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SHORT COMMUNICATION

Hans-Friedrich Eicke
Holger Hammerich

Temperature-controlled change of charge transport mechanisms in nonionic water-in-oil microemulsions

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H.-F. Eicke (✉) · H. Hammerich
Institut für Physikalische Chemie
Dept. Chemie, Universität Basel
4056 Basel, Switzerland
e-mail: hans-friedrich.eicke@unibas.ch

Abstract The temperature-controlled transition from the Stokes charge transport of aqueous nanodroplets to the intrinsic conduction of nanodroplet clusters in nonionic microemulsions was studied. Two different charge transport processes apparent from a minimum value of the conductance have been simulated based on straightforward physical models. Their predictions compare favourably with the observations.

Keywords Nonionic pentaethylene glycol monoalkyl ethers · Water-in-oil microemulsions with added electrolyte · Charge transport processes · Temperature dependence of transport mechanisms · Modelling of transport mechanisms

Introduction

A feature frequently observed conductometrically with ionic and nonionic water-in oil microemulsions, where the latter contain minute amounts of an electrolyte (dispersed in the aqueous core of the nanodroplets), is the transition of the Stokes charge transport of nanodroplets to intrinsically conducting nanodroplet clusters [1–4]. In the case of nonionic systems a prerequisite is sufficient stability of the droplet phase with respect to neighbouring phases in the presence of small amounts of electrolyte. Although the general mechanisms leading to the observed conductance minimum accompanied with charge transport processes are similar in both types of microemulsions, we will restrict the discussion to nonionic systems where more experimental material is at our disposal. One starts from a dispersion of aqueous nanodroplets covered by nonionic surfactants in a medium of low dielectric constant. Decreasing the temperature of the system results in a monotonic decrease in the electrical conductivity, which passes, at a particular temperature, through a minimum value of the conductivity followed by a large nonmonotonous increase in the conductance, eventually adopting a typical percolation threshold. This observation suggests the occurrence of this minimum region by two conduction processes, one of which describes the transport of charged nanodroplets, while the other is attributed to the intrinsic conduction of nanodroplet clusters. It should be emphasised that the experimental temperature range considered here is significantly above that of the percolation transition, i.e., at least 0.5 K.

Experimental

Nonionic surfactants (pentaethylene glycol monoalkyl ethers), i.e., $C_{12}E5$ and $C_{14}E_5$ purity above 98% GC, and the electrolytes LiBr, NaCl, sodium formiate, sodium acetate, sodium capronate and sodium laurate were obtained from Fluka, puriss. All the compounds were used as received.

The concentration of nanodroplets in oil (o) is given by the mass fraction of water (w) and surfactant (s), $c_w = (w + s)/(w + s + o)$, which was kept constant at $c_w = 0.256$. The size of the nanodroplets is controlled by the water-to-surfactant mass ratio, $r_w = w/s$. More specifically, the nanodroplet radius, R_{nd}, is related to the molar water-to-surfactant ratio, $w_o = (M_s/M_w)r_w$, where M_s and M_w are the molecular weights, by [5] $R_{nd} = 3(w_o v_w + v_s)/A_{head}$. $v_w \approx 30 \times 10^{-30}$ and $v_s \approx 340 \times 10^{-30}$ m^3 are the molecular volumes of water and pentaethylene glycol, and $A_{head} \approx 56 \times 10^{-20}$ m^2 [6] is the average interfacial area of the polar head of the nonionic surfactants. Five electrolyte molecules per nanodroplet were added, i.e., about 3.4×10^{-2} moldm^{-3}, with respect to the aqueous phase of the nonionic microemulsion.

Measurements of the electrical conductivity, σ, were carried out in a sealed-plate condenser-type glass cell with two rectangular Pt electrodes of 5 × 10 mm and a gap width of 2 mm. The cell also contained a magnetic stirrer to eliminate temperature differences in the conductance cell. It was immersed in a temperature bath, which was adjusted to ± 0.04 K. The conductance was determined by an autobalancing alternating current conductance bridge (Radiometer Copenhagen, type CDM 83), which operates between 73 and 50 kHz to reach maximal sensitivity between 2×10^{-8} and 1.3 S. These frequencies are well outside the Maxwell–Wagner frequency, $\sigma/\varepsilon\varepsilon_0$, of the systems studied.

Results and discussion

A moderately concentrated dispersion of nanodroplets (volume fraction $\Phi \approx 0.19$), i.e., a nonionic water-in-oil microemulsion containing minute amounts of electrolytes with varying hydrocarbon chain lengths, can always be studied in a monodisperse nanodroplet state within a particular temperature region. Considering Fig. 1 for the case where pentaethylene glycol tetradecyl ether was used as surfactant, we observe two obviously different branches of the plot within the temperature interval studied. In the lower temperature region two different phenomena occur; the plot splits into individual graphs dependent on the physicochemical properties of the electrolytes added and the conductivities increase according to a power law. Increasing temperatures produce a rather small increase in the conductivities, which develop in a linear fashion within the temperature interval studied. The general trend of the graphs of Fig. 1 is also found in the case shown in Fig. 2, where pentaethylene glycol dodecyl ether was used as the nonionic surfactant. The spread of the steep portions of the σ plots is less pronounced. Sodium acetate was studied at two concentrations (ratio 1:5 per nanodroplet). The lower concentration showed 20% higher conductivity. Hence, this additive behaves like a weak electrolyte in the aqueous core as was to be expected. The typical strong electrolytes, i.e., sodium chloride and lithium bromide, display similar behaviour, although lithium bromide has a higher conductivity at the same temperature.

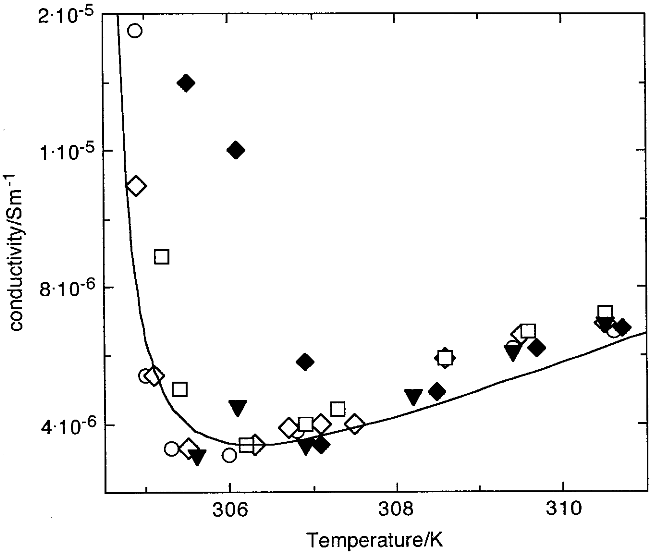

Fig. 1 Temperature-dependent electrical conductivity of pentaethylene glycol tetradecyl ether/aqueous electrolyte (3.4×10^{-2} moldm^{-3})/isooctane water-in-oil microemulsions. Electrolytes: LiBr (*circles*), HCOONa (*open diamonds*), CH_3COONa (*squares*), $CH_3(CH_2)_4COONa$ (*down triangles*), $CH_3(CH_2)_{10}COONa$ (*filled diamonds*)

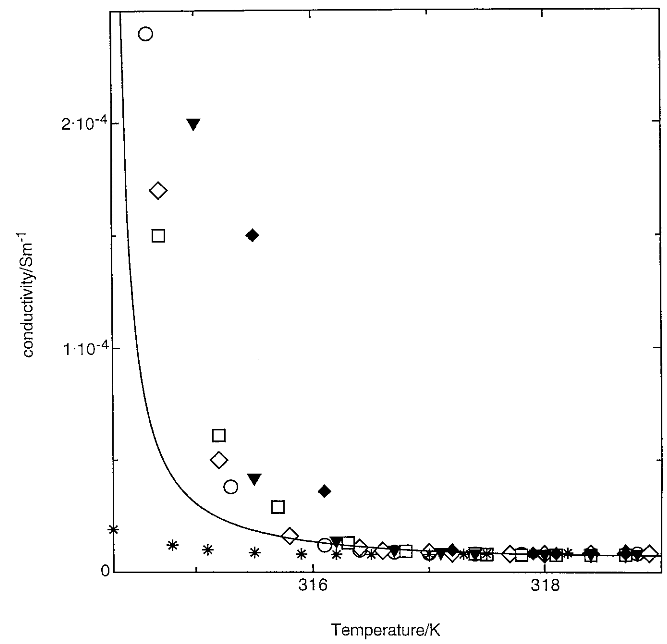

Fig. 2 Temperature-dependent electrical conductivity of pentaethylene glycol dodecyl ether/aqueous electrolyte (3.4×10^{-2} moldm^{-3})/isooctane water-in-oil microemulsions. Electrolytes: (open triangle) NaCl, (filled diamond) LiBr, (open circle) HCOONa, (open diamond) CH_3COONa, (open square) CH_3COONa (6.8×10^{-3} moldm^{-3}), (star) $CH_3(CH_2)_{10}COONa$

The lower-temperature region again displays a differentiated appearance of the conductivity plot compared to the higher-temperature portion of the diagram, where individual properties of the electrolytes are obliterated. This observation supports our view to distinguish two conduction mechanisms; At higher temperatures (surfactant dependent), the nanodroplets tend to exist in a monomeric state. At lower temperatures, nanodroplet clusters are formed, which possess an intrinsic conductance via lipophilic barriers between the aqueous nanodroplets (Fig. 3). The apparent constancy of the conductivities in the higher-temperature region (Fig. 2) is possibly due to an earlier aggregation of the nanodroplets with a concomitant contribution of the intrinsic conduction. A possible mechanism of charge transport was discussed in Ref. [7].

We describe here the more regular case as displayed in Fig. 1 (which has been also frequently observed with

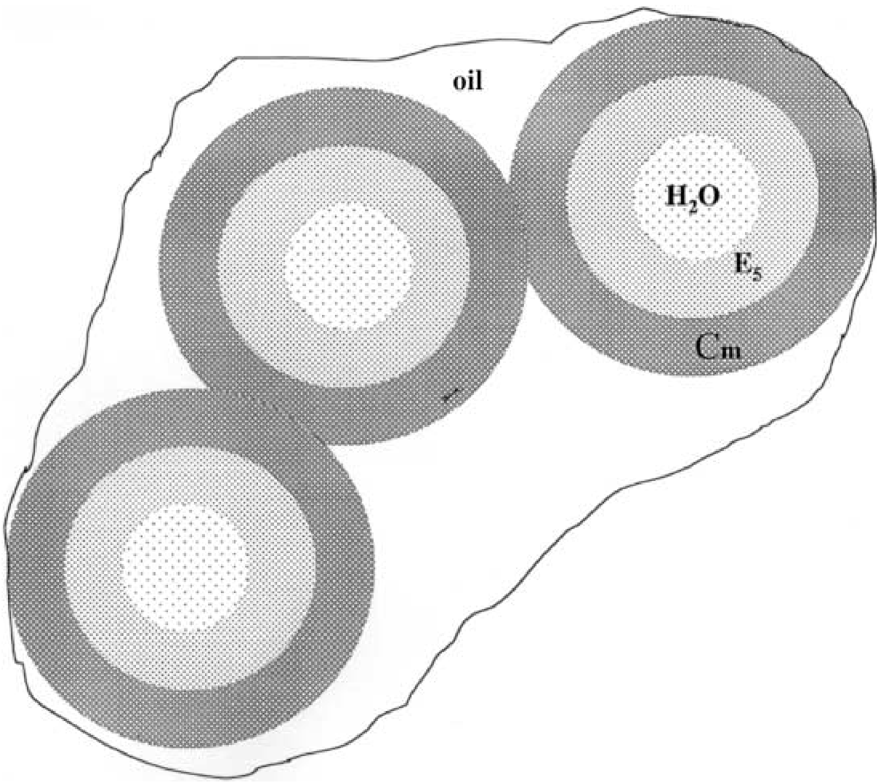

Fig. 3 Nanodroplet cluster (or section of a larger cluster) in oil (isooctane). *Light* and *dark cross-hatched areas* represent pentaethylene glycol (E_5) and tetradecyl or dodecyl ether (C_m)

Aerosol OT in apolar media), i.e., the low conducting, monotonically with temperature increasing, conductivity range. According to earlier experience we assume that the nanodroplets carry charges owing to spontaneous number fluctuations of the ions residing on the droplets [8, 9]. The model predicts under the given experimental conditions (on the average five electrolyte molecules per nanodroplet) that about 40% of the droplets carry an excess charge. The fluctuation model yields under the prevailing conditions an electrical conductivity, i.e.,

$$\sigma_{\mathrm{nd}} = (\varepsilon\varepsilon_0 k_{\mathrm{B}} T / 2\pi\eta)\left(\Phi/R^3\right), \tag{1}$$

where ε is the relative dielectric constant of the dispersion medium, ε_0 the influence constant, k_{B} Boltzmann's constant, η the viscosity of the medium, R the nanodroplet radius, and Φ the volume fraction of droplets. According to this model it is understood that the different electrolytes added to the nanodroplets do not display any other effect but charging the nanodroplets [8]. This is obvious from the experiments.

The lower-temperature region as defined earlier is attributed to a temperature-controlled aggregation process leading to nanodroplet clusters of various sizes, which eventually form an infinite cluster at the percolation temperature. From the experiments it was concluded that such clusters exhibit an intrinsic conduction process [10], which involves the transition of charges (molecular ions) from the aqueous core of the nanodroplets to the hydrocarbon bilayers. Such bilayers form nanodroplet clusters, probably by interdigitation of the long hydrocarbon tails of neighbouring droplets. The clusters are at each particular temperature in a dynamic equilibrium, forming larger clusters and breaking into smaller ones.

The membrane transport of charges (ions) within the clusters is controlled by the ion distribution between the aqueous core (aqueous phase) of the nanodroplets and the lipophilic barrier (barrier phase). One starts, accordingly, by equating the electrochemical potentials of the transferable ions in both phases; thus,

$$\eta_{\mathrm{i}}^{\mathrm{core}} = \eta_{\mathrm{i}}^{\mathrm{barrier}}. \tag{2}$$

The potential and concentration dependence of the electrochemical potentials is explicitly written as

$$z_{\mathrm{i}} e_0 \varphi^{\mathrm{core}} + \mu_{\mathrm{i0}}^{0\mathrm{core}} + k_{\mathrm{B}} T \ln c_{\mathrm{i}}^{\mathrm{core}} = z_{\mathrm{i}} e_0 \varphi^{\mathrm{barrier}} + \mu_{\mathrm{i0}}^{0\mathrm{barrier}} + k_{\mathrm{B}} T \ln c_{\mathrm{i}}^{\mathrm{barrier}}. \tag{3}$$

The ratio of the respective ion concentrations in the two phases is, accordingly,

$$\ln \frac{c_{\mathrm{i}}^{\mathrm{barrier}}}{c_{\mathrm{i}}^{\mathrm{core}}} = -\frac{z_{\mathrm{i}} e_0 \Delta\varphi + \Delta\mu_{\mathrm{i0}}^0}{k_{\mathrm{B}} T}, \tag{4}$$

where $\Delta\varphi = \varphi^{\mathrm{barrier}} - \varphi^{\mathrm{core}}$ is the difference of the electrostatic potential of the barrier and the aqueous droplet phases. $\Delta\mu_{\mathrm{i0}}^0 = \mu_{\mathrm{i0}}^{0\ \mathrm{barrier}} - \mu_{\mathrm{i0}}^{0\ \mathrm{core}}$ is the chemical standard potential of transfer of the ions in the lipophilic barrier and the aqueous core of the nanodroplets, respectively.

z_i is the valency of the cation or anion, e_0 the elementary charge, and $k_B T$ the thermal energy of the system.

Lipophilic anions are expected to possess a rather small chemical potential in the lipophilic barrier range and, hence, substantially reduce the nominator of Eq. (4), thus giving rise to an increase in the electrical conductivity at almost constant thermal energy.

According to Eq. (4) $c_i^{\mathrm{core}} = c_i^{\mathrm{barrier}}$ at $\Delta\varphi = -\Delta\mu_{i0}^0/z_i e_0$. $\Delta\varphi$ is equal to $\Delta\varphi_0$ for zero surface charge plus a term proportional to the charge, q, of the aqueous core of the nanodroplet divided by the capacity of a sphere of radius r_w (core radius), i.e.,

$$\Delta\varphi = \Delta\varphi_0 + q/(4\pi\varepsilon\varepsilon_0 r_W), \tag{5}$$

where ε is the relative dielectric constant of the lipophilic barrier and ε_0 the absolute dielectric constant. $\Delta\varphi_0$ is determined by the nature of the coexisting phases [aqueous core and lipophilic barrier (hydrocarbon tails)]. The charge of the aqueous core is equal to the negative value of the space charge $< c_i^{\mathrm{barrier}} >$ surrounding each core within the cluster. The latter corresponds to the average anion concentration within the barrier phase. This follows from physical reasoning, i.e., anions are frequently more lipophilic, particularly if they carry hydrocarbon moieties as discussed here. More quantitatively, the alkyl chain length controls the anion solubility in the hydrocarbon barrier region [11, 12]. With increasing chain length $\mu_{i0}^{0\mathrm{barrier}}$ decreases, yielding a negative $\Delta\mu_{i0}^0$ and hence diminishes the nominator of the right-hand side of Eq. (4).

The rather striking increase in the electrical conductivity, however, is due to approaching the critical percolation threshold temperature (T_c), which is still distinctly different from the temperatures studied here. Since percolation phenomena announce themselves before the proper percolation threshold by increasing clustering of nanodroplets (to chains), we describe the temperature dependence of the cluster conductivity by a $(aT\text{–}T_c)^{-1}$ term, where a is a suitable constant. It is thus assumed that this process is described by a second-order phase transition [13]. The exponent corresponds to the classical value of the "generalised susceptibility" [14], since the measurements were made sufficiently far (earlier) from the critical regime.

The total conductivity of the nanodroplet clusters can now be written according to Eq. (4) (see also Ref. [10]), i.e.,

$$\begin{aligned}\sigma^{\mathrm{cluster}} &= \alpha e_0 (c_{\mathrm{anion}}^{\mathrm{core}} u_{\mathrm{anion}}^{\mathrm{core}} + c_{\mathrm{cation}}^{\mathrm{core}} u_{\mathrm{cation}}^{\mathrm{core}}) \frac{A_{\mathrm{contact}}}{R_{\mathrm{nd}} d_{\mathrm{barrier}}} \\ &\quad \times \exp\left[-(z_i e_0 \Delta\varphi + \Delta\mu_{i0}^0)/k_B T\right] \frac{\Phi}{a|T - T_c|} \\ &= \alpha e_0 c_{i0}^{\mathrm{core}} (u_{\mathrm{anion}}^{\mathrm{core}} + u_{\mathrm{cation}}^{\mathrm{core}}) \frac{R_{\mathrm{nd}}}{d_{\mathrm{barrier}}} \\ &\quad \times \exp(-\Delta \mathrm{E}/k_B T) \frac{\Phi}{a|T - T_c|},\end{aligned} \tag{6}$$

where α is the degree of dissociation of electrolytes in the aqueous core, c_{i0} the weighed-in concentration of electrolyte, $u_{\mathrm{anion}}^{\mathrm{core}}$, $u_{\mathrm{cation}}^{\mathrm{core}}$ are the mobilities of the dissociation products of the added electrolyte, d_{barrier} the width of the lipophilic barrier between two aqueous cores, $\Delta E = z_i e_0 \Delta\varphi + \Delta\mu^0{}_{i0}$, $A_{\mathrm{contact}} \approx \mathrm{R}_{\mathrm{nd}}^2$, and R_{nd} is the radius of the nanodroplets.

With increasing length of the lipophilic chain the anion mobility in the aqueous core will become small compared to that of the cation (Na^+). The intrinsic conductivity of the clustered state is, accordingly,

$$\sigma^{\mathrm{cluster}} \cong \alpha e_0 c_{i0}^{\mathrm{core}} u_{\mathrm{cation}}^{\mathrm{core}} \frac{R_{\mathrm{nd}}}{d_{\mathrm{barrier}}} \exp(-\Delta E/k_B T) \frac{\Phi}{a|T - T_c|}. \tag{7}$$

The overall conductivity of the two contributions, i.e., Eqs. (1) and (7) is

$$\begin{aligned}\sigma(T) &\cong \alpha e_0 c_{i0}^{\mathrm{core}} u_{\mathrm{cation}}^{\mathrm{core}} \frac{R_{\mathrm{nd}}}{R_{\mathrm{nd}} d_{\mathrm{barrier}}} \exp(-\Delta E/k_B T) \frac{\Phi}{a|T - T_c|} \\ &\quad + \frac{\varepsilon\varepsilon_0 k_B (T - T_c)}{2\pi\eta} \frac{\Phi}{R^3}.\end{aligned} \tag{8}$$

The first term of Eq. (8) simulates the strong increase of the intrinsic conductivities of the nanodroplet clusters. The second term describes the low conducting Stokes transport of charged (monomeric) nanodroplets. The latter is seen to become negligibly small approaching the critical regime as is obvious from the experiments.

Figs. 1 and 2 show fits of Eq. (8) to a representative set of data points yielding reasonable agreement not only with the overall trend of the plots but also with the experimental data.

We emphasise the effect of chain length of the added electrolytes on the onset temperature of the steep increase of the intrinsic conductivities and their distribution with respect to the temperature scale. It might be surprising that the typical strong electrolytes display a similar course of the plot as the lipophilic weak electrolytes. This is probably due to the size of the hydration shell of the former, which is comparable to the size of the lipophilic ions. Hence the free energy of transfer would be comparable for both types of ions [15]. We are well aware that with further decreasing of the temperature, clusters with interconnected networks of chains of nanodroplets in mutual contact will form where the conductivity depends on the connectivity of the system [9], which does not permit quantitative evaluations of the conductivity.

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