

Nonmonotonic Electric Conductivity by Alkyl-chain Variation of an Ionic Additive in Percolated Nonionic W/O-Microemulsions

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Sparsely distributed ionic surfactants (sodium *n*-alkyl sulfonates) with varying alkyl chains in a nonionic ($C_{14}E_5$) w/o-microemulsion were studied. A nonmonotonic electrical conductivity as a function of chain length has been observed at the critical percolation temperature of the system. A model is proposed that assumes a mutually affecting chain length dependence of the degree of dissociation of the ionic surfactants and of its solubility in the hydrocarbon medium. The calculated plots are in reasonable agreement with the experimental data.

Introduction

Charge transport in thermodynamically stable water-in-oil (w/o) microemulsions stabilized by ionic or mixtures of ionic and nonionic surfactants at the critical percolation limit and sufficiently far away from this limit have been frequently studied.^{1–5} In the former case, fractal properties of ramified clusters dominate the transport properties, whereas in those systems sufficiently far away from the percolation limit (i.e., in the percolated state), the aqueous nanometer sized droplets are expected to form a nonfractal, three-dimensional network suspended in an oil continuum. The properties of these latter materials have been the subject of theoretical and experimental investigations for more than a century. Landauer⁶ has given a comprehensive review of this development.

In this investigation, we suppose that equilibrium properties of the sparsely added ionic surfactant to an otherwise nonionic w/o microemulsion, i.e., dissociation and distribution equilibria of the ionic surfactant in the apolar inter-droplet regions (see Figure 1), are essential.

The experimental conductivity plots show a curious pattern, that is, a nonmonotonic dependence on the chain length of sodium *n*-alkyl sulfonate, which was added to a nonionic ($C_{14}E_5$) w/o microemulsion. The plots pass through maxima, the positions of which are slightly controlled by the dielectric dispersion medium. The same behavior is observed if the critical percolation temperature has been plotted against the chain length of the *n* alkyl sulfonate.⁷

Materials and Measurements

Nonionic w/o microemulsions were prepared from pentaethylene glycol tetradecyl ether, $C_{14}E_5(s)$, purity > 98% GC. The weight fraction was chosen as $(w + s)/(w + s + o) = 0.256$, $r_w = w/s = 1$ throughout this study, which determines the concentration of the aqueous nanodroplets in oil and their sizes. Univalent ionic surfactants, that is, sodium salts of *n*-alkyl sulfonic acids $H(-CH_2-)_nSO_3^- Na^+$, $1 \leq n \leq 18$, were added to the microemulsion to yield a 3×10^{-3} molar solution (about 5 electrolyte molecules/nanodroplet). All electrolytes and iso-octane, *n*-octane, and *n*-decane were of highest purity and obtained from Fluka. The water was deionized and distilled twice.

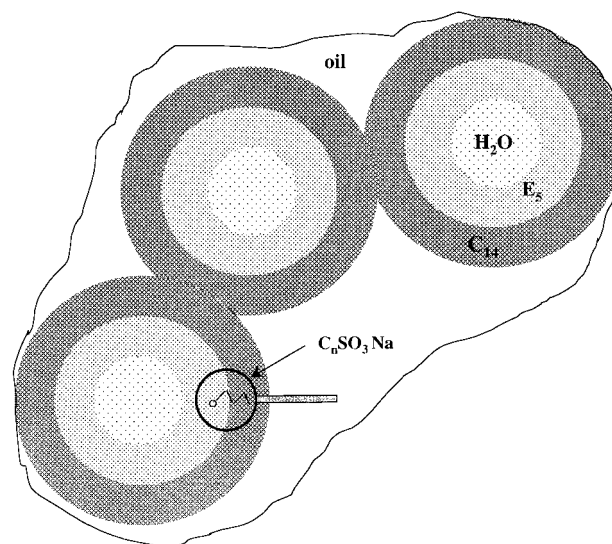


Figure 1. Part of aqueous nanodroplet cluster with overlapping C_{14} (=tetradecyl) regions; E_5 = penta-ethylene glycol; and C_nSO_3Na = sodium *n*-alkyl sulfonate.

Measurements of the electrical conductivity (σ) were carried out in a hermetically sealed plate condenser-type glass cell with two rectangular Pt electrodes of 5×10 mm and a gap width of 2 mm. The cell was also be equipped with a magnetic stirrer to avoid temperature gradients. It was immersed in a temperature bath, which could be adjusted to within ± 0.04 K. An auto-balancing ac bridge (Radiometer Copenhagen, CDM83), which operates at 73 Hz and 50 kHz to reach maximal sensitivity between 2×10^{-8} and 1.3 S, determined the conductance of the sample. These frequencies are outside the Maxwell–Wagner frequency $\sigma/\epsilon\epsilon_0$ of the studied systems.

The inflection points of the temperature-dependent conductivity plots were taken to indicate the percolation temperature T_c . The experimental error of this determination is estimated to stay below 0.1 K on the average.

Results and Discussion

Sodium monoalkyl sulfonates with varying chain length from C_1 to C_{18} were added to the nonionic w/o microemulsion at

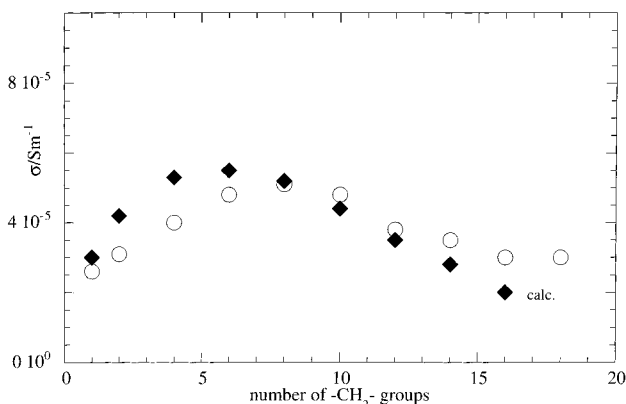


Figure 2. Electrical conductivity of a nonionic/ionic w/o microemulsion against n -alkyl chain length ($\infty(-\text{CH}_2-)_n$) of an ionic surfactant: water/ C_{14}E_5 , $H(-\text{CH}_2-)_n\text{SO}_3\text{Na}/i$ -octane, $T_{c,\text{max}} = 306$ K. Open circles = experimental points, filled diamonds = calculated according to eqs 15 and 16.

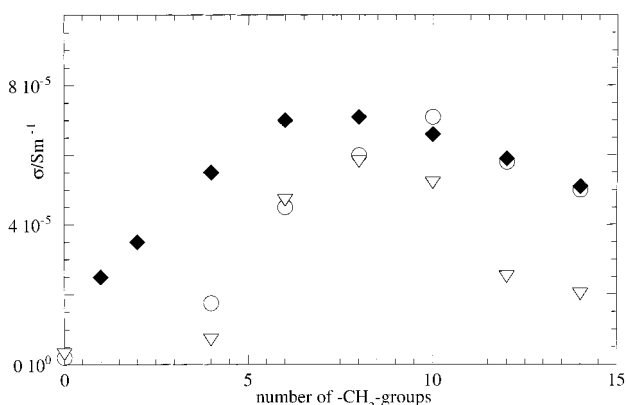


Figure 3. Electrical conductivities of a nonionic/ionic w/o microemulsion against n -alkyl chain length ($\infty(-\text{CH}_2-)_n$) of the ionic surfactant: water/ C_{14}E_5 , $H(-\text{CH}_2-)_n\text{SO}_3\text{Na}/n$ -octane (or n -decane), $T_{c,\text{max}} \approx 311$ K. Open circles = system in n -octane, open triangles = system in n -decane; filled diamonds = calculated points according to eqs 15 and 16.

constant ratio of $H(-\text{CH}_2-)_n\text{SO}_3^-\text{Na}^+$ and C_{14}E_5 molecules. The percolation temperature passes through a maximum⁷ as does the conductivity at the threshold indicating two opposing effects, which govern the aggregation processes of the nanodroplets.

Figure 2 shows the electrical conductivity of n -alkyl sulfonates against the alkyl chain length at the percolation temperature of water/ C_{14}E_5 , $H(-\text{CH}_2-)_n\text{SO}_3^-\text{Na}^+ /i$ sooctane w/o microemulsions containing 3×10^{-3} molar sulfonates. The slightly asymmetric plot passes through a maximum at C_6 – C_8 if isooctane is the dispersion medium. With further increase of the chain length, the conductivity drops to lower values and seems to become constant at and beyond C_{16} . Replacing isooctane by n -octane or n -decane keeping the composition of the microemulsion otherwise constant shifts the maxima toward larger tail lengths of the alkyl sulfonates (Figure 3).

As already mentioned in the Introduction, the following discussion is concerned with the formation of charges, that is, the dissociation of the ionic surfactants in the w/o (C_{14}E_5 -covered) interface. No detailed information on the structure is required. The mobility of the individual aqueous nanodroplets is not considered because Stokes transport of the droplets is not relevant.⁷

We thus assume equilibrium between the water/oil interface and the oil phase with regard to the exchangeable ionic species, that is, the anions (n -alkyl sulfonates). Accordingly, we equate

the electrochemical potentials of the anion in both phases

$$\eta_a^{\text{intf}} = \eta_a^{\text{oil}} \quad (1)$$

Equation 1 is explicitly written, that is

$$-e_o\varphi^{\text{intf}} + \mu_a^{\circ,\text{intf}} + k_B T \ln c_a^{\text{intf}} = -e_o\varphi^{\text{oil}} + \mu_a^{\circ,\text{oil}} + k_B T \ln c_a^{\text{oil}} \quad (1a)$$

where e_o are the elementary charge, $\mu_a^{\circ,\text{intf}}$, $\mu_a^{\circ,\text{oil}}$ the standard potentials of the anion in the respective states, c_a^{intf} , c_a^{oil} the anion concentrations at the interface and in the oil phase, and φ^{intf} , and φ^{oil} the electrical potentials of the interface and oil phases. From eq 1a one obtains

$$c_a^{\text{oil}} = c_a^{\text{intf}} \exp\left\{-\frac{e_o\Delta\varphi + \Delta\mu_a^{\circ}}{k_B T}\right\} \quad (2)$$

c_a^{intf} is in particular the anion concentration in the oil at zero charge of the nanodroplet and $\Delta\mu_a^{\circ} = 0$. The latter term is the standard free energy of transfer of an anion from the interface into the oil phase.

Generally, $c_a^{\text{intf}} = \alpha c_{\text{io}}^{\text{intf}}(n)$ is the exchangeable anion concentration in the w/o interface of the nanodroplets. α is the degree of dissociation of the ionic surfactants. $c_{\text{io}}^{\text{intf}}(n)$ is part of the ionic surfactant, which is—chain length-dependent—adsorbed in the w/o interface. The latter can be related to the total weighed-in amount of the ionic surfactant via mass balance and equilibrium distribution of the ionic surfactant between the w/o interface and the oil phase. Thus, from the equilibrium condition

$$\mu_{\text{io}}^{\text{intf}} = \mu_{\text{io}}^{\text{oil}} \quad (3)$$

one obtains the ratio of the equilibrium concentrations of the ionic surfactant in the oil phase and the w/o interface, that is

$$\frac{c_{\text{io}}^{\text{oil}}}{c_{\text{io}}^{\text{intf}}} = \exp\left\{-\frac{\mu_{\text{io}}^{\circ,\text{oil}}(n) - \mu_{\text{io}}^{\circ,\text{intf}}(n)}{k_B T}\right\} \quad (4)$$

The standard states of the chemical potentials μ_{io}° of the ionic surfactant are chain length-dependent. In accordance with other authors,^{7,8} it is assumed that $\mu_{\text{io}}^{\circ,\text{oil}}/k_B T = a - bn$ and $\mu_{\text{io}}^{\circ,\text{intf}}/k_B T = cn$; that is, $\mu_{\text{io}}^{\circ,\text{oil}}$ decreases with increasing chain length, whereas $\mu_{\text{io}}^{\circ,\text{intf}}$ increases with chain length. $-\Delta\mu_{\text{io}}^{\circ}/k_B T$ (eq 4) may then be expressed by $-a + dn$ ($d = b + c$), where a and d are considered as free parameters to fit the experimental data. They are related to the properties of the hydrocarbon medium and the solubility of the ionic surfactant in this environment.

Equation 4 will now be combined with the mass balance, that is

$$c_{\text{io}}^{\text{intf}} = c_{\text{io}}^{\text{tot}} - c_{\text{io}}^{\text{oil}} \quad (5)$$

to yield

$$c_{\text{io}}^{\text{intf}} = \frac{c_{\text{io}}^{\text{tot}}}{1 + \exp\left\{-\frac{\Delta\mu_{\text{io}}^{\circ}(n)}{k_B T}\right\}} \quad (6)$$

From eqs 6 and 2, we derive the anion concentration in the oil phase, the most relevant quantity to model the electrical

conductivity of the system. Hence

$$c_a^{\text{oil}} = \frac{\alpha c_{\text{io}}^{\text{tot}}}{1 + \exp\left\{-\frac{\Delta\mu_{\text{io}}^{\text{o}}(n)}{k_B T}\right\}} \exp\left[-\frac{e_o \Delta\varphi + \Delta\mu_a^{\text{o}}}{k_B T}\right] \quad (7)$$

$\Delta\varphi$ is related with the charge of the nanodroplet by

$$\Delta\varphi = q/4\pi\epsilon_o\epsilon r_{\text{nd}} \quad (8)$$

where q is equal to the negative value of the space charge around each nanodroplet with radius r_{nd} ; $\epsilon_o\epsilon$ in the absolute dielectric constant of the nanodroplet. This space charge corresponds to the (average) anion concentration in the oil phase. Since the ion concentration in the oil is very small only average values of the concentration have to be considered.¹⁰ For the same reason, it appears justified to attach to $\Delta\varphi$ a mean value. $\Delta\mu_a^{\text{o}}$ will be neglected with respect to the first term in the nominator. It turned out that this exponential is rather close to 1 under the prevailing experimental conditions (i.e., very low ion concentration in oil).

What remains is to find a quantitative expression to evaluate the degree of dissociation (α) to calculate the anion concentration in the oil phase. This may be achieved by the ideal lattice gas model,¹² which is applied to the scattered ionic surfactants in the w/o interface in equilibrium with the oil phase. Two subsystems, that is, the nonionic w/o interface of the nanodroplets with few scattered ionic surfactants at fixed sites and an ideal gas of ions (the dissociation products) in a volume V are considered to describe the dissociation equilibrium of the above system.

One assumes, accordingly, an ideal 2-dimensional lattice gas consisting of ν ionic surfactant molecules bound to fixed sites (in the interface) of which ξ are dissociated, that is

$$Z_1(\nu, \xi, T) = \frac{\nu!}{\nu!(\nu - \xi)!} \exp\left[-\frac{\xi \Delta\epsilon}{k_B T}\right] \quad (9)$$

where $\Delta\epsilon$ is the energy of dissociation, and T is the temperature of the system. From the partition function one finds, considering Stirlings' approximation in the thermodynamic limit and the degree of dissociation $\alpha = \xi/\nu$

$$F_1 = \nu(\alpha \Delta\epsilon + k_B T(\alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha))) \quad (10)$$

The other subsystem, which is in equilibrium with the lattice gas, consists of ξ ions in the volume V at temperature T , hence

$$Z_2(\xi, V, T) = \frac{1}{\xi!} \left[\frac{V}{\lambda^3}\right]^\xi \quad (11)$$

where $\lambda = h/(2\pi m k_B T)^{1/2}$; h is Planck's constant, and m is the mass of an ionic surfactant molecule.

From eq 11, we obtain by applying again Stirlings' approximation and introducing the degree of dissociation, that is

$$F_2 = \alpha \nu k_B T \left[-\ln \frac{V}{\xi \lambda^3} + \ln \alpha - 1 \right] \quad (12)$$

Equilibrium of the two subsystems demands $F_1 + F_2 = \min(\alpha)$, that is

$$\Delta\epsilon + k_B T \left(\ln \alpha - \ln(1 - \alpha) - k_B T \ln \frac{V}{\nu \lambda^3} + k_B T \ln \alpha \right) = 0 \quad (13)$$

or,

$$\ln \frac{\alpha^2}{1 - \alpha} = -\frac{\Delta\epsilon - k_B T \ln \frac{V}{\nu \lambda^3}}{k_B T} \quad (14)$$

If $\alpha \ll 1$ eq 14 can be approximated by

$$\alpha \approx \exp(-\Delta\epsilon/2k_B T) \sqrt{\frac{V}{\nu}} \frac{(2\pi m_{\text{CH}_2} k_B T)^{3/4}}{h^{3/2}} n^{3/4} \quad (14a)$$

Equation 14a involves a further approximation. The mass of the ionic surfactant is $m_{\text{polar head}} + n m_{\text{CH}_2}$. The first constant term has been neglected. This approximation improves with increasing number of $-\text{CH}_2-$ groups. Taking this for granted eq 14a shows that the degree of dissociation grows as a power law of the number of $-\text{CH}_2-$ groups.

To conform to the low experimental conductivity, the degree of dissociation has to be rather small (considering all other contributions from anion mobility and weighed-in concentration). Such a small value of α demands a large energy of activation ($\Delta\epsilon$) and, regarding solely electrostatic interactions, thus a small dielectric constant of the interfacial region where the ionic surfactants are accumulated. Such a physical situation has been discussed in ref 7 referring to the same nonionic w/o microemulsion. The pentaethylene oxide moiety of C_{14}E_5 in the aqueous nanodroplets forms a medium of low dielectric constant (about 10–15), in which the polar parts of the ionic surfactants are imbedded. Inserting eq 14a into eq 7 allows one, finally, to calculate the anion concentration in the hydrocarbon phase. Thus

$$c_a^{\text{oil}} \cong \frac{\text{const } c_{\text{io}}^{\text{tot}} n^{3/4}}{1 + e^{-a+dn}} \quad (15)$$

where

$$\text{const} = \exp(-\Delta\epsilon/k_B T) \sqrt{(V/\nu)} (2\pi m_{\text{CH}_2} k_B T)^{3/4} h^{3/2} \exp\{- (e_o \Delta\varphi + \Delta\mu_a^{\text{o}})/k_B T\}$$

A comparison with experimental data can now be made by explicitly calculating the electrical conductivity, that is

$$\sigma = c_a^{\text{oil}} u_a F \quad (16)$$

where F is the Faraday constant, and $u_a = e_o/6\pi\eta r_a$ is the mobility of the anions with radius r_a . The viscosity η is taken from literature data¹³ and estimated to be about 4×10^{-2} Pa s. According to Träuble and Sackmann,¹⁴ steroid molecules possess low diffusion coefficients ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$) in phospholipid bilayers. Considerably larger diffusion coefficients are reported for small anions. This will be all the more true in bilayerlike lamellar crystalline phases with shorter chain length (C_{14}). The bilayers, which are here considered have shorter chain length but are interdigitated (if two nano-droplets approach each other) with a consequently considerable resistance regarding diffusion.

The plots (see Figures 2 and 3) can reasonably be fitted by suitably selected materials parameters a and d to show the typical features of the experimental plots in the range of chain lengths studied.

As seen from the Figures, the calculated chain length-dependent electrical conductivity can be satisfactorily fitted to the experimental plots (Figures 2 and 3). In view of the approximations involved, particularly at small chain lengths and the range of the experimental data, the agreement is adequate.

As already mentioned, the experimentally observed solvent dependence could only be considered by empirical parameters.

Conclusion

It is shown that a model assuming a molecular weight (\propto chain length) dependent dissociation and oil solubility of a sparsely added ionic surfactant to an otherwise nonionic w/o microemulsion in the percolated state may result in nonmonotonic electrical conductivity plots against *n*-alkyl chain length.

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