Electrical Conductance Behavior of Oil-in-Water Microemulsions Stabilized by Sodium Dodecyl Sulfate and 1-Butanol

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The specific conductivity of several oil-in-water (o/w) microemulsions (MEs) stabilized by sodium dodecyl sulfate and 1-butanol was measured at 25 °C as functions of the volume fraction of oil (ϕ_0) and the molar ratio of water to surfactant (R). The oils used are octane, benzene, toluene, carbon tetrachloride, chloroform, cyclohexane, xylene, and nitrobenzene. The conductivity data were explained by the modified Bruggeman equation in the entire experimental range of ϕ_0 in the case of octane and nitrobenzene and in a limited range of ϕ_0 in the case of other oils. The value of the slope of this equation, f, is found to depend on (i) the concentration of surfactant or the R value, (ii) the nature of the oil, and (iii) the nature and number of substituents, if the oil is a substituted benzene. The specific conductivity data of o/w MEs of $R = 120$ and 100 were also analyzed in the light of the mixed electrolyte model, and the values of aggregation number, counterion binding constant, and radius of droplet were computed.

Introduction

The electrical conductance of a microemulsion (ME) can provide us with information about the structure and dimensions of droplets. Most of the electrical conductance measurements of MEs are made in the water-in-oil (w/o) region due to the occurrence of the percolation phenomenon. In MEs, to study any of their physical properties, different composition paths are available due to the presence of generally four components. Relatively much less study has been made about the electrical conductance behavior of MEs stabilized by ionic surfactants in the oil-in-water (o/w) region by varying R (molar ratio of water to surfactant). Particularly, the Bruggeman equation[1−3] used for describing the conductance behavior of o/w MEs stabilized by nonionic surfactants has not been examined critically for its applicability to o/w MEs stabilized by ionic surfactants. Recently, a model known as the mixed-electrolyte model (MEM) has been used to analyze the electrical conductance data of ionic surfactants in aqueous,[4−6] molten,[7] and mixed-solvent media.[8] It would be worthwhile to examine the application of the MEM to explain the electrical conductance behavior of o/w MEs.

Keeping the above points in mind, we have made conductivity measurements of MEs containing sodium dodecyl sulfate (SDS), 1-butanol, and eight different oils at R values of 120, 100, 85, and 75.

Experimental Section

SDS and 1-butanol used in this study are of the same grade as used in our earlier study.[8] Eight MEs were prepared using octane (SD, AR grade, assay 99.7%), benzene (Merck, assay 99.7%), toluene (Merck, assay 99.5%), carbon tetrachloride (Merck, assay 99.8%), chloroform (Merck, HPLC grade, assay 99%), cyclohexane (Merck, HPLC grade, assay 99.7%), *m*-xylene (Merck), and nitrobenzene (Merck) as oils, and they were named as OCT, BEN, TOL, CTC, CHF, CYH, XYL, and NTB, respectively. Double-distilled water (conductivity = 2 μS cm^{-1}) was used throughout. Stock micellar solutions of various R values were prepared by mixing appropriate amounts of SDS, 1-butanol, and water such that the weight ratio of surfactant to cosurfactant (1-butanol) is 0.446. Conductivity measurements were made at 1 kHz using a Wayne-Kerr B905 automatic precision bridge and a cell of cell constant 102.4 m^{-1}. In an actual experiment, a known volume of micellar solution of a particular R value containing SDS, 1-butanol, and water was taken in a sample tube and was placed in a thermostat (INSREF make) maintained at 25 ± 0.01 °C. Oil was added to this mixture in installments by using a calibrated Finn pipet. The contents were mixed thoroughly after each addition of oil and were allowed to attain the desired temperature before measuring the conductivity. The addition of oil was continued till the mixture exhibited opalescence.

Results and Discussion

The measured values of the specific conductivity, κ, of the MEs are presented in the form of plots of $(\kappa/\kappa_0)^{2/3}$ versus ϕ_0 (Figures 1−4). κ_0 and ϕ_0 denote the specific conductivity of the water + SDS + 1-butanol phase of a particular R value and the volume fraction of oil, respectively. The purpose of plotting $(\kappa/\kappa_0)^{2/3}$ versus ϕ_0 is discussed below.

The modified Bruggeman equation[1−3] for spherical droplets is of the form

$$(\kappa/\kappa_0)^{2/3} = (1 - f\phi_0) \qquad (1)$$

The value of the empirical parameter f is reported[2,3] to be >1 in o/w MEs stabilized by nonionic surfactants and is attributed to the hydration of the droplets. Only in the case of MEs containing unhydrated spherical droplets is f considered to be equal to 1. By plotting $(\kappa/\kappa_0)^{2/3}$ versus

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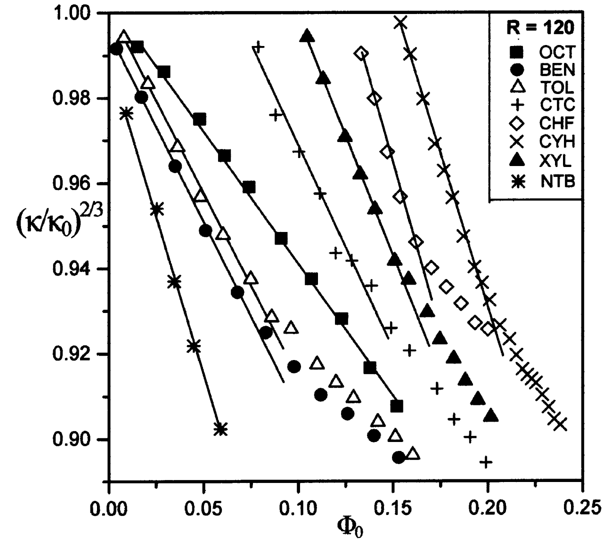

Figure 1. Variation of $(\kappa/\kappa_0)^{2/3}$ of microemulsions of $R = 120$ with Φ_0. The ordinate and abscissa scales are 0.89−1.0 and 0−0.25 for OCT (■), 0.895−1.0 and 0.015−0.275 for BEN (●), 0.89−1.0 and 0.01−0.275 for TOL (△), 0.88−1.01 and −0.1−0.275 for CTC (+), 0.90−1.0 and −0.25−0.25 for CHF (◇), 0.83−1.0 and −0.4−0.275 for CYH (×), 0.88−1.0 and −0.15−0.25 for XYL (▲), and 0.93−1.0 and 0.01−0.25 for NTB (∗), respectively.

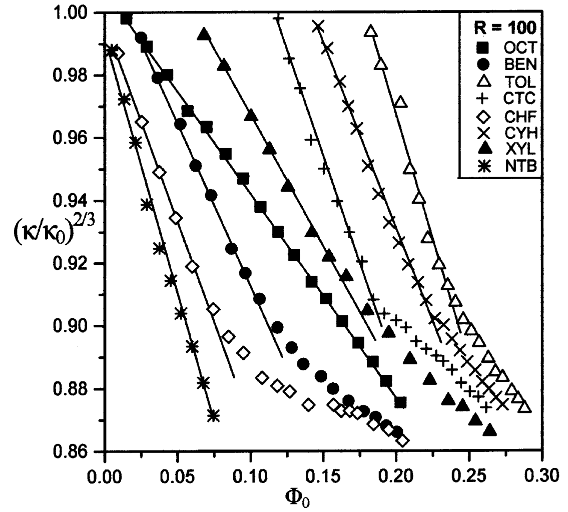

Figure 2. Variation of $(\kappa/\kappa_0)^{2/3}$ of microemulsions of $R = 100$ with Φ_0. The ordinate and abscissa scales are 0.86−1.00 and 0−0.3 for OCT (■), 0.85−1.0 and −0.01−0.35 for BEN (●), 0.84−1.0 and −0.15−0.35 for TOL (△), 0.825−1.00 and −0.35−0.35 for CTC (+), 0.89−1.00 and 0.01−0.35 for CHF (◇), 0.775−1.00 and −0.1−0.35 for CYH (×), 0.85−1.00 and 0.01−0.25 for XYL (▲), and 0.90−1.00 and 0.01−0.35 for NTB (∗), respectively.

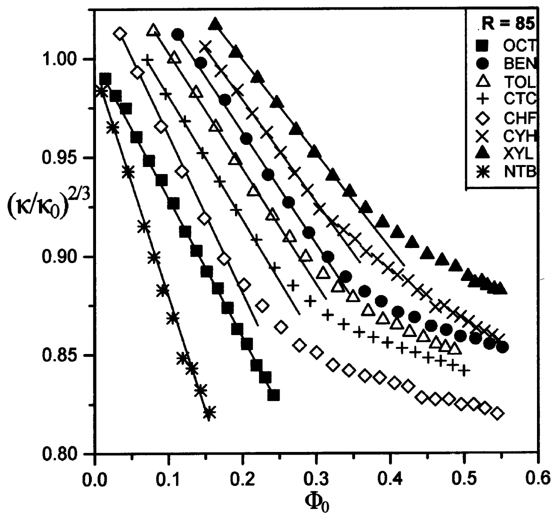

Figure 3. Variation of $(\kappa/\kappa_0)^{2/3}$ of microemulsions of $R = 85$ with Φ_0. The ordinate and abscissa scales are 0.8−1.025 and 0−0.6 for OCT (■), 0.75−1.0 and −0.04−0.3 for BEN (●), 0.75−1.0 and −0.025−0.35 for TOL (△), 0.73−1.025 and −0.025−0.4 for CTC (+), 0.83−1.00 and 0.0−0.35 for CHF (◇), 0.65−1.025 and −0.1−0.4 for CYH (×), 0.7−1.00 and −0.08−0.3 for XYL (▲), and 0.87−1.02 and 0.01−0.4 for NTB (∗), respectively.

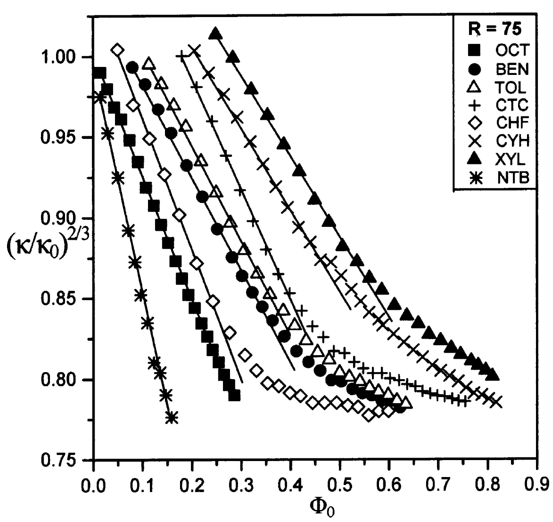

Figure 4. Variation of $(\kappa/\kappa_0)^{2/3}$ of microemulsions of $R = 75$ with Φ_0. The ordinate and abscissa scales are 0.75−1.025 and 0−0.9 for OCT (■), 0.725−1.025 and −0.02−0.45 for BEN (●), 0.725−1.025 and −0.04−0.45 for TOL (△), 0.7−1.025 and −0.08−0.45 for CTC (+), 0.775−1.00 and 0.0−0.5 for CHF (◇), 0.65−1.025 and −0.1−0.45 for CYH (×), 0.8−1.00 and −0.1−0.35 for XYL (▲), and 0.87−1.02 and 0.01−0.6 for NTB (∗), respectively.

ϕ_0, it is, therefore, possible to examine the applicability of eq 1 to the MEs under study.

From the viscosity study, some of the MEs under consideration are known[9] to be o/w type and to have spherical oil droplets. In view of this, an attempt has been made to analyze the κ data of all the MEs under study by using eq 1. In the case of MEs whose droplets are nonspherical, the fitting of κ data to eq 1 is of empirical nature only. From Figures 1−4, it is evident that in the case of MEs containing octane and nitrobenzene the plots of $(\kappa/\kappa_0)^{2/3}$ versus ϕ_0 are linear in the entire experimental range of ϕ_0 whereas in the other MEs deviation from linearity occurs at higher ϕ_0 values. Such a deviation from eq 1 at higher values of ϕ_0 was reported[3] to occur in o/w MEs stabilized by nonionic surfactants also. The upper limits of ϕ_0 up to which eq 1 is valid are denoted by ϕ_c, and its values for the different MEs are given in Table 1. The ϕ_c value increases as the R value of MEs decreases. The values of f for the different MEs of $R = 120$, 100, 85, and 75 were obtained by least-squares fitting the κ data lying in the range $\phi_0 \leq \phi_c$ to eq 1 and are listed in Table 1. Although a linear shape of the plots of $(\kappa/\kappa_0)^{2/3}$ versus ϕ_0 indicates the validity of eq 1 below ϕ_c, the values of f are found to be less than 1 in many of the MEs under study (Table 1). Bisal et al.[3] observed a value of f less than 1 only in some of the exceptional o/w MEs stabilized by Triton X-100 and hexylamine. The κ data of such exceptional o/w

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Table 1. Values of *f* Obtained from Equation 1 for Different MEs at Various *R* Values and at 25 °C[a]

system	R				R_1
	120	100	85	75	
OCT	0.614	0.640	0.707	0.753	
BEN	0.780 (0.083)	0.906 (0.091)	1.056 (0.138)	1.146 (0.167)	90.4
TOL	0.760 (0.087)	0.863 (0.123)	0.982 (0.138)	1.132 (0.138)	83.7
CTC	0.682 (0.107)	0.860 (0.138)	1.060 (0.145)	1.284 (0.138)	88.6
CHF	0.726 (0.057)	0.874 (0.074)	0.990 (0.099)	1.123 (0.130)	84.0
CYH	0.790 (0.123)	0.895 (0.091)	0.991 (0.152)	1.071 (0.167)	84.1
XYL	0.719 (0.091)	0.834 (0.115)	0.944 (0.138)	1.017 (0.167)	76.34
NTB	0.974	1.014	1.113	1.182	103.27

[a] The values of ϕ_c, which is the value of ϕ_0 up to which eq 1 holds good, are given in parentheses.

MEs were described by Bisal et al.[3] using the reduced form of the Maxwell equation which is given by

$$(\kappa/\kappa_0) = 2(1 - \phi_0)/(2 + \phi_0) \qquad (2)$$

Equation 2 can be derived by multiplying κ_0 by $(1 - \phi_0)$ and $1/(1 + \phi_0/2)$ in order to account for the dilution and obstruction effects, respectively,[10] on the conductance of an o/w ME due to the addition of an oil. Equation 2 is, however, found to be inadequate to explain the conductance behavior of the MEs under consideration.

On the basis of viscosity data, it has been observed[9] that in OCT, BEN, and TOL of $R = 85$ and 75 a phase transition from o/w to either bicontinuous or w/o ME takes place when ϕ_0 lies in the range of ~0.1−0.15. In the case of BEN and TOL, the values of ϕ_c estimated from Figures 3 and 4 are comparable to their ϕ_0 values at which phase transition is reported to take place.[9] It is, however, surprising to find that conductivity data are not so sensitive to the phase transition expected in MEs of $R = 85$ and 75.

From Table 1, the following inferences can be made: (i) The value of *f* for OCT is the lowest compared to other oils and remained less than 1 at all the four *R* values. (ii) When the oils used are substituted benzenes, the value of *f* depends on the nature and number of the substituents. (iii) The value of *f* increases as the *R* value decreases. From the plot of *f* versus *R* (Figure 5), the values of *R* where *f* becomes equal to 1 (denoted by R_1) are estimated for the different MEs, which indicates the dependence of the *f* value on the surfactant concentration in a ME. The above inferences suggest that the value of *f* is controlled by several factors. The hydration of the polar head of the surfactant depends on the structural parameters of the interfacial film of surfactant, which changes with the nature of the oil. For instance, penetration of oil into the hydrophobic region of the surfactant affects the area per polar head, which in turn affects its hydration. Thus, despite several factors affecting *f*, hydration may be considered to be the main factor which controls the value of *f*.

Although an attempt has been made above to explain the specific conductance data of o/w MEs in the light of eq 1 based on the effective medium theory, a more quantitative approach would be to determine the specific conductivity of such MEs from the additive contribution of their constituent ionic species. Such an attempt was recently made by Aveyard et al.[10] in o/w MEs stabilized by AOT. The o/w MEs under study are considered to consist of (i) monomeric dodecyl sulfate ions produced by the complete dissociation of SDS monomers having a concentration equal to the critical micelle concentration (cmc), (ii) charged droplets, and (iii) counterions released by the dissociation of SDS monomers and droplets. Therefore, κ of an o/w ME can be written as

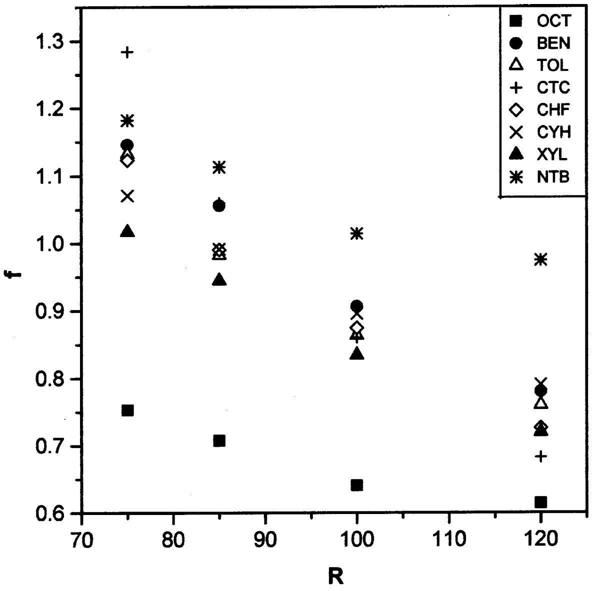

Figure 5. Variation of the *f* parameter of eq 1 as a function of *R*.

$$\kappa = \kappa_{DS} + \kappa_{Na} + \kappa_d = \lambda_{DS}c_{DS} + \lambda_{Na}c_{Na} + \lambda_d c_d \qquad (3)$$

κ_{DS}, κ_{Na}, and κ_d are the specific conductivities of the dodecyl sulfate ion (DS^-), sodium counterion (Na^+), and ionic droplets, respectively. λ and c terms refer to molar ionic conductivities and concentrations of the ionic species, respectively. By applying the mixed electrolyte model[4−8] to o/w MEs, the molar conductance of an ionic surfactant in a ME medium, Λ_{ME}, can be written as

$$\Lambda_{ME} = \Lambda_{mono}(c_0/c_t) + \Lambda_d(c_d/c_t) \qquad (4)$$

where Λ_{mono} is the molar conductance of the monomer and Λ_d is that of the droplet. c_0 is the cmc of the surfactant in the continuous medium, and c_t is the total concentration of the ionic surfactant in the ME. It has been approximated that the concentrations of DS^- and Na^+ ions obtained from the dissociation of monomers remain constant in the ME and are equal to c_0. c_d is estimated as

$$c_d = (c_t - c_0)/n \qquad (5)$$

where n is the number of surfactant molecules present in a droplet. Equation 4 can be written as

$$\Lambda_{ME} = [\lambda_{DS} + \lambda_{Na}](c_0/c_t) + [\lambda_d + \lambda_{Na}n(1 - \beta)](c_d/c_t) \qquad (6)$$

In the above eq 6, β is the counterion binding constant

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and $n(1-\beta)$ is the number of moles of Na^+ ion released by the dissociation of 1 mol of droplet. Since $\kappa = \Lambda_{\mathrm{ME}}c_{\mathrm{t}}$, we obtain an expression for κ as

$$\kappa = \lambda_{\mathrm{DS}}c_0 + \lambda_{\mathrm{Na}}[c_0 + c_{\mathrm{d}}n(1-\beta)] + \lambda_{\mathrm{d}}c_{\mathrm{d}} \tag{7}$$

Equation 7 is equivalent to eq 3. It is therefore clear that the mixed electrolyte model can be used in the case of o/w MEs also. Initially, before the addition of oil the system consists of SDS, butanol, and water. Applying the Debye–Hückel–Onsager approach to account for ion–ion or droplet–droplet interactions, the specific conductance, κ_0, of the ME with no oil can be written as

$$\kappa_0 = [\Lambda_1^0 - A_1I^{1/2}/(1 + B_0a_1)]c_0 + [\Lambda_{\mathrm{d}}^0 - A_{\mathrm{d}}I^{1/2}/(1 + B_0a_{\mathrm{d}})]c_{\mathrm{d}}n(1-\beta) \tag{8}$$

In eq 8, Λ_i^0 and a_i correspond to the limiting equivalent conductivities and effective sizes, respectively, of monomer ($i = 1$) and droplet ($i = \mathrm{d}$). I is the ionic strength, and the remaining terms of eq 8 are represented by the following relations:

$$B_0 = [8\pi N_{\mathrm{A}}e_0{}^2/(10^3\epsilon k_{\mathrm{B}}T)]^{1/2}\mathrm{I}^{1/2} \tag{9}$$

$$A_i = \{2.801 \times 10^6|z_+z_-|q\Lambda_i^0/[(\epsilon T)^{3/2}(1 + q^{1/2})]\} + \{41.25(|zz_+| + |z_-|)/[\eta(\epsilon T)^{1/2}]\} \tag{10}$$

$$q = [|z_+z_-|(\lambda_+^0 + \lambda_-^0)]/[(|z_+| + |z_-|)(|z_+\lambda_-^0| + |z_-\lambda_+^0|)] \tag{11}$$

In eq 9, k_{B} is the Boltzmann constant, T is the absolute temperature, N_{A} is the Avogadro number, e_0 is the electronic charge, and ϵ is the dielectric constant of the medium. In the expressions for A_i ($i = 1$ or d) and q, z_j and λ_j^0 refer to the effective charge and limiting equivalent conductivity of ionic ($j = +$ or $-$) species, respectively, and η is the viscosity of the dispersing medium. The added oil is considered to cause (i) swelling of the ionic micelles, (ii) dilution of the ME, and (iii) obstruction for the conductance of smaller ions. Since monomer concentration is assumed to have a constant value equal to c_0, dilution due to the added oil does not change c_0 value. On the other hand, due to dilution c_{t} will become $c_{\mathrm{t}}(1 - \phi_0)$ after the addition of oil. The expression for κ therefore becomes

$$\kappa = [\Lambda_1^0 - A_1I^{1/2}/(1 + B_0a_1)]c_0 + [\Lambda_{\mathrm{d}\phi}^0 - A_{\mathrm{d}\phi}I^{1/2}/(1 + B_0a_{\mathrm{d}\phi})]c_{\mathrm{d}\phi}n_\phi(1-\beta) \tag{12}$$

where $A_{\mathrm{d}\phi}$, $c_{\mathrm{d}\phi}$, $\Lambda_{\mathrm{d}\phi}^0$, n_ϕ, and $a_{\mathrm{d}\phi}$ are the values of A_{d}, c_{d}, Λ_{d}^0, n, and a_{d}, respectively, in the ME having volume fraction of oil $= \phi_0$. $c_{\mathrm{d}\phi}$ is determined from the relation

$$c_{\mathrm{d}\phi} = [c_{\mathrm{t}}(1 - \phi_0) - c_0]/n_\phi \tag{13}$$

During computation, the obstruction effect of the droplet on the conductivity of smaller ions (DS^- and Na^+) was taken into account in eq 12 in a manner similar to that reported by Aveyard et al.[10] 1-Butanol is reported[11,12] to have nearly 1 mol dm^{-3} solubility in water, and therefore in the continuous medium the concentration of butanol is taken to be equal to 1 mol dm^{-3}. The remaining amount of butanol is considered to be present in the droplet phase.[11,13,14] On the basis of the reported studies[8,15–17] on water + butanol + SDS systems, the values of c_0, Λ_1^0, and η of the continuous medium at 25 °C are taken to be 0.005 × 10^3 mol m^{-3}, 69 × 10^{-4} S m^2 equiv^{-1}, and 0.0011 Pa s, respectively. The dielectric constant of the water + butanol continuous medium at 25 °C was estimated to be 77.0 by using the additivity principle. The dielectric relaxation studies[18–21] carried out in the recent past on mixtures of water with methanol, ethanol, and 1-propanol have shown the presence of composition-dependent dynamical structures in these mixtures. In light of this, the method adopted here for estimating the dielectric constant of the water + butanol system is, no doubt, an approximate one. Therefore, there is scope for improving the fitting of conductivity data to the mixed electrolyte model if a better value of the dielectric constant of the water + butanol system is available. The limiting ionic conductivity of dodecyl sulfate ion, λ_{DS}^0, in the continuous medium containing water + butanol was estimated using the Stokes–Einstein equation

$$\lambda_i^0 = z_ie_0F/(6\pi\eta r_i) \tag{14}$$

To get the value of λ_{DS}^0 from eq 14, we substituted for the radius of the dodecyl sulfate ion (r_{DS}) the value calculated from the Tanford equation,[22]

$$r_{\mathrm{DS}} = [(3/4\pi)(27.4 + 26.9 \times 12)]^{1/3} \tag{15}$$

After λ_{DS}^0 was computed in this fashion, the value of the limiting ionic conductivity of sodium ion, λ_{Na}^0, in the dispersing phase was obtained as $\Lambda_1^0 - \lambda_{\mathrm{DS}}^0$. The radius of the counterion (r_{Na}) in the dispersing medium was calculated by substituting in turn the value of λ_{Na}^0 in eq 14. It is difficult to determine experimentally the radius of the droplet, r_{d}. Therefore, by presuming volume to be additive, we first calculated the volume of one droplet, v_{d}, as

$$v_{\mathrm{d}} = (27.4 + 26.9 \times 12)n_\phi + n_{\mathrm{cs}}v_{\mathrm{cs}} + \phi_0/n_{\mathrm{d}} \tag{16}$$

A mean radius for the droplet was then assigned by approximating the volume of the droplet to be spherical. Thus $r_{\mathrm{d}} = (3v_{\mathrm{d}}/4\pi)^{1/3}$. In eq 16, n_{cs} is the number of butanol molecules in a droplet, v_{cs} is the molecular volume of butanol, and n_{d} is the number of droplets per unit volume of ME. Deviation from eq 16 may arise depending upon the packing conditions of surfactant, cosurfactant, and oil in a droplet. λ_{d}^0 was calculated from eq 14 after substituting the value of r_{d} for r_i. The values of Λ_{d}^0, a_1, and a_{d} were obtained using the relations $\Lambda_{\mathrm{d}}^0 = \lambda_{\mathrm{d}}^0 + \lambda_{\mathrm{Na}}^0$, $a_1 = r_{\mathrm{DS}} + r_{\mathrm{Na}}$, and $a_{\mathrm{d}} = r_{\mathrm{d}} + r_{\mathrm{Na}}$. To compute the specific conductivity from eqs 8 and 12, it is required to feed the values of aggregation number n or n_ϕ, which is the number of surfactant molecules in a droplet, and the counterion binding constant, β. Moreover, the ionic strength has to

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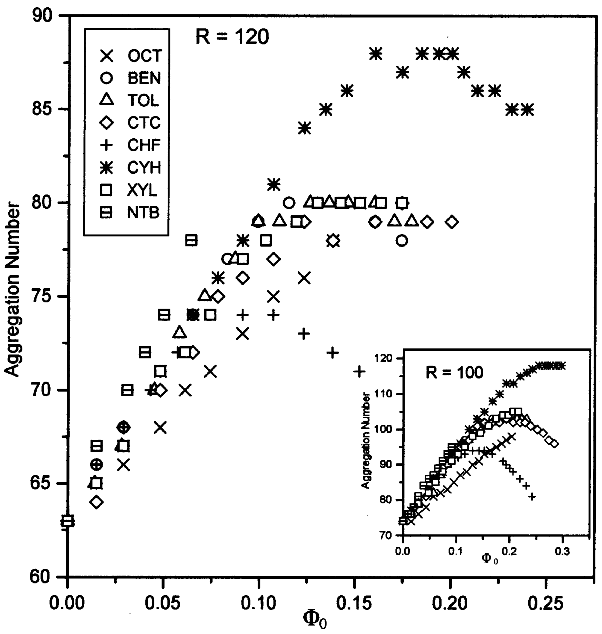

Figure 6. Computed values of the aggregation number of SDS in the different microemulsions as a function of the volume fraction of oil. The symbols used are the same for microemulsions of $R = 120$ and $R = 100$ (inset).

be calculated by an appropriate expression. Data fitting was done through an iteration program and by using any one of the four models for I reported in the earlier studies.[4,5] It was, however, found that none of the four models for I used earlier[4,5] was suitable for the data fitting. The data fitting was therefore made by estimating ionic strength from the relation

$$I = c_0 + c_d n_\phi(1 - \beta) \quad (17)$$

In this expression for I, the contribution to ionic strength from the ionic droplets has been included but by considering a droplet of charge $n_\phi(1 - \beta)$ as equivalent to $n_\phi(1 - \beta)$ monomers of unit charge. Such type of contribution to the ionic strength by ionic micelles was reported earlier by McBain and Searles.[25] Data fitting was first made by including the obstruction effect. The values of β and n_ϕ that gave best agreement between the experimental and calculated values of κ were chosen. The computed values of n_ϕ, λ_d^0, and r_d for the different MEs of $R = 120$ and 100 are presented in Figures 6–8, respectively. Values of n_ϕ, λ_d^0, and r_d for the MEs of $R = 120$ and 100 at some selected values of ϕ_0 are also given in Tables 2 and 3. In the case of MEs of both $R = 120$ and 100, with an increase in ϕ_0, λ_d^0 decreases in OCT, increases in NTB, and passes through a maximum in the remaining MEs (Figure 7).

The computed value of β was found to be 0.2 ± 0.1 in the case of all the MEs of $R = 120$ and 100. Decrease of β by the addition of butanol to surfactant solutions has been reported.[16,23,24] The study made by Lawrence and Pearson[23] had revealed that the value of β decreases as butanol concentration increases and attains an almost constant value equal to ~0.1 when butanol concentration becomes more than ~1.5 mol dm^{-3}. In the MEs of $R = 120$ and 100, the butanol concentration is >2.5 mol dm^{-3} and hence the value of $\beta = 0.2 \pm 0.1$ obtained from the present

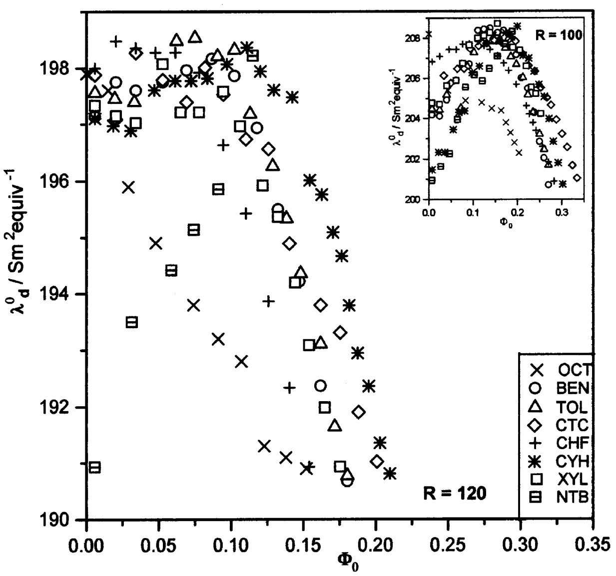

Figure 7. The limiting equivalent ionic conductivity of droplets of the different MEs as a function of the volume fraction of oil. The symbols used are the same for MEs of $R = 120$ and $R = 100$ (inset). The ordinate scales are 190–199 ($R = 120$) and 200–209 ($R = 100$) for OCT (×), 184–202 ($R = 120$) and 201–217 ($R = 100$) for BEN (○), 184–201 ($R = 120$) and 200–217 ($R = 100$) for TOL (△), 180–201 ($R = 120$) and 185–220 ($R = 100$) for CTC (◇), 178–201 ($R = 120$) and 175–220 ($R = 100$) for CHF (+), 181–203 ($R = 120$) and 201–220 ($R = 100$) for CYH (∗), 186–201 ($R = 120$) and 201–215 ($R = 100$) for XYL (□), and 197–206 ($R = 120$) and 207–219 ($R = 100$) for NTB (divided square), respectively; the abscissa scale is 0–0.35 for all MEs of $R = 120$ and 100 except for NTB in which case it is 0–0.2.

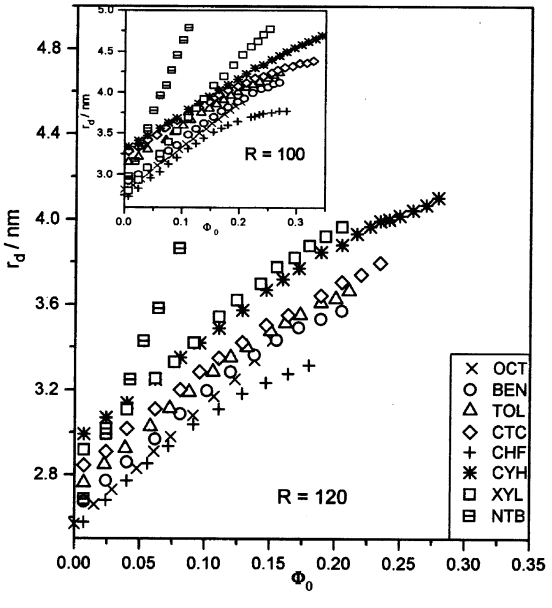

Figure 8. Radii of the droplets of the different MEs as a function of the volume fraction of oil. The symbols used are the same for MEs of $R = 120$ and 100 (inset). The ordinate scales are 2.5–5.0 ($R = 120$) and 2.6–5.0 ($R = 100$) for OCT (×), 2.4–5.0 ($R = 120$) and 2.5–5.0 ($R = 100$) for BEN (○), 2.3–5.0 ($R = 120$) and 2.2–5.0 ($R = 100$) for TOL (△), 2.2–5.0 ($R = 120$) and 2.0–5.0 ($R = 100$) for CTC (◇), 2.5–5.0 ($R = 120$) and 2.7–5.0 ($R = 100$) for CHF (+), 2.0–5.0 ($R = 120$) and 1.9–5.0 ($R = 100$) for CYH (∗), 2.2–4.5 ($R = 120$) and 2.7–4.2 ($R = 100$) for XYL (□), and 2.5–3.5 ($R = 120$) and 2.7–3.5 ($R = 100$) for NTB (divided square), respectively; the abscissa scale is 0–0.35 for all MEs of $R = 120$ and 100.

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Table 2. Computed Values of n_ϕ, λ_d^0 (S m^2 equiv^{-1}), and r_d (nm) for the Different Microemulsions of $R = 120$ at Some Selected Values of ϕ_0 and 25 °C[a]

parameter	OCT	BEN	TOL	CTC	CHF	CYH	XYL	NTB
ϕ_0	0.015	0.015	0.014	0.015	0.015	0.015	0.015	0.015
$n_\phi \pm 2$	63	66	65	64	66	65	65	67
$10^4\lambda_d^0$	197.9	199.1	197.7	196.1	199.1	197.6	197.6	200.4
r_d	2.57	2.67	2.66	2.64	2.67	2.66	2.66	2.69
ϕ_0	0.048	0.048	0.045	0.048	0.043	0.048	0.048	0.031
$n_\phi \pm 2$	68	71	70	70	70	71	71	70
$10^4\lambda_d^0$	194.9	199.1	198.1	197.7	198.6	199.1	199.1	201.3
r_d	2.83	2.87	2.85	2.86	2.84	2.87	2.87	2.79
ϕ_0	0.123	0.145	0.146	0.160	0.123	0.200	0.152	0.050
$n_\phi \pm 2$	76	80	80	79	73	88	80	74
$10^4\lambda_d^0$	191.3	192.2	192.0	188.6	187.6	192.1	191.0	202.7
r_d	3.25	3.40	3.40	3.44	3.21	3.74	3.43	2.92
ϕ_0	0.152	0.174	0.179	0.200	0.152	0.239	0.174	0.064
$n_\phi \pm 2$	80	78	79	79	71	85	80	78
$10^4\lambda_d^0$	190.9	185.3	185.4	182.3	180.3	182.9	187.5	205.0
r_d	3.43	3.48	3.52	3.61	3.29	3.87	3.51	3.03

[a] $\beta = 0.2 \pm 0.1$ and at $\phi_0 = 0$, $n_\phi = 63 \pm 2$, $10^4\lambda_d^0 = 197.9$, and $r_d = 2.57$.

Table 3. Computed Values of n_ϕ, λ_d^0 (S m^2 equiv^{-1}), and r_d (nm) for the Different Microemulsions of $R = 100$ at Some Selected Values of ϕ_0 and 25 °C[a]

parameter	OCT	BEN	TOL	CTC	CHF	CYH	XYL	NTB
ϕ_0	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.010
$n_\phi \pm 2$	74	76	76	75	77	77	76	76
$10^4\lambda_d^0$	205.4	208.1	208.1	206.8	209.5	209.5	208.1	209.1
r_d	2.87	2.90	2.89	2.88	2.91	2.91	2.90	2.88
ϕ_0	0.107	0.103	0.111	0.107	0.103	0.107	0.103	0.048
$n_\phi \pm 2$	87	95	96	95	92	96	93	86
$10^4\lambda_d^0$	205.6	215.6	215.3	214.9	212.1	216.0	213.3	215.0
r_d	3.37	3.46	3.50	3.47	3.42	3.48	3.43	3.14
ϕ_0	0.152	0.177	0.180	0.206	0.152	0.206	0.160	0.065
$n_\phi \pm 2$	93	103	103	102	94	113	101	89
$10^4\lambda_d^0$	205.0	211.4	211.1	205.9	206.1	216.8	212.4	215.4
r_d	3.62	3.84	3.85	3.94	3.63	4.08	3.75	3.24
ϕ_0	0.203	0.231	0.231	0.283	0.242	0.296	0.216	0.091
$n_\phi \pm 2$	98	102	103	96	81	118	105	95
$10^4\lambda_d^0$	202.3	202.2	203.1	188.9	179.3	207.1	207.4	217.8
r_d	3.88	4.04	4.06	4.17	3.79	4.53	4.02	3.41

[a] $\beta = 0.2 \pm 0.1$ and at $\phi_0 = 0$, $n_\phi = 74 \pm 2$, $10^4\lambda_d^0 = 208.2$, and $r_d = 2.82$.

data fitting is close to the experimental value reported by Lawrence and Pearson.[23]

The values of n obtained in the case of MEs of $R = 120$ ($n = 63 \pm 2$) and 100 ($n = 74 \pm 2$) for $\phi_0 = 0$, that is, for the water + butanol + SDS system, are in good agreement with the values measured by Almgren and Swarup[26] using the steady-state fluorescence quenching method. Furthermore, the n_ϕ values obtained from the present data fitting for OCT, BEN, and TOL of $R = 120$ and 100 at the maximum ϕ_0 are comparable to those estimated from their viscosity data.[9] The increase in n_ϕ with an increase in ϕ_0 is in accordance with the observation made by Zana.[27] However, in the region of $\phi_0 > \phi_c$ the value of n_ϕ either remains almost constant or tends to decrease. The values of n_ϕ obtained by excluding the obstruction effect were found to be generally more by about 10 than that shown in Figure 6 (Tables 2 and 3).

The analysis of conductivity data in the above fashion using the mixed electrolyte model has been done here only for MEs of $R = 120$ and 100. Such an analysis of the κ data of MEs of $R = 85$ and 75 has not been done because of the possibility of phase change in these MEs. Furthermore, in MEs of $R = 120$ and 100 we made an attempt to account for the interdroplet interactions using an interaction parameter, α, instead of the Debye−Hückel−Onsager treatment as reported by Aveyard et al.[10] This was done by writing the conductivity of the droplet as

$$\lambda_d = \lambda_d^0(1 + \alpha\phi_0) \qquad (18)$$

where λ_d^0 was obtained from eq 14. Aveyard et al.[10] found that in a heptane−AOT−water (NaCl solution) o/w ME the conductivity data could be explained satisfactorily by using the Debye−Hückel−Onsager treatment to account for ion−ion interactions of smaller ions and eq 18 with $\alpha = 55$ to account for interdroplet interactions. However, in the MEs of $R = 120$ and 100 which are being investigated here eq 18 failed and only the Debye−Hückel−Onsager treatment is found to be suitable to account for both ion−ion interactions of smaller ions and interdroplet interactions.

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