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SHORT COMMUNICATION

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# Water droplet charging process in water-in-oil microemulsions: an electrical conductivity study

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**Abstract** The electrical conductivity $\sigma$ of water-in-oil microemulsions formulated with AOT in pentane, heptane, decane and carbon tetrachloride was investigated in a wide range of composition and temperature. Assuming an Arrhenius-type temperature dependence of the conductivity, from the slopes of the linear portions of the plots $\ln(\sigma)$ vs. $1/T$, the equilibrium constant $K$ of the overall kinetic reaction yielding the droplet ionization has been evaluated as a function of the water-to-surfactant molar ratio, $W$. The activation energies of the whole conductivity process lie in the range 25–40 kJ mol$^{-1}$, depending on the characteristics of the oil phase. These values suggest that the ionization of the water droplets, responsible of the observed conductivity, is caused by the exchange of the droplet content ($Na^+$ ions in aqueous solution, deriving from surfactant molecule dissociation), when droplets coalesce and then redisperse.

**Key words** Microemulsions – electrical conductivity

## Introduction

The electrical conductivity properties of water-in-oil microemulsions, in the single phase region, have been extensively investigated during the last few years [1–3] and a well-defined picture of the various mechanisms involved has been drawn. Two different regimes, according to microemulsion composition and temperature, have been evidenced and different theoretical models have been proposed.

In the low-temperature region, below the upper transition temperature, and for low fractional volume of the water droplets (well below the percolation threshold), the electrical conductivity is due to the transport of charged water droplets [4–8], whose ionization is caused by a charging mechanism driven by spontaneous thermal fluctuations. This process provides exchange of the water droplet content when droplets approach each other, fuse to form a short-lived droplet dimer and then redisperse. According to these theories, the migration of charged droplets in an external electric field is the main conductivity mechanism in dilute microemulsions, responsible of the observed electrical conductivity.

At higher temperatures and higher volume fractions, when a clusterization process takes place, a different transport mechanism prevails and, because of charge hopping (surfactant hopping model [9]) or formation of transient water channels [10], a sharp increase in conductivity, over orders of magnitude, is observed. This process has been analyzed as a percolation process and is due to the transition from a conductivity mechanism due to motion of charged water droplets forced by an external field, to a conductivity regime dominated by the motion of charged carriers (surfactant anion) within connected clusters of the water droplets or by motion of surfactant counterions (such as $Na^+$ ions) within water channels, giving rise to water clusters upon opening of the surfactant layers.

Recently, we have studied the electrical conductivity behavior of water-in-oil microemulsions [11] formulated with four different oil phases (three alkanes, i.e. *n*-pentane, *n*-heptane, *n*-decane and carbon tetrachloride) in the one-phase region of the phase diagram, well below percolation, where the conduction is attributed to a charge fluctuation mechanism. Our findings give further support to this view, showing how the proposed charge fluctuation models [4–8] furnish an overall description in good agreement with the experimental results.

Having established that the mechanism responsible for the electrical conductivity in appropriate regions of the phase diagram is that of the charge fluctuation, the detailed process that gives rise to charged droplets, even at low volume fraction, must be further investigated.

As pointed out by Luisi et al. [12], there are two views about the mode by which the charge fluctuation mechanism works, producing charged droplets starting from a complete electroneutral system.

The first mechanism is due to transient fusion of two adjacent droplets to form a short-lived dimer-droplet, where ions (counterions) can randomly redistribute, giving rise to separate charged droplets when two new isolated droplets are formed. The effectiveness of this mechanism depends on the fusion rate constant and on the lifetime of the fused species, in order to allow the aqueous content to be randomly redistributed by diffusion.

The second mechanism involves the diffusion of a surfactant molecule through the bilayer formed by the surfactant tails of two adjacent, but non-fusing, droplets. Furthermore, although improbable, a different mechanism may be proposed, involving ion (counterion) diffusion through the surfactant layer and the oil phase, when droplets are in contact without having coalesced.

All these mechanisms impart the microemulsions with the appropriate degree of ionization to allow the electrical conductivity to be several folds higher than that of the oil phase, as experimentally observed.

However, so far, the mechanism of charge fluctuation in microemulsions remains not completely understood and no conclusive indications emerge to establish which of the two above mechanisms is the preferred one.

To this end, the temperature dependence of the exchange kinetics as viewed from the electrical conductivity properties could furnish some help. With this objective, we have measured the temperature dependence of the low-frequency electrical conductivity of different microemulsions, over the whole single phase region, by varying the water-to-surfactant molar ratio $W$, and consequently the droplet sizes, and by changing the oil component.

In this note, we report on the activation energies $\Delta E$ for the electrical conductivity of the systems investigated, derived by considering the conduction as an activated process following an Arrhenius law. These values, in the range 25–40 kJ $mol^{-1}$, depending on the oil phase, provide strong support for a mechanism involving a kinetic exchange process of the droplet aqueous content as the preferred one.

## Experimental

The electrical conductivity measurements were performed on different AOT/water/oil microemulsion systems for three alkanes, i.e. *n*-pentane, *n*-heptane, *n*-decane and for carbon tetrachloride. The composition of the microemulsions investigated is characterized by the water-to-surfactant molar ratio $W = [H_2O]/[AOT]$, ranging from 2 to 25, and by the fractional volume $\Phi$ of the surfactant-coated water droplets, kept constant at a value of $\Phi = 0.1$, throughout the experiments. AOT [sodium bis(2-ethylhexyl)sulfosuccinate] was purchased from Sigma Chem. Co. [St. Louis, MO] and used as received. The alkanes and $CCl_4$ were supplied by Aldrich, USA. All these chemicals were used without further purification. Deionized water with a conductivity of about 2–5 $10^{-6}\,\Omega^{-1}\,cm^{-1}$ was used for all the sample preparations. The temperature range investigated was within 5 and 65 °C; for some microemulsions, the upper temperature limit was reduced because of the phase separation and the boiling temperature of the oil phase.

The electrical conductivity of the microemulsions was measured as a function of temperature by means of low-frequency Impedance Analyzer Hewlett-Packard mod. 4192A, at the frequency of 10 kHz. In the frequency range up to about 100 kHz–1 MHz, the electrical conductivity of microemulsions does not display any marked dependence on frequency and our measurements thus refer to the low-frequency limit value.

## The microemulsion conductivity as due to charge fluctuation mechanism

Independently of the mechanism of the droplet charging, the electrical conductivity due to the drift of an ensemble of non-interacting water droplets, each of them with an electric charge ($ze$), at concentration $n(z)$, is given by

$$\sigma = \frac{e^2}{6\pi\eta R_d}\sum_z z^2 n(z) \ , \qquad (1)$$

where $\eta$ is the viscosity of the continuous phase, $R_d$ the hydrodynamic radius of the water droplet and the sum is over all possible values of the charges. Assuming that the concentration $n(z)$ of droplets with a charge larger than unity ($z = \pm 1$) is negligible, the average, steady state, electrical conductivity can be written as

$$\sigma = \frac{e^2 z^2}{6\pi\eta R_d} \langle n(z) \rangle \ , \tag{2}$$

where $\langle n(z) \rangle = \langle n^+ \rangle + \langle n^- \rangle$ is the average equilibrium concentration of charged droplets, respectively with $z = +1$ and $-1$. The stoichiometry of the equilibrium and the electroneutrality of the whole system implies that $\langle n^+ \rangle = \langle n^- \rangle$.

The concentration $\langle n^+ \rangle$, or equivalently $\langle n^- \rangle$, is related to the rate coefficients of the equilibrium which yields between uncharged and charged droplets during their Brownian movements.

The process governing the exchange of charge between the water core of two adjacent droplets can be described by two elementary steps, associated with the temporary formation of a transient aggregate and its subsequent breakdown into two separate droplets with a random charge distribution, according to the reaction

$$n_0 + n_0 \underset{k_r}{\overset{k_d}{\Leftrightarrow}} (2n_0) \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} \langle n^+ \rangle + \langle n^- \rangle \ , \tag{3}$$

where the rate constants $k_d$, $k_r$ and $k_1$, $k_{-1}$ refer to the dimer formation and to those dissociations that are effective in the charging process, respectively.

In the steady-state condition, from the appropriate rate equation $\mathrm{d}\langle n^+ \rangle/\mathrm{d}t = 0$, the concentration $\langle n^+ \rangle$ is given by

$$\langle n^+ \rangle = n_0 \sqrt{\frac{k_d k_1}{k_r k_{-1}}} \ , \tag{4}$$

and the electrical conductivity can be written as

$$\frac{\sigma}{\Phi} = \frac{e^2 z^2}{4\pi^2 \eta R_d^4} \frac{1}{2 + \sqrt{\dfrac{k_r k_{-1}}{k_d k_1}}} \ , \tag{5}$$

where $\Phi = (4/3)\pi R_d^3 (n_0 + 2\langle n^+ \rangle)$ is the fractional volume of the surfactant-coated water droplets.

Since the equilibrium constant $K = (k_d k_1 / k_r k_{-1})$ of the overall process can be related to the excess free energy $\Delta E$ associated to the charging of a neutral droplet, according to the relation

$$K \equiv \frac{k_d k_1}{k_r k_{-1}} = \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{6}$$

and assuming for $\Delta E$ the Born energy

$$\Delta E = \frac{e^2 z^2}{4\pi\varepsilon_0 \varepsilon R_d} \ . \tag{7}$$

Eq. (5) leads to be the fundamental relation obtained by Hall [5], when $z$ is limited to $z = \pm 1$. Here, $k_B T$ is the thermal energy and $\varepsilon_0 \varepsilon$ the dielectric constant of the oil phase.

On the other hand, if no invocation is made of any specific mechanism of droplet charging, Eq. (5) can be used to have an evaluation of the equilibrium constant $K$ and hence the free energy $\Delta E$ involved in the process, when the value of the reduced conductivity $\sigma/\Phi$ is experimentally determined.

## Results and discussion

At low volume fraction $\Phi$, well below the percolation threshold and in absence of any relevant droplet aggregation (formation of extended clusters), the mobility of the charged droplets is controlled by the viscosity of the oil phase and their migration under the influence of an external electric field can therefore be described as an activation process analogous to the ion transport in the bulk aqueous phase. In these conditions, the activation energy of the overall charge transport process can be derived from an Arrhenius plot of the electrical conductivity.

At low volume fractions $\Phi$ as those investigated, ($\Phi = 0.1$), all the microemulsion systems studied here behave in absence of any clusterization process and the conductivity varies linearly with the droplet concentration. This behavior, in the case of AOT/water/$CCl_4$ microemulsion, at some selected temperatures, is shown in Fig. 1. The other microemulsion systems behave similarly.

Typical dependencies of the electrical conductivity $\sigma$ as a function of the temperature $T$ for the four microemulsions investigated are shown in Fig. 2. The plots show the region where $\ln(\sigma)$ varies linearly with $1/T$. Deviations from a constant slope generally occur as the temperature and/or the water-to-surfactant molar ratio $W$ increases, indicating that a new process takes place, as the clusterization proceeds. As an example, the full behavior is reported in Fig. 3, in the case of AOT/water/*n*-decane microemulsions, where the conductivity curves are shown over the whole temperature interval investigated, from 5 up to 65 °C. Moreover, in Fig. 3, the intervals where the Arrhenius process holds are also indicated.

In these systems, the dependence of the average radius $R_c$ of the water core on the molar ratio $W$ is given by

$$R_c = \left(\left(\frac{3V}{a_0}\right) W + \frac{3V_H}{a_0}\right) , \tag{8}$$

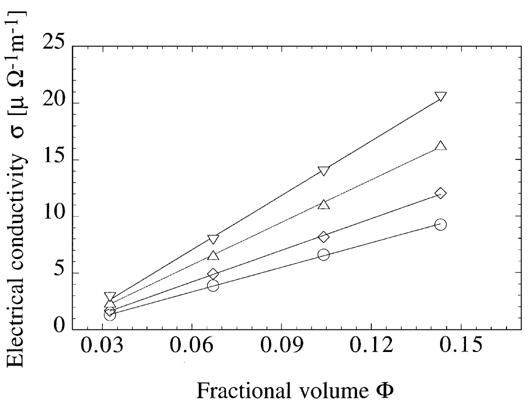


**Fig. 1** The electrical conductivity $\sigma$ of AOT/water/$CCl_4$ microemulsion system as a function of the volume fraction $\Phi$, at some selected temperatures: (○) $T = 10\,°C$; (◇) 20 °C; (△) 30 °C; (▽) 40 °C; The absence of droplet–droplet interactions is revealed by the linear increase of $\sigma$ as a function of $\Phi$

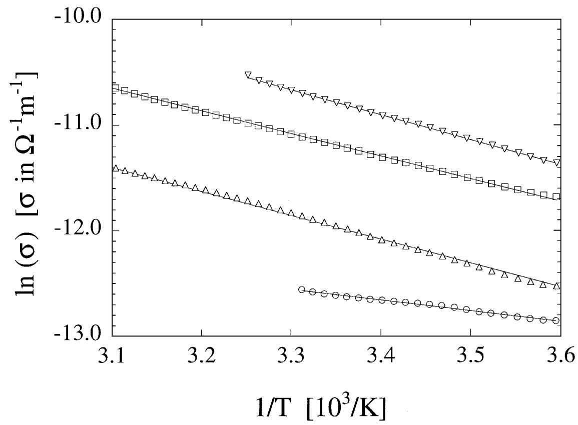
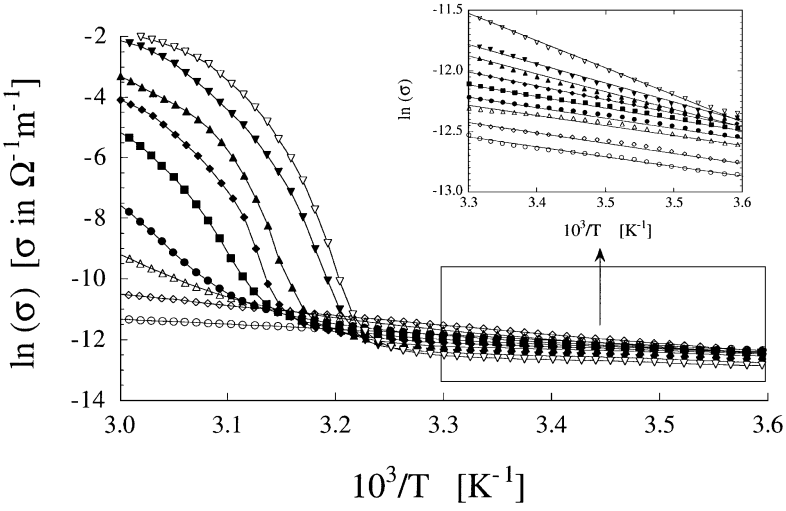


**Fig. 2** Arrhenius plot of the four microemulsion systems investigated at the selected water-to-surfactant molar ratio $W = 7$ and at the fractional volume of the dispersed phase $\Phi = 0.1$. (△) AOT/water/$CCl_4$; (▽) AOT/water/*n*-pentane; (□) AOT/water/*n*-heptane; (○) AOT/water/*n*-decane. From the slopes, the activation energies of the conductive process may be determined

**Fig. 3** Arrhenius plot for AOT/water/*n*-decane microemulsion systems at some selected water-to-surfactant molar ratios $W$ and at the fractional volume of the dispersed phase $\Phi = 0.1$. (○): $W = 3$; (◇): 7; (△): 9; (●): 10; (■): 12; (◆): 14; (▲): 16; (▽): 20. From the slopes, the activation energies of the conductive process may be determined. Deviation from a straight line occurs at higher temperatures and at higher $W$ values, when a different conductive process due to clusterization prevails. The inset shows the region where an activated process described by an Arrhenius law holds



where $V$ is the volume of an individual water molecule, $V_H$ the average volume occupied by a head group and $a_0$ is the area occupied by the surfactant head group. Since the size distribution of the water droplets is well described by the Schultz distribution function, depending on a width parameter $Z$, the root-mean-square deviation of the radius $R_c$ from its mean is given by $\sigma_R = R_c/(1 + Z)^{1/2}$. For the microemulsions studied, the polydispersity index of the droplets has been evaluated, on the basis of neutron scattering measurements, to be relatively small, of the order of $\sigma_R/R_c = \Delta R_c/R_c \approx 0.2$. Hence, to a first approximation, the polydispersity effects can be neglected.

The hydrodynamic radius $R_d$ can be calculated according to the relation

$$R_d = R_c + \delta\ , \tag{9}$$

where $\delta = 1.05\,\text{nm}$ is the length of an AOT molecule without $SO_3^-$ group.

The equilibrium constant $K$ (Eqs. (5) and (6)) or conversely the free energy $\Delta E$ (Eq. (6)), has been evaluated by means of a non-linear least-squares fitting procedure. The results are shown in Fig. 4. As can be seen, microemulsions formulated with alkanes (*n*-pentane, *n*-heptane, *n*-decane) and with carbon tetrachloride behave similarly, the energy $\Delta E$ decreasing monotonically from values of about

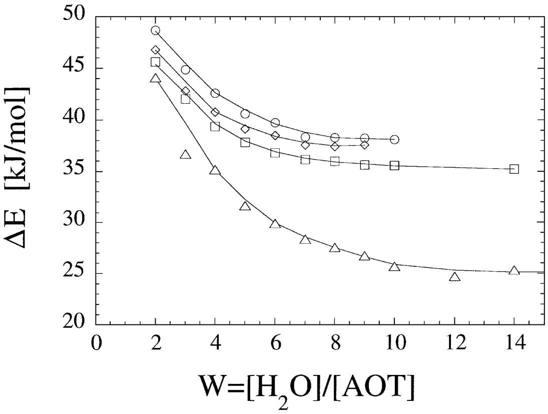


**Fig. 4** The excess free energy $\Delta E$ derived from the linear portion of the plot $\ln(\sigma)$ vs. $1/T$, according to Eqs. (5) and (6), as a function of the water-to-surfactant molar ratio $W$, for the four microemulsion systems investigated: (○): AOT/water/CCl$_4$; (◇): AOT/water/*n*-pentane; (□): AOT/water/*n*-heptane; (△): AOT/water/*n*-decane

45–50 kJ mol$^{-1}$ to values of about 35–40 kJ mol$^{-1}$, in the case of *n*-pentane, *n*-heptane and carbon tetrachloride and to values of about 25 kJ mol$^{-1}$ in the case of *n*-decane, as the water-to-surfactant molar ratio $W$ increases from 2 to 15.

For low values of $W$, i.e. when there are few water molecules for each AOT molecule and therefore for each Na$^+$ ion in the core droplet, the water molecules are preferably involved in the ion hydration (ion salvation) and are tightly bound to the Na$^+$ ion and the whole aqueous environment is quite rigid. For microemulsions in this composition range, the water core of each droplet is relatively small and the hydrated ions (Na$^+$ counterions) are bound to the surfactant layer and are thus immobilized. In these conditions, a larger energetic contribution is required to allow the droplet charging process to be effective. Similar evidences have been observed by Verbeeck et al. [13] for different cations. As $W$ is increased and the amount of water exceeds that of the surfactant headgroup hydration, water begins to form a pool in the core of the droplets and, during the droplet collision to form an encounter pair, is able to exchange quite rapidly from one to another droplet, giving rise to the charge fluctuation mechanism. This picture is clearly evidenced by the initial decrease of $\Delta E$, at low $W$ values, until a constant value is reached at approximately $W = 6$–$7$.

As can be seen in Fig. 4, the value of the energy $\Delta E$ at the first appearance of free water in the droplet cores ranges for all the microemulsions investigated from 35–40 to 25 kJ mol$^{-1}$. These values provide strong support for a mechanism involving droplet ionization as due to Na$^+$ ion exchange during the transient fusion of the water droplets, as consequence of the opening of the interfacial layer. Activation energies of the order of 20–30 kJ mol$^{-1}$, as those approximately found in the systems investigated, fall in the range of activation energy for ions in aqueous medium [14], providing suggestions in favour of the view that the charging of the water droplets occurs when droplets come close enough that they fuse, form a transient dimeric aggregate and then redisperse.

As far as the other mechanisms are concerned, it must be pointed out that both of them (surfactant anion hopping or counterion (Na$^+$ ions) diffusion) require a more energetic contribution than that evaluated from the conductivity behavior in the Arrhenius regime. Diffusion of surfactant counterions, Na$^+$ in this case, through the hydrophobic region in the vicinity of two non-fusing droplets requires energies of the order of 120–150 kJ mol$^{-1}$ [15, 16]. On the other hand, if the droplet ionization mechanism is due to the hopping of surfactant anions from one droplets to another, as in the Huang et al. model [17], the activation energy should be of the order of 70–80 kJ mol$^{-1}$ [18, 19], assuming for the diffusion coefficient of the surfactant in a typical AOT microemulsion a value of $D = 5 \times 10^{-10}$ m$^2$ s$^{-1}$ [19]. On the basis of these estimates, these mechanisms should be discarded.

To evaluate the effectiveness of the charge fluctuation from the solubilizate exchange mechanism between water droplets, the rate constant of the second order chemical reaction yielding droplet coalescence should be known. For water/AOT/oil microemulsion systems, Fletcher et al. [20, 21] found for the rate constant values of the order of $1$–$5 \times 10^7$ l mol$^{-1}$ s$^{-1}$, largely independent of the different indicator reactions investigated (electron transfer, proton transfer and metal–ligand complexation) but dependent on the water-to-surfactant molar ratio $W$ and on temperature. On the other hand, using the steady-state solution of the diffusion problem [22], the rate constant for the encounters between a primary particles and those surrounding it can be evaluated to be of the order of $5 \times 10^{11}$ l mol$^{-1}$ s$^{-1}$. This means that one in about $10^3$ encounters results in a randomization of the ion content between droplets, i.e. only the more energetic collisions are able to establish a water channel through which ions (counterions) can diffuse and requilibrate.

The dependence of the observed asymptotic value of $\Delta E$ on the chain length of the oil component reflects the increasing flexibility, and thus the higher permeability, of the resulting interfacial layer. For example, the one-phase stability region of AOT/water/oil microemulsions shifts towards lower temperatures at higher alkane chain length, indicating an increased interaction between water droplets. As pointed out by Huang et al. [17], as the oil chain length increases, the difference between the oil molecules and the surfactant decreases, thus favoring an oil–surfactant packing that increases the attraction between droplets and they coalesce. This effect is particularly evident with *n*-decane whose chain length is almost similar to the chain length of the surfactant molecule. On the other hand, in the case of carbon tetrachloride, where the interdigitation of the surfactant tails and the solvent molecules is sterically unfavourable, the process requires a little higher energy.

Further investigations over a wide range of droplet radii with oil phases of different chemical properties are needed to draw an ultimate conclusion and to put the different behaviors observed in perspective.

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