3, where a straight line is found in the range of medium values of ϕ.

For higher concentrations the equation

$$\sigma \alpha (\phi - \phi_p) \qquad [2]$$

fits the conductivity data (3). Figures 4 to 7 show this relation. The valid range of Eq. [2] overlaps with that of Eq. [1].

From the effective medium theory, the conductivity for a binary composite can be expressed as (3, 7, 13, 14)

$$\frac{\sigma - \sigma_c}{3\sigma} = \frac{\sigma_d - \sigma_c}{\sigma_d + 2\sigma} \phi, \qquad [3]$$

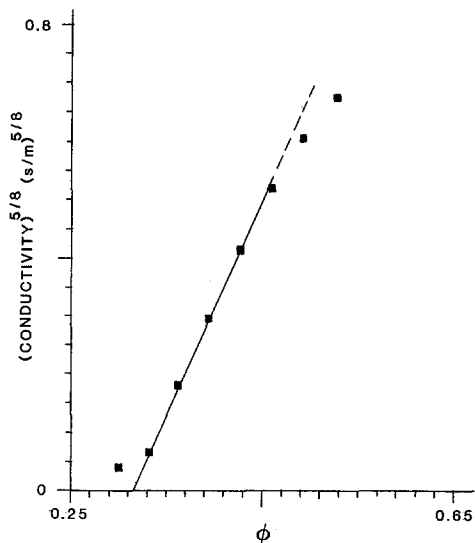where σ_c and σ_d are the conductivities of the continuous phase and disperse phase, respec-

FIG. 3. Conductivity$^{5/8}$ versus volume fraction of water added. (See Eq. 1).

tively. For the present systems σ_d is much larger than σ_c, since the continuous phase is oil which shows almost zero conductivity. Thus the above equation can be reduced to

$$\sigma = \tfrac{3}{2}\sigma_d(\phi - \tfrac{1}{3}).\qquad [4]$$

FIG. 5. Conductivity versus $(\phi - \tfrac{1}{3})$ for the system containing SDS, hexylamine (Ha), heptane (Hp), and water, with the ratio Hp/Ha = 25/75 (W/W) and the ratio SDS/(Hp + Ha) = 20/80 (W/W).

Obviously, the plot of σ against $(\phi - \tfrac{1}{3})$ should be a straight line passing through the origin and with a slope equal to $3\sigma_d/2$ if the conduc-
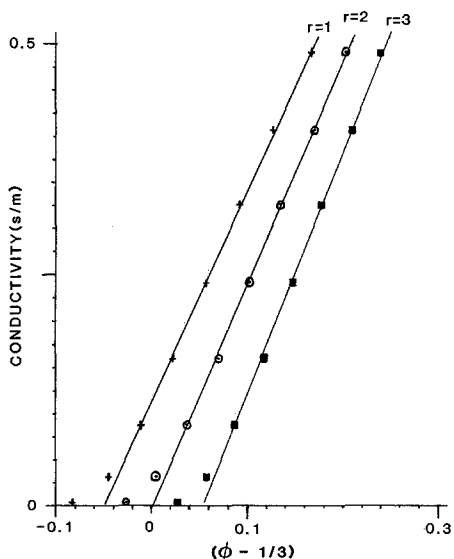

FIG. 4. Conductivity versus $(\phi - \tfrac{1}{3})$ for the system containing SDS, hexylamine (Ha), and water, with the ratio SDS/Ha (W/W) equal to 20/80.
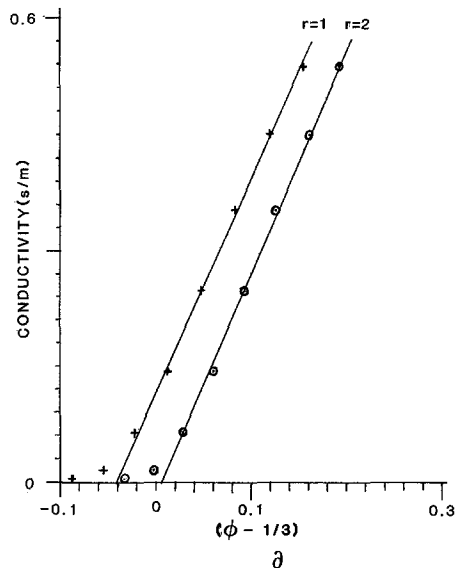

FIG. 6. Conductivity versus $(\phi - \tfrac{1}{3})$ for the system containing SDS, hexylamine (Ha), heptane (Hp), and water, with the ratio Hp/Ha = 25/75 and the ratio SDS/(Hp + Ha) = 15/85.
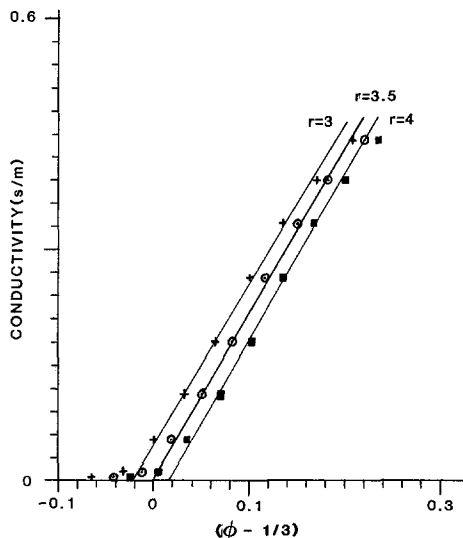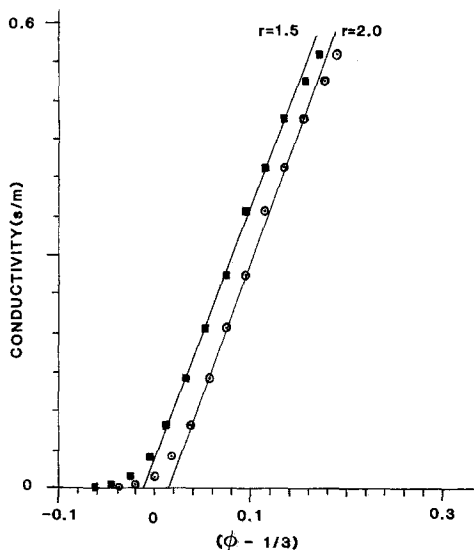
FIG. 7. Conductivity versus $(\phi - \frac{1}{3})$ for the system containing SDS, hexylamine (Ha), heptane (Hp), and water, with the ratio Hp/Ha = 37.5/62.5 and the ratio SDS/(Hp + Ha) = 20/80.

tivity behavior of the system obeys the equation. Comparing Eq. [4] with Eq. [2], it seems that the percolation threshold is equal to $\frac{1}{3}$.

Since the volume fraction ϕ of the disperse phase is not obtained directly from these experiments, it is necessary to calculate it from the weight fractions. To do this, the following assumptions have been made.

(a) All SDS is in the interphase between the water core and oil phase.

(b) The cosurfactant hexylamine distributes among the continuous phase (oil), interphase, and disperse phase (water core). However, the solubility of hexylamine in water is negligible (less than 1% at 25°C) so that the amine is considered to be present only in the interphase and in the oil phase.

(c) The interphase is composed of SDS and hexylamine. Thus the average ratio of SDS molecules to hexylamine molecules, r, in the interphase is given by

$$r = N_{Ha}^{int}/N_{SDS},$$

where N_{Ha}^{int} is the mole number of hexylamine

in the interphase and N_{SDS} is the mole number of SDS in the system.

With the above model we can derive a formula to calculate the volume fraction of the disperse phase:

$$\phi = \frac{V_d}{V_t} = \frac{\rho_t}{\rho_d} [f_{SDS} + f_{Ha}^{int} + f_{H_2O}]$$

$$= \frac{\rho_t}{\rho_d} \left[f_{SDS} \left(1 + r\frac{M_{Ha}}{M_{SDS}} \right) + f_{H_2O} \right], \quad [5]$$

where ρ_t and ρ_d are the densities of the microemulsion system and the disperse phase (water droplets). The weight fractions of SDS and water in the system are f_{SDS} and f_{H_2O}, respectively, while the weight fraction of hexylamine in the interphase is f_{Ha}^{int}. M_{Ha} and M_{SDS} are the molecular weights of hexylamine and SDS. As an approximation, the value of ρ_d can be taken as 1.0 g/ml since the density of water at 25°C is near 1.0 g/ml, that of SDS is 1.16 g/ml (15), and that of hexylamine is 0.766 g/ml. With this equation, we are able to evaluate the volume fraction of water droplets (water core plus interphase) if an appropriate value of the structural parameter r is chosen. Hence we can plot σ against $(\phi - \frac{1}{3})$ as shown in Figs. 4 to 7. From these figures, it is seen that the parameter r can be determined by fitting the experimental data with the reduced effective medium Eq. [4], that is, by trying different values of r until the straight line passes through the origin. From Eq. [4] the conductivity of the disperse phase, σ_d, can be calculated from the slope of the straight line. Data from systems with the ratio of SDS to (Ha + Hp) equal to 20/80 are plotted in Fig. 8. It is interesting that σ_d shows a linear relation to the ratio by weight between SDS and hexylamine in the system. This result confirms the previous assumption that all SDS is essentially present in the interphase. Since SDS is ionic and largely ionized in contact with the water core, the conductivity of the disperse phase, σ_d, will increase with increasing concentration of SDS in the system. A similar result was observed by Clausse et al. (3).
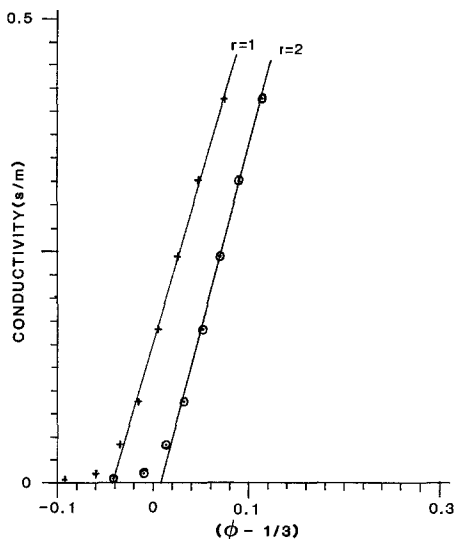
FIG. 8. Conductivity versus $(\phi - \frac{1}{3})$ for the system containing SDS, hexylamine (Ha), heptane (Hp), and water, with the ratio Hp/Ha = 50/50 and the ratio SDS/(Hp + Ha) = 20/80.

It may be questioned how the parameter r can remain unchanged while the water content varies over a rather wide range and the ratio of SDS to hexylamine is held constant. This can be interpreted qualitatively. When water concentration increases, the size of water droplets becomes larger whereas their number decreases due to clustering of small droplets, so that it is possible to maintain the constant ratio of hexylamine to SDS in the interphase during the addition of water. The constancy of r is actually in agreement with the result observed by Lagues and co-workers (6) and Shah et al. (16). A quantitative interpretation of this observation will be given later.

It is noted that the parameter r increases when the ratio of hexylamine to SDS increases. For example, in Figs. 5 and 6, r increases from about 2.0 to 3.5 when the ratio Ha/SDS changes from 60/20 to 63.75/15 for the systems with Ha/Hp equal to 75/25. This is understandable because, for a given amount of water (assume that the water droplet is spherical), the surface area of the water core is fixed, if the system is monodisperse. To cover this area, more hexylamine molecules will be

needed if there are not enough SDS molecules available. Since the area of the polar head of the hexylamine molecule is smaller than that of the SDS molecule, r will increase rapidly with the ratio Ha/SDS. Similar results have been obtained for other systems with different ratios of Ha/(Ha + HP). The increase in r with increasing ratio Ha/SDS also explains the increase in σ_d with increasing SDS/Ha since SDS is ionic while hexylamine is largely nonionized and conduction is due mainly to SDS. For a droplet with a given radius, if there are more SDS molecules in the interphase, then there are fewer hexylamine molecules. Therefore the conductivity of the droplet (disperse phase), σ_d, increases.

We mentioned above that the parameter r is a constant when water content varies if the ratio SDS/Ha is kept constant and that the reason for this is due to the increase in water droplet size and to the decrease in droplet number. We now interpret this by quantitative calculations.

To evaluate the radius of water droplets, we assume that the microemulsions are monodisperse and that the water cores are spherical.
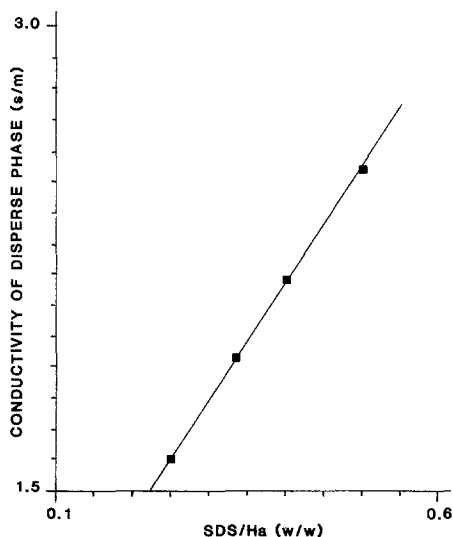

FIG. 9. Conductivity of disperse phase versus the ratio SDS/Ha for the microemulsion systems with the ratio SDS/(Hp + Ha) = 20/80.

Thus the total volume of water droplets is given by

$$V_d = 4\Pi R^3 N_d/3 \qquad [6]$$

and the total surface area of these droplets is

$$A_d = 4\Pi R^2 N_d, \qquad [7]$$

where R and N_d are the radius and the number of water droplets, respectively. Combining these two equations gives

$$A_d = 3V_d/R = 3W_d/(R\rho_d). \qquad [8]$$

On the other hand, A_d can be obtained from consideration of the polar head area of the amphiphilic molecules covering the surface of the water cores, assuming that the interphase is a monolayer film. Thus

$$A_d = N_{SDS}N_A A_{SDS} + N_{Ha}^{int}N_A A_{Ha}$$

$$= N_{SDS}N_A(A_{SDS} + rA_{Ha}), \qquad [9]$$

where N_A is Avogadro's number, A_{SDS} and A_{Ha} are the areas of the polar heads of an SDS and a hexylamine molecule, respectively.

Combine the last two equations to obtain

$$R = 3W_d/[N_A\rho_d N_{SDS}(A_{SDS} + rA_{Ha})], \qquad [10]$$

where

$$W_d = W_{SDS} + W_{Ha}^{int} + W_{H_2O}$$

$$= N_{SDS}M_{SDS} + N_{Ha}^{int}M_{Ha} + W_{H_2O}$$

$$= N_{SDS}(M_{SDS} + rM_{Ha}) + W_{H_2O}.$$

Thus

$$R = \frac{3[M_{SDS} + rM_{Ha} + W_{H_2O}/N_{SDS}]}{N_A\rho_d(A_{SDS} + rA_{Ha})}$$

$$= \frac{3[M_{SDS} + rM_{Ha} + (f_{H_2O}/f_{SDS})M_{SDS}]}{N_A\rho_d(A_{SDS} + rA_{Ha})}, \qquad [11]$$

where f_{H_2O} and f_{SDS} have been defined in Eq. 5. From conductivity data fitted by the reduced effective medium Eq. 4, the parameter r can be obtained when the ratio of Ha to SDS is held constant. Then if the following values are taken (17),

$$\rho_d \cong 1.0\,g/ml$$

$$A_{SDS} \cong 35\,Å^2$$

$$A_{Ha} \cong 25\,Å^2,$$

we can calculate the radius of the water droplets for each composition. The results of two sample calculations are shown in Fig. 10 for the system with SDS/(Ha + Hp) = 20/80 and the system with SDS/(Ha + Hp) = 15/85 while the ratio of hexylamine to heptane is equal to 75/25 for both of the systems. These calculated results of microemulsion droplet sizes are in good agreement with those commonly reported in the literature (10, 12). We see that the radius of water droplets is increasing with water weight fraction. Note that this radius increases more rapidly in the high water content range than in the low water content range.

It is easy to show that the number of water droplets per unit volume of microemulsion is given by

$$\tilde{N}_d = \frac{N_d}{V_t} = 3\phi/(4\Pi R^3). \qquad [12]$$

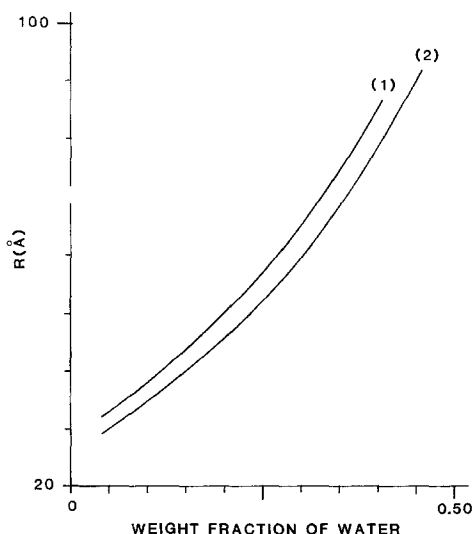Thus the total surface area of droplets per unit volume of microemulsion is

FIG. 10. Radius of microemulsion droplets with the ratio Hp/Ha = 25/75 and the ratio SDS/(Hp + Ha) = 20/80 (1) and 15/85 (2).

$$\tilde{A}_d = 4\Pi R^2 \tilde{N}_d. \qquad [13]$$

The calculated results of $\tilde{N}_d$ and $\tilde{A}_d$ for the systems corresponding to Fig. 10 are shown in Figs. 11 and 12. It is seen that $\tilde{N}_d$ decreases with water weight fraction, and $\tilde{A}_d$ decreases with water content almost linearly. This is because the decrease in $\tilde{N}_d$ outweighs the increase in radius. The general tendency of R and $\tilde{N}_d$ to change with water content is in agreement with the results obtained by Baker and coworkers for a different system using a light-scattering technique (5). However, their results show that the radius of water droplets decreases with increasing surfactant concentration. In contrast, for the present systems, R increases with increasing SDS concentration. This difference might be ascribed to the difference in microemulsion character since their system is an "S" type as designated by Clausse and co-workers (7), characterized by a phase diagram in which the W/O and O/W areas are disjointed and separated by a composition zone over which viscous and turbid systems are formed.
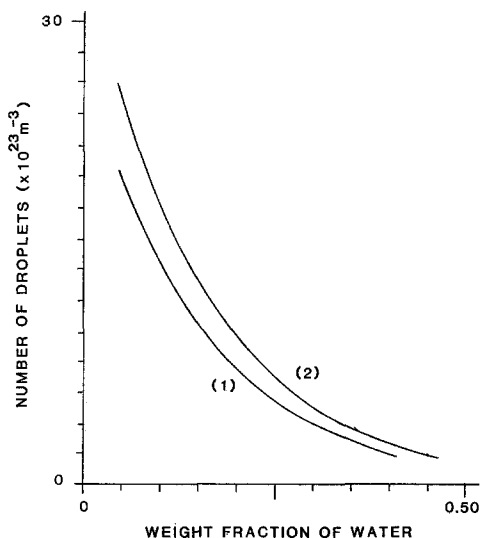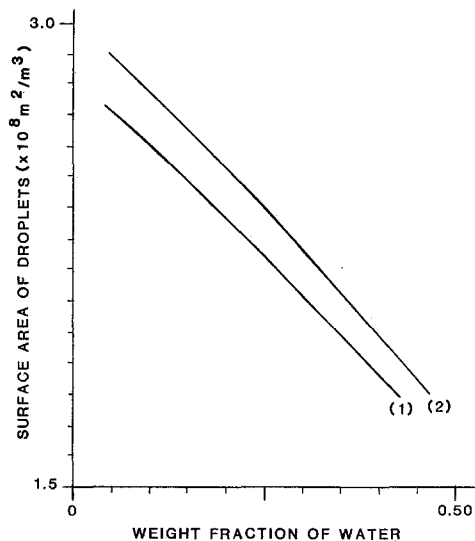

FIG. 12. Variation of surface area of droplets per unit volume of microemulsion with weight fraction of water for the system with the ratio Hp/Ha = 25/75 and the ratio SDS/(Hp + Ha) = 20/80 (1) and 15/85 (2).

SUMMARY

For the present microemulsion systems, conductivity behavior can be described by the percolation and effective medium theories. In particular, the important parameter, r, of water droplet structure in microemulsions can be found by fitting the experimental data with the effective medium formula. The conductivity of disperse phase (water droplets) can be obtained also. With the parameter r, approximate calculations of water droplet size and the number and surface area of droplets per unit volume of microemulsions are possible.

ACKNOWLEDGMENTS

FIG. 11. Variation of number of droplets per unit volume of microemulsion with weight fraction of water for a system with the ratio Hp/Ha = 25/75 and the ratio SDS/(Hp + Ha) = 20/80 (1) and 15/85 (2).

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