ELSEVIER

Biophysical Chemistry 58 (1996) 29–37

Biophysical Chemistry

Interfacial charge transport in water-in-oil microemulsions stabilized by ionic–non-ionic surfactant mixtures

Hans-Friedrich Eicke *, Wolfgang Meier

Institut für Physikalische Chemie, Dept. Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Received 14 November 1994; revised 14 March 1995; accepted 28 March 1995

Abstract

Interfacial charge transport and mobility have been studied in system-spanning nanodroplet clusters formed in water-in-oil microemulsions stabilized by non-ionic–ionic surfactant mixtures. An unexpectedly large reduction in the counterion mobility was derived from a two-step adsorption process which described the Langmuir-plot-like conductivity isotherm remarkably well. It also conformed very satisfactorily to mobility data of the sodium bis-2-ethylhexylsulfosuccinate (AOT) counterion derived from frequency-dependent dielectric dispersion measurements with singly dispersed nanodroplets of the same system as used with the cluster studies. The activation energy attributed to the counterion mobility allowed one to calculate approximately the minimum distance between the (positive) counterion in the bulk and the surfactant anion in the interface.

Keywords: Water-in-oil microemulsions; Interfacial charge transport; Surfactants; Nanodroplets; Ion mobility

1. Introduction

Water-in-oil or oil-in-water microemulsions, i.e., thermodynamically stable mixtures of oil, water and surfactants, are discriminated according to their major component (*w*ater or *o*il). They are isotropic and homogeneous on a macroscopic scale but heterogeneous on a molecular scale as they are divided into water and oil domains separated by a surfactant monolayer. Their structure depends crucially on the water to oil ratio. For high oil or water content, nanometre-sized droplets form which appear conceptually simple and, hence, have found widespread applications as models in all branches of natural sciences. A spherical nanometer-sized water or brine droplet of a w/o microemulsion covered by a monolayer of ionic or non-ionic lipids might be viewed as a crude model of a primitive cell. Such model depends, of course, on the properties to be studied. In the case of charge and potential distributions, such primitive models proved indeed valuable. A considerable bulk of literature exists on hydrophobic particles in aqueous environment stabilized by electric double layers [1]. The opposite case, i.e., water-in-oil dispersions, has received much less attention which might be partly due to more intrinsic experimental difficulties [2]. Here one has to realize that all ions are confined to the nanodroplet, where we now

---

* Corresponding author.

SSDI 0301-4622(95)00083-6

distinguish bulk (the aqueous phase) and interface with the accumulated lipids.

From simple physical arguments, one has to conclude that the counterions (of the lipid ions residing in the oil/water interface) are expelled from the aqueous (dispersed) phase by virtue of their charges with equal signs. Since this phase can be made practically to contain no other ions, it can be considered to be homogeneous. One expects, therefore, a compressed electrical double layer in the interface with virtually no ion exchange between the aqueous and oil phases. If charges accumulate in the oil/water interface, surface conduction may be anticipated. Thus one of the questions to be addressed refers to how physical properties change in passing from bulk to surface conductance in these systems.

It is interesting to note that an analogous physical situation has been considered by Schwarz [3] with regard to charged latex particles dispersed in an aqueous electrolyte. This theoretical model explained the experimental data of Schwan et al. [4] on polystyrene spheres in KCl solutions remarkably well by assuming that the interfacial charges cannot exchange with those in the bulk of the solution. In other words, a tightly bound ionic double layer has been considered which was, however, criticized later on in the literature for being ad hoc [5]. Instead, in more recent theoretical treatments [5–7], the Gouy–Chapman, i.e., the diffuse double layer model, has been favored. The thin double layer approximation [5], $\delta \ll R, \delta$ being the thickness of the double layer and R the radius of the spherical particle, emerged from this latter treatment. Characteristically, the relaxation time of the polarization is now controlled by the bulk diffusion coefficient of the ions, while in Schwarz' model it describes the time needed for the charges to diffuse along the surface over the size of the particle. Other advances beyond that of the bound double layer model may be found in the literature [5].

In spite of these improvements which present – at least conceptually – an important progress for aqueous dispersions, we have good reasons to believe that oil continuous dispersions may form an example where the (relative crude) assumptions of Schwarz' theory are reasonably fulfilled.

We want to show that electric conductivity measurements at the onset of the system-spanning nanodroplet clusters and within the singly dispersed nanodroplet regime can be interpreted consistently by assuming interfacial conductivity within a strongly compressed interfacial electric double layer.

2. Experimental

2.1. Materials

Ionic surfactant, AOT (sodium bis-2-ethylhexylsulfosuccinate, > 99%), non-ionic surfactant, pentaethyleneglycol monododecylether, i.e., $C_{12}E_5$ (> 98% GC), *n*-octane (pract.), and deionized, twice distilled water were used. All chemicals were obtained from Fluka.

2.2. Phase diagrams

Samples were equilibrated while being stirred in a water bath, which was thermostated within 0.02 K. Phase separation took place between minutes and hours. In all cases lyotropic liquid crystals, identified by cross-polarizers, were formed. The concentration unit is the mass fraction of water (w) and surfactant (s) and oil (o), i.e. $c_w = (w+s)/(w+s+o)$. The size of the nanodroplets (generally the characteristic correlation length of the system) is controlled by $r_w = w/s$. $r_w = 1$ and $c_w = 0.256$ are used in this work if not otherwise stated.

2.3. Conductivity measurements

Conductivity measurements were carried out with a plate condenser type glass cell, with two rectangular Pt electrodes of 5 × 10 mm and a gap width of 2 mm. Conductance was determined by an auto-balancing conductance bridge (Radiometer, Copenhagen, instrument type CDM 83) between 1.3 S and 2×10^{-8} S and 73 Hz and 50 kHz. The frequency-dependent impedance measurements were made with a Hewlett-Packard HP 4192 A Impedance Analyzer in the frequency range $10–1.3 \times 10^7$ Hz. A thermostated measuring cell was specially constructed to fit the characteristic parameters of the HP 4192 A instrument by Drs. H. Meier and F.A. Sauer, MPI für Biophysik, Frankfurt/M.

The inflection point positions of the conductivity plots of the system-spanning nanodroplet clusters were obtained by evaluating the first and second derivative of the experimental data via standard computational procedures. Verification with geometric inflection point determinations confirmed the remarkable accuracy of the evaluated data. The main uncertainty of the experimental data evolves from the temperature-dependent solubility of the surfactants.

3. Results and discussion

The study of oil/water interfaces is advantageously and conveniently carried out in thermodynamically stable emulsions. In case of conductivity measurements, which are to trace charge transport in the interface, a system-spanning nanodroplet cluster of such an emulsion has to be studied. This state can either consist of an infinite cluster of nanometre-sized droplets or of bicontinuous paths of oil and water spanning the whole cluster [8]. We are concerned with droplet clusters and singly dispersed droplets if low-frequency dielectric measurements are carried out.

We have stabilized our emulsions by a mixture of non-ionic and ionic surfactants keeping the total oil/water interface constant. The charge density could be adjusted by changing the composition of the interface. This was feasible because the surface area per surfactant was approximately the same for both surfactant types used in this investigation. In case of droplet size variation the charge density was kept constant. The ionic surfactant was the sole charge source in the system, i.e. ionic impurities could be kept at an arbitrary low level.

Specific conductivities (σ) at the system-spanning cluster threshold as a function of temperature and different molar fractions of ionic surfactants (AOT) were determined (see Fig. 1a and b). The inflection point of the conductivity plot has been considered usually [9] to correspond to a percolation-like phase transition threshold of the system. Since number and size of the nanodroplets were kept constant, the critical temperature where the onset of cluster formation is located, was uniquely determined by the composition of the surfactant mixture in the interface.

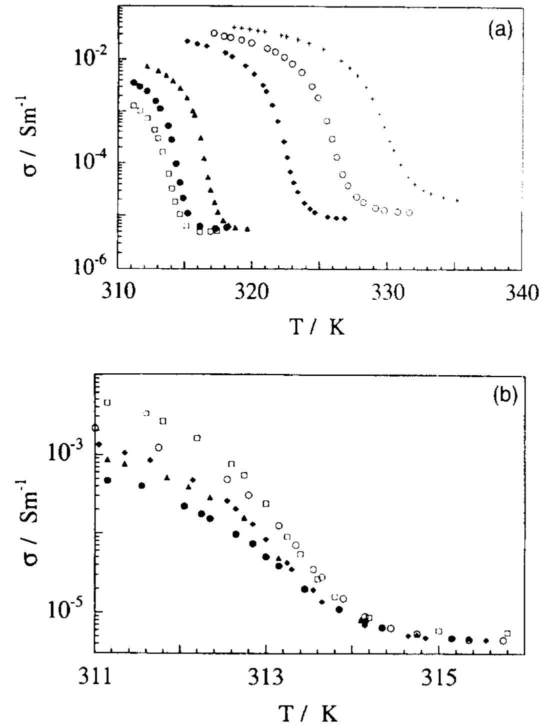

Fig. 1. (a) Typical set of experimental conductivities σ of H_2O–AOT, $C_{12}E_5$–n-octane as a function of temperature T for varying interfacial molar fractions of ionic surfactant (AOT), $X_{\mathrm{electrolyte}}$: (+) 8.28×10^{-3}; (○) 5.76×10^{-3}; (◆) 4.14×10^{-3}; (△) 1.66×10^{-3}; (●) 8.28×10^{-4}; (□) 2.48×10^{-4}. (b) Typical set of experimental conductivities σ of the system $NaCl_{aq}$–$C_{12}E_5$–n-octane as a function of temperature T of non-ionic surfactant covered nanodroplets and solubilized brine of different molar fractions $X_{\mathrm{electrolyte}}$ (○) 9×10^{-5}; (◆) 1.8×10^{-4}; (△) 2.7×10^{-4}; (●) 3.6×10^{-4}; (□) 9×10^{-4}.

Accordingly, in order to study how droplet size (and hence interfacial curvature) influences the specific conductivity, the temperature dependence of σ – subject to varying droplet sizes – has to be eliminated. Hence, in order to reduce the specific conductivity to isothermal conditions (referring to an arbitrary reference temperature) one expands σ into a Taylor series of two variables to first order [10], i.e.

$$\sigma = \sigma_0 + (\partial\sigma/\partial r_{\mathrm{w}})_T (r_{\mathrm{w}} - r_{\mathrm{w},0}) + (\partial\sigma/\partial T)_{r_{\mathrm{w}}} (T - T_{\mathrm{c},0}) \qquad (1)$$

where $r_{\mathrm{w},0}$ and $T_{\mathrm{c},0}$ are some (hypothetical) reference states of nanodroplets [containing no free (independently exchangeable) water [11]] and the critical temperature at this composition. $(\partial\sigma/\partial r_{\mathrm{w}})_T$ might

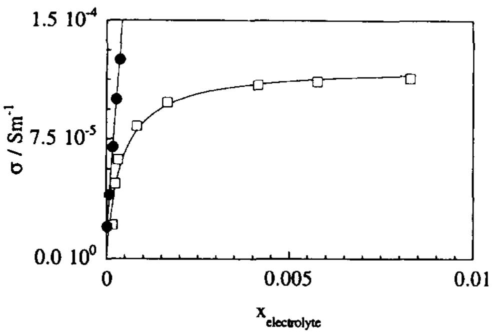

Fig. 2. Isothermal conductivities σ of $NaCl_{aq}$–$C_{12}E_5$–*n*-octane and H_2O–AOT,$C_{12}E_5$–*n*-octane at system spanning cluster thresholds (313 K = ref. temp, see text) against mole fraction of electrolyte ($X_{electrolyte}$ = mole electrolyte/mole surfactant). (●) NaCl; (□) AOT: best fit to experimental data with Eq. 10: $u_{Na^+} = 10^{-10}$ m^2 V^{-1} s^{-1}, $\Gamma_0 = 2 \times 10^{-8}$ mol m^{-2}; $K_1 K_2 = 54$. Size of experimental points denotes error bars.

be called an ''isothermal droplet size coefficient'' of the specific conductivity, $(\partial\sigma/\partial T)_{r_w}$ is the temperature coefficient of the specific conductivity at constant droplet size, and $(\partial\sigma/\partial r_w)_{perc}$ is the droplet size coefficient at the respective critical temperature. The droplet size coefficient is accessible from experimentally determinable expressions, i.e.

$$(\partial\sigma/\partial r_w)_T = (\partial\sigma/\partial r_w)_c - (\partial\sigma/\partial T)_{r_w}(dT/dr_w)_c \tag{2}$$

where $(dT/dr_w)_c$ in Eq. 2 describes the shift of the critical temperature with varying droplet size.

Thus we have plotted the (isothermal) conductivities at the onset of cluster formation of aqueous nanodroplets covered by a binary non-ionic/ionic surfactant mixture ($C_{12}E_5$–AOT) in *n*-octane against the molar fraction of ionic surfactant $x_{electrolyte}$ (see Fig. 2). A strongly bended plot results indicating that the conductivity becomes constant with increasing weighed-in amount of ionic surfactant. The reason for this behavior is that at $x_{electrolyte} \rightarrow 0$ the counterions are distributed in the aqueous bulk phase of the nanodroplets. If the conductance increases with rising amounts of ionic surfactants, the (equally charged) counterions of the surfactant are expelled from the bulk of the nanodroplets towards their interfaces. It appears instructive at this place to plot also in the same diagram the specific conductivity of nanodroplets in the clustered state covered solely by non-ionics but containing varying concentrations of brine ($x_{electrolyte}$). A straight line is observed extending up to $x_{electrolyte} = 1.8 \times 10^{-3}$; its slope is about twice that of the initial slope of the $C_{12}E_5$–AOT system. The difference is plausible because in case of nanodroplets with mixed lipid monolayers only the counterion (Na^+) contributes to the conductivity, while the surfactant anion of AOT is immobilized in the interface. For the brine system there exists no preferential adsorption of either ion and the plot obeys Ohms law.

For example, the value $x_{electrolyte} = 1.8 \times 10^{-3}$ corresponds to a 0.1 M aqueous electrolyte solution. It has a specific conductivity of 1.4 S m^{-1} at 313 K [11] from which we derive $\sigma^{313}_{0.1\,M\,NaCl} = 0.196$ S m^{-1} considering a volume fraction of water of 0.140 in the ternary system. The experimental conductivity of this microemulsion is, however, 5.90×10^{-4} S m^{-1} at the same temperature. Hence the conductivity of the microemulsion is smaller by a factor of about 300. This reduction could be attributed to an activation energy ΔE_A of about 15 kJ mol^{-1} at 313 K to overcome the surfactant bilayer between the nanodroplets. In comparing this value with the theoretically predicted figure at room temperature [12], we have to assume a considerable temperature dependence of ΔE_A. This is supported by another set of observations (cf. [10]) where we studied $C_{14}E_5$ with solubilized aqueous sodium chloride solutions at the system spanning cluster formation threshold in *n*-octane at 298 K. The cluster formation was clearly identified from viscosity measurements, however, no increase in conductivity could be detected. We interpret this observation as a rather convincing argument in favour of the nanodroplet picture [13].

Concerning the bended plot it is proposed to consider more closely the role played by the interface on the charge distribution in these systems. We suggest, therefore, a two-stage adsorption process, consisting of an adsorption–desorption equilibrium and a dissociation step, i.e.

$$\mathrm{A(oil)} \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \mathrm{A(ads)} \underset{k_2'}{\overset{k_2}{\rightleftarrows}} \mathrm{A^-_{aq}(ads)} + \mathrm{Na^+_{aq}} \tag{3}$$

where A is the surfactant electrolyte and the rate constants k_1, k_1', k_2 and k_2' refer to the coupled processes. The rate equation with respect to A(ads) reads

$$d\Gamma_A/dt = k_1 x_A\left(\Gamma_0^0 - \Gamma_j\right) - k_1'\Gamma_{A(\text{ads})} - k_2\Gamma_{A(\text{ads})} + k_2'\Gamma_j \quad (4)$$

where x_A is the mole fraction of A, Γ_A(ads) its interfacial concentration, Γ_0^0 the interfacial concentration of "empty sites" available to the AOT molecules (which can be adjusted a priori in this experiment) and Γ_j the interfacial concentration of the AOT anions.

A second-rate equation describing the dissociation rate of the AOT molecules can be written as

$$d\Gamma_j/dt = k_2\Gamma_{A(\text{ads})} - k_2'\Gamma_j \quad (5)$$

Assuming that the adsorption equilibrium (Eq. 4) is adjusted, i.e. $d\Gamma_A/dt = 0$, we combine this equation with Eq. 5 to obtain

$$d\Gamma_j/dt = \frac{k_1 k_2}{k_1' + k_2} x_A\left(\Gamma_0^0 - \Gamma_j\right) + \left(\frac{k_2}{k_1' + k_2} - 1\right)k_2'\Gamma_j \quad (6)$$

If $k_2 \ll k_1'$, i.e. the rate of dissociation is small compared to the rate of adsorption of surfactant electrolyte, we get

$$d\Gamma_j/dt \approx \frac{k_1 k_2}{k_1'} x_A\left(\Gamma_0^0 - \Gamma_j\right) - k_2'\Gamma_j \quad (7)$$

The assumption of adsorption equilibrium of the AOT anion in the interface yields

$$\Gamma_j = \frac{\Gamma_0^0 x_A}{1/K_1K_2 + x_A} \quad (8)$$

One thus obtains a typical Langmuir adsorption isotherm with respect to the AOT anion. We have also set $K_1 = k_1/k_1'$ and $K_2 = k_2/k_2'$. As the specific conductivity is defined by

$$\sigma = \alpha c F(u_+ + u_-) \quad (9)$$

where α is the degree of dissociation, F the Faraday constant and u_j the mobilities of the ions. As $\alpha c = c_j$ is the ion concentration and, due to electroneutrality, $c_jV_{\text{nd}} = \Gamma_jS_{\text{nd}}$ (where V_{nd} and S_{nd} are the volume and surface of a *nano**d**roplet*), we obtain

$$\sigma \approx \Gamma_j F u_+ (S/V)_{\text{nd}} \quad (10)$$

if one assumes that only the anion of AOT is adsorbed onto the interface in the AOT concentration range considered and its contribution to the overall conductivity is negligible (compare the initial slopes in Fig. 2). Hence, the specific conductivity finally reads

$$\sigma \approx \frac{\Gamma_0^0 x_A}{1/K_1K_2 + x_A}(S/V)_{\text{nd}} F u_{\text{Na}^+} \quad (11)$$

For $x_{\text{AOT}} \ll x_{\text{C12E5}}$ a further approximation is feasible within a mean field approach [14] based on the assumption that the oil/water interface is covered by a saturated surfactant monolayer [2], i.e.

$$(S/V)_{\text{nd}} \approx \phi_s/l_s \quad (12)$$

where ϕ_s is the volume fraction of the non-ionic surfactant and l_s the length of the surfactant molecule as long as the droplet size is determined by the non-ionic surfactants. We thus obtain to higher order

$$\sigma \approx \frac{\Gamma_0^0 x_A}{1/K_1K_2 + x_A}(\phi_s/l_s) F u_{\text{Na}^+}(x_A) \quad (13)$$

where u_{Na^+} is a function of x_A according to the above outlined idea. For $x_A \to 0$ $u_{\text{Na}^+} \to u_{\text{Na}^+}^0$, its value at infinite dilution, 6.9×10^{-8} m^2 V^{-1} s^{-1} [11], while in the saturation regime u_{Na^+} is obtained under the condition $x_A \gg (K_1K_2)^{-1}$. Two limiting cases are observed, i.e. for $x_A \gg 1/K_1K_2$ one obtains

$$\sigma \approx \Gamma_0^0(\phi_s/l_s) F u_{\text{Na}^+} \quad (14)$$

and for $x_A \ll 1/K_1K_2$, Eq. 13 reduces to

$$\sigma \approx K_1K_2\Gamma_0^0(\phi_s/l_s) F u_{\text{Na}^+}(x_A) x_A \quad (15)$$

From Eq. 14 one can deduce directly an approximate value of u_{Na^+} which is about 1.0×10^{-10} m^2 V^{-1} s^{-1}. With $u_{\text{Na}^+} = u_{\text{Na}^+}^0$ (diluted aqueous droplet phase) and a weighed-in interfacial concentration $\Gamma_0^0 = 2 \times 10^{-8}$ mol m^{-2} one derives from Eq. 15 a value for the product K_1K_2 of ca. 54. A comparison of the just determined mobility of the sodium ion

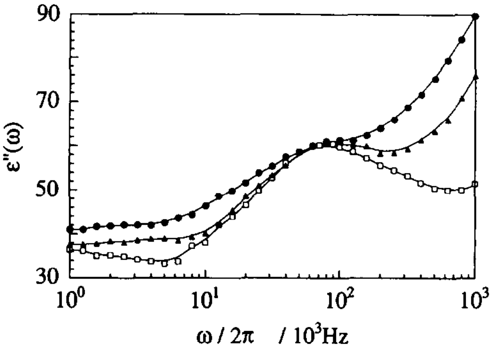

Fig. 3. Low-frequency dielectric loss measurements of singly dispersed nanodroplets of H_2O–AOT,$C_{12}E_5$–*n*-octane (see text). Parameter: interfacial molar fraction of AOT/nanodroplet: (●) 8.3×10^{-4}; (△) 1.67×10^{-3}; (□) 4.14×10^{-3}.

with $u^0_{Na^+}$ at the same temperature (313 K) demonstrates the remarkable retardation by a factor of 680 of the sodium counterion mobility of AOT under these conditions.

It is interesting to note that we found the same low mobility value in a dispersion of droplets of the kind just discussed, however, far away from the nanodroplet cluster regime by carrying out dielectric dispersion measurements in the low-frequency range [3]. Fig. 3 shows the dielectric loss, i.e. $\{G(\omega) - G(\omega \to 0)\}/\omega C_v$, ($G(\omega)$ being the frequency dependent conductance and C_v the capacity of the empty cell) against the applied frequency. The parameter of the plot corresponds to different surface concentrations of AOT ($= \Gamma_{AOT}$). Note the theoretically predicted rather low frequency and the relative insensitivity of ε''_{max} (Γ_{AOT}) on the AOT concentration. According to Schwarz' model, i.e. $u_j = (\pi e R^2 f)/k_B T$ (u_j = counterion mobility of *j*th ion and R the aqueous core radius of the nanodroplet and $f = \omega/2\pi$ the applied frequency), we derive a mobility of the counterion $u_{Na^+} \approx 1.5 \times 10^{-10}$ m^2 V^{-1} s^{-1} in remarkably good agreement with the value deduced from conductivity measurements in the infinitely clustered state of the microemulsion. A simple physical argument is at hand to conclude that the ion distribution is rather compressed within a small distance from the charged interface (small Debye screening length) and, hence, the interfacial conduction is expected to experience a considerable retardation: the aqueous nanodroplet presents a conducting sphere in a non-conducting medium. Hence charges with equal sign in the droplet tend to accumulate at the oil/water interface (largest mutual ion–ion distance).

The energy of activation of the specific conductivity (in the infinitely clustered state) as inferred from the saturation regime is 46 kJ mol^{-1}, which is significantly larger than the value found for very low electrolyte concentrations which corresponds to the interdroplet charge transport. If we assume that the ion transport in the isolated droplet and the interconnected (percolated) droplets along the interface follows the same mechanism, we attribute to the counterion motion along the interface an activation energy (E_c), i.e., $u_+ = u^0_+ \exp(-E_c/RT)$, where u^0_+ is the value of u_+ at $E_c \to 0$ and at the infinite diluted bulk state of the electrolyte solution (Fig. 4). This activation energy is of electrostatic origin. The counterion within the semi-diffuse double layer must overcome the potential barriers between the discrete charges in the interface in order to follow the applied electric field. The height of the potential well multiplied by the charge of the counterion is the activation energy E_c, i.e., $e^2/4\pi\varepsilon_0\varepsilon_r\delta$. From this expression an approximate minimum distance between the counterion and the AOT anion in the interface can be obtained. Adopting the experimental value of the activation energy of 46 kJ mol^{-1} and taking $\varepsilon^{313}_{H20} \leq 10$ one derives an average minimum distance of about 5×10^{-10} m, i.e., an extremely compressed ionic double layer.

A further clue to assume interfacial charge trans-

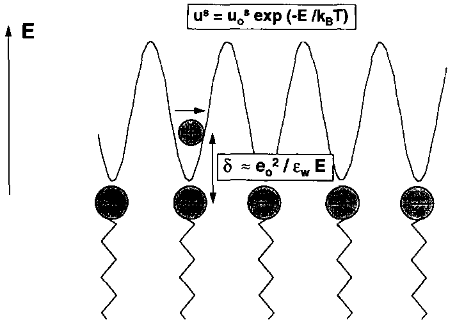

Fig. 4. Simplified model of interfacial charge transport of surfactant counterions. δ = closest distance between surfactant and counterions; ε_w = dielectric constant of water in electric double layer; E = electrostatic potential energy; u^s = ion mobility in interface.

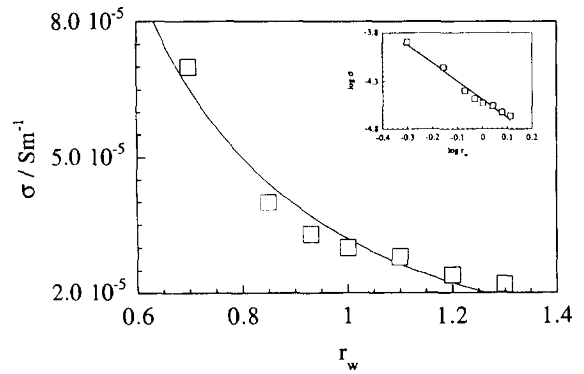

Fig. 5. Isothermal conductivity σ of H_2O–AOT,$C_{12}E_5$–n-octane against $r_w = m_{H2O} / m_{surfactant}$. Solid line is fitted with r_w^{-2} (r_w is nanodroplet radius R). Inset shows logarithmic plot of best fit with $r_w^{-1.9}$. Size of experimental points denotes error bars.

port in the infinite nanodroplet cluster regime stems from another set of measurements using the same system as for the construction of the Langmuir plot-like isotherm. Fig. 5 shows isothermal specific conductivities against the nanodroplet radii covered by a mixed ionic–non-ionic surfactant layer at constant interfacial charge density ($c^s_{\text{ionic}}/c^s_{\text{non-ionic}} = 8.3 \times 10^{-3}$ corresponding to a surface charge of about 10^{-8} C m^{-2}). This is again done by replacing non-ionic surfactants ($C_{12}E_5$) by ionic surfactants (AOT) as both possess approximately the same equilibrium area/surfactant. The plot exhibits a surprising shape: the specific conductivity varies as R_{nd}^{-2} (more exact -1.9, see inset) indicating that the resistance of the system varies proportional to the surface of the spheres. This result brings the concept of the interfacial charge transport into prominence and contrasts clearly with the strictly linear radius dependence observed with nanodroplets covered by non-ionic surfactants and containing brine [10]. An appropriate theoretical model of this situation starts by applying a phase equilibrium to the sodium ions by assuming the Debye screening length to be very small compared with R_{sphere}. Hence, one proceeds to solve a one-dimensional potential distribution, a "linear box model" (see Appendix) [15], which predicts a reciprocal R_{nd}^2 dependence of the counterions c_j, and thus of the specific conductivity, i.e.

$$c_j \approx 2\varepsilon\varepsilon_0 RT/z^2e^2N_A^2R_{\text{nd}}^2 \propto \sigma \qquad (16)$$

where R is the gas constant, ε, ε_0 the relative dielectric constant and the permittivity of the vacuum, N_A Avogadro's constant, z the valency of the counterion, and e the elementary charge. This result is remarkable and confirms the assumption of interfacial charge transport in the here considered microemulsions.

4. Conclusions

Mobility, charge production and ion transport were investigated in aqueous nanodroplets covered by mixtures of ionic and non-ionic surfactants. They were studied in the singly dispersed state or at the onset of a system-spanning cluster. Increasing amounts of surfactant electrolyte in the mixed surfactant monolayer let the isothermal conductivity plot strongly bend adopting a Langmuir-like isotherm. A two-step adsorption process describes the σ-plot remarkably well and allows one to derive a counterion mobility almost three orders of magnitude smaller than its value in bulk solution at the same temperature and electrolyte concentration. This value conforms remarkably well to mobility data of the AOT counterions obtained from frequency-dependent dielectric dispersion measurements with singly dispersed nanodroplets of the same system. It has also been observed that the conductivity of an infinite cluster with nanodroplets covered by mixed monolayers varies with the inverse second power of their radii in agreement with a "linear box model", thus demonstrating the proportionality of the electric resistance and the surface areas of the nanodroplets. We conclude that the Debye screening length is small hence the semi-diffuse double layer is highly compressed. This is taken to be the reason for the reduced mobility and low surface conductivity.

Acknowledgements

The authors are grateful to B. Fedtke, H. Hammerich and Y. Hauger for help with the experiments. One of the authors (H.F.E.) acknowledges frequent discussions with F. Sauer, MPI für Biophysik, Frankfurt/M concerning the here addressed problems and a careful reading of the manuscript by Prof. R. Schilling, Institute of Theoretical Physics, University of Mainz. This work has been supported by the Swiss National Science Foundation.

Appendix A

A phase equilibrium between the interface of the nanodroplets and their aqueous bulk phase is considered with regard to the sodium ions (counterions of AOT), i.e.

$$\eta_+ = \overline{\mu}_+ + RT \ln c_+ + zeN_A\phi \tag{1A}$$

where η_+ is the electrochemical potential of counterions in the interface, $\overline{\mu}_+$ a reference electrochemical potential, R the gas constant, c_+ the concentration of counterions in the bulk (droplet) phase, z the valency of the counterion, e the elementary charge, N_A Avogadro's constant and ϕ the potential of the bulk phase. Eq. 1A can be rewritten as

$$c_+ = c_{+0}\exp\{(-zeN_A\phi + \mathrm{const} - \overline{\mu}_+)/RT\} \tag{2A}$$

or

$$c_+ = c_{+0}\exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right)\right\} \tag{3A}$$

where $\tilde{\phi} = (zeN_A/RT)\phi$, $\tilde{\phi}_0 = (zeN_A/RT)\phi_0$, c_{+0} is some reference counterion concentration in the nanodroplet (see below) and the origin of the coordinate system is taken to be in the oil/water interface. Eq. 3A is combined with Poisson's Eq. 4A

$$-\mathrm{d}^2\phi/\mathrm{d}x^2 = (zeN_A/\varepsilon\varepsilon_0)c_+ \tag{4A}$$

and written in dimensionless quantities using $\xi = \kappa x$, (with κ the Debye screening length) we obtain

$$-\mathrm{d}^2\tilde{\phi}/\mathrm{d}\xi^2 = \exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right)\right\} \tag{5A}$$

Integration of Eq. 5A yields

$$\frac{1}{2}\left(\mathrm{d}\tilde{\phi}/\mathrm{d}\xi\right)^2 = \exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right)\right\} - \mathrm{const} \tag{6A}$$

As a boundary condition we have $(\mathrm{d}\tilde{\phi}/\mathrm{d}\xi)_{\xi=\xi_R} = 0$ at the center of the sphere $(x = R)$, hence

$$\mathrm{const} = \exp\left\{-\left(\tilde{\phi}_{(\xi=\xi_R)} - \tilde{\phi}_0\right)\right\} \tag{7A}$$

Since we are free to choose the constant potential $\tilde{\phi}_0$ at $\xi = \xi_R$ we take $\tilde{\phi}_{(\xi=\xi_R)} = \tilde{\phi}_0$ and get from Eq. 6A or

$$\left(\mathrm{d}\tilde{\phi}/\mathrm{d}\xi\right) = -\sqrt{2\left[\exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right\} - 1\right]} \tag{8A}$$

The second integration is carried out by introducing $z = \tilde{\phi} - \tilde{\phi}_0$, whence the final result is

$$\sqrt{2}\,\mathrm{arctg}\left(\exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right)\right\} - 1\right)^{1/2} = \xi - \xi_R \tag{9A}$$

A further boundary condition is fixed by the physical state at the interface of the nanodroplet, i.e.

$$\left(\mathrm{d}\tilde{\phi}/\mathrm{d}\xi\right)_{\xi=0} = \Gamma\kappa/c_{+0} \tag{10A}$$

where Γ denotes the saturated monolayer with a particular surface concentration of ionic surfactant in mol m^{-2}.

In order to calculate the counterion concentration, we start out by differentiating Eq. 9A, i.e.

$$-\left(\mathrm{d}\tilde{\phi}/\mathrm{d}\xi\right)\exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right)\right\} = \sqrt{2}\left(\mathrm{tg}(\xi - \xi_R)/\sqrt{2}\right)\left\{1 + \mathrm{tg}^2(\xi - \xi_R)/\sqrt{2}\right\} \tag{11A}$$

Eq. 10A inserted into Eq. 11A yields

$$-\Gamma\kappa/c_{+0}\exp\left\{-\left(\tilde{\phi} - \tilde{\phi}_0\right)\right\} = \sqrt{2}\left(\mathrm{tg}[\xi - \xi_R]/\sqrt{2}\right)\left(1 + \mathrm{tg}^2[\xi - \xi_R]/\sqrt{2}\right) \tag{12A}$$

Again Eq. 12A can be substituted into Eq. 9A, thus yielding

$$\frac{\sqrt{2}\,\Gamma\kappa}{c_{+0}}\mathrm{tg}\frac{\xi_R - \xi}{\sqrt{2}} - 1 = 0 \tag{13A}$$

The counterion concentration is contained in κ. At the oil/water interface (surface of the nanodroplet) we have the boundary condition $\xi = 0$, hence

$$\sqrt{2}\,\xi_R\,\mathrm{tg}\,\xi_R = 1 \tag{14A}$$

if we adopt the condition $c_{+0}R \leq \Gamma$.

$$c_j \approx 2\varepsilon\varepsilon_0 RT/z^2e^2N_A^2R^2 \,\alpha\, \sigma \tag{16A}$$

where R is the gas constant, ε, ε_0 the relative dielectric constant and the permittivity of the vacuum, N_A Avogadro's constant, z the valency of the counterion, and e the elementary charge.

References

[1] H.R. Kruyt (Ed.), Colloid Science, Vol. 1, Elsevier, Amsterdam, 1952; F. Franks (Ed.), Water a Comprehensive Treatise, Vol. 4, Plenum Press, New York, 1975, Chaps. 2 and 4; S.S. Dukhin and V.N. Shilov, Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes, Wiley, New York, 1974; M. Clausse, in P. Becher (Ed.), Encyclopedia of Emulsion Technology, Vol. 1, Marcel Dekker, New York/Basel, 1983.

[2] G. Seelig, in P.L. Luisi and B.E. Straub (Eds.), Reverse Micelles, Plenum Press, New York, 1984, p. 209f.

[3] G. Schwarz, J. Phys. Chem., 66 (1962) 2636.

[4] H.-P. Schwan, G. Schwarz, J. Maczuk and H. Pauly, J. Phys. Chem., 66 (1962) 2626.

[5] W.C. Chew and P.N. Sen, J. Chem. Phys., 77 (1982) 4683.

[6] S.S. Dukhin and B.V. Derjaguin in E. Martijevic (Ed.), Surface and Colloid Science, Vol. 7, Wiley, New York, 1974.

[7] M. Fixman, J. Chem. Phys., 72 (1980) 5177.

[8] M. Borkovec, H.-F. Eicke and B. DasGupta, J. Phys. Chem., 93 (1989) 314; M. Kahlweit, R. Strey, D. Haase, et al., J. Colloid Interface Sci., 118 (1987) 436.

[9] H.-F. Eicke, R. Hilfiker and H. Thomas, Chem. Phys. Lett., 125 (1986) 295.

[10] H.-F. Eicke, W. Meier and H. Hammerich, Langmuir, 10 (1994) 2223.

[11] Landolt Börnstein, Vol. 2 and 7, Springer, Berlin, 1960.

[12] A. Parsegian, Nature, 221 (1969) 844; R.C. McDonnald, Biochim. Biophys. Acta, 448 (1976) 193.

[13] H.-F. Eicke in I.D. Robb (Ed.), Microemulsions, Plenum Press, New York, 1982.

[14] J. Jouffroy, P. Levinson and P.G. de Gennes, J. Phys. (Paris), 43 (1982) 1241.

[15] F.A. Sauer, personal communication.