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Electric conductivity near the percolation transition of a nonionic water-in-oil microemulsion

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Abstract

The electric conductivity of a nonionic water-in-oil microemulsion has been measured in the presence of small amounts of carrier electrolyte. Two distinct regimes can be distinguished: the conductivity increases linearly for small nanodroplet concentration, while it decreases above a critical value. The qualitative change occurs close to a concentration where the system is known to have formed a system-spanning *nonconducting* cluster of nanodroplets. This behaviour of the conductivity is shown to agree well with predictions of percolation theory for aggregating charged nanodroplets.

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1. Conductometric measurements in microemulsions

Measuring the electric conductivity of ionic [1–3] water-in-oil (W/O) microemulsions has become a standard technique. Under appropriate conditions, conductometry allows one to extract information about the concentration of charge carriers, that is, the degree of dissociation, or about the size of the carriers via their mobilities. For not too small concentrations of surfactant (S) the conductivity is dominated by Stokes transport of nanodroplets or monomers, i.e., individual nanometer-sized water droplets separated by surfactants from the surrounding oil. The formation of a system-spanning (or ‘infinite’) cluster in ionic microemulsions, for example, is marked by a steep increase of the conductivity: the Stokes process is superseded by the hopping of charged surfactants from one droplet of the cluster to another [4]. Even aspects of the elementary

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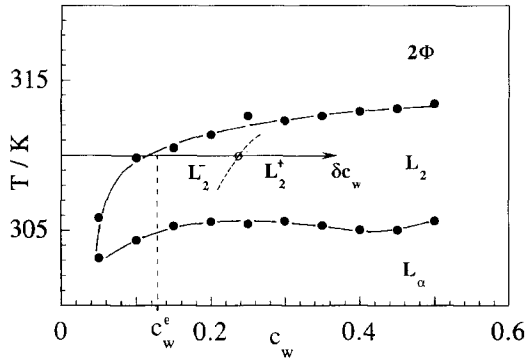


Fig. 1. Phase diagram of the W/O microemulsion. The electric conductivity has been measured for parameter values corresponding to a segment of the horizontal line in the L_2 phase of the system. The droplet concentration δc_w is given relative to the emulsification failure at c_w^e , close to the boundary between the phase 2Φ and the microemulsion L_2 . The open circle shows the critical concentration of nanodroplets, δc_w^* , where the behaviour of the electric conductivity of the sample indicates the formation of a system-spanning cluster. Presumably, there is a whole *line* (dashed) where percolation occurs, dividing the L_2 phase into two parts, L_2^\pm , which are distinguished by the (non-) existence of an ‘infinite’ cluster.

process of charge formation in micromulsions become accessible experimentally [5]. For ionic surfactants, charge formation is driven by fluctuation processes of intrinsic electrolytes.

The purpose of this work is to study the conductivity of a specific W/O microemulsion with *nonionic* surfactant molecules, that is, a ‘nonionic microemulsion.’ Its phase diagram, shown in Fig. 1, is easily determined visually. Three domains can be distinguished: the monophasic microemulsion L_2 , the two-phase domain 2Φ , where water and a three-component phase coexist, and the lamellar, lyophilic liquid–crystal phase, denoted by L_α . Emulsification sets in for concentrations c_w of water and surfactant above c_w^e , that is, close to the boundary between the phase 2Φ and the microemulsion L_2 . Below this value nanodroplets have not yet formed corresponding to an ‘emulsification failure’ [6,7]. From now on, droplet concentration and conductivity will be given relative to their values in this state. Thus, one has $c_w = c_w^e + \delta c_w$ and $\sigma = \sigma^e + \delta\sigma$, where at temperature $T = 310$ K numerically one has $c_w^e \simeq 0.13$ and $\sigma^e \simeq 3.5 \times 10^{-7} (\Omega\text{m})^{-1}$.

In addition, the presence of a system-spanning cluster has been detected for this system [8] by measuring the dynamic viscosity as a function of the volume fraction of *n*-octane, $(1 - \delta c_w)$. The viscosity increases sigmoidally with increasing δc_w and shows an inflection point at about $\delta c_w^* = 0.15$. Up to this point the dependence of the viscosity on the concentration follows the Saitô–Bedeaux relation [9,10] which is a strong indication that a system-spanning cluster of nanodroplets has formed.

Nanodroplets are known to exist as individual entities over the whole concentration range studied here as has been shown experimentally for similar systems [11,12]. However, the surfactants being *nonionic* [13], small amounts of an electrolyte must be added to provide the charges necessary for the charge transport. It is important to note

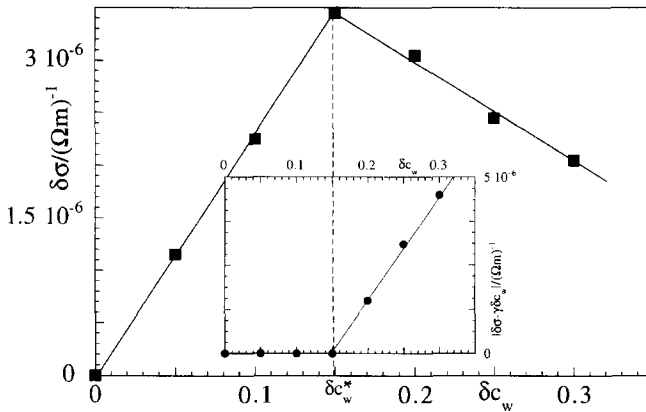


Fig. 2. Measured values of the specific electric conductivity $\delta\sigma$ against the concentration of nanodroplets, δc_w . Inset: Deviation $|\delta\sigma - \gamma\delta c_w|$ of the conductivity $\delta\sigma$ from a linear dependence on the concentration δc_w with a slope $\gamma = 2.3 \times 10^{-5} (\Omega\text{m})^{-1}$ as a function of the concentration δc_w .

that the infinite cluster of the *nonionic* microemulsion studied here is *nonconductive*: the surfactants do not provide charges to be transported easily along the cluster.

The experiments reported here correspond to parameter values on the horizontal line in the L_2 phase of Fig. 1, with δc_w varying between 0 and 0.3. The measured values of the isothermal specific electric conductivity $\delta\sigma$ are shown in Fig. 2 as a function of the concentration of the aqueous nanodroplets, δc_w . The conductivity increases linearly with the weighed-in concentration of the nanodroplets, reaches a maximum at a critical value, δc_w^* , and decreases strongly. The inset shows the deviation of the conductivity $\delta\sigma$ from a linear dependence on δc_w with a slope $\gamma = 2.3 \times 10^{-5} (\Omega\text{m})^{-1}$.

The presence of a macroscopic cluster will again strongly influence the conductivity of a microemulsion if the charge transport is solely due to the motion of finite aggregates through the viscous medium. Its formation at the critical concentration δc_w^* effectively immobilizes a substantial part of the charge carriers: the monomers being attached to the system-spanning cluster can no longer contribute to the Stokes transport. This picture being correct, a reasonable description of the measurements should be possible in terms of percolation theory. The model presented below attempts to describe the conductivity near the critical concentration δc_w^* in terms of a percolation transition.

2. Experimental

Microemulsions were prepared by mixing appropriate weight fractions of surfactant, brine (1 mol/m³ NaCl in water), and oil. C₁₄E₅ (pentakis(ethyleneglycol)mono (tetradecyl)-ether) (purity 99.8%) and *n*-octane(oil) were obtained from Fluka; water was bidistilled. The weight fractions $(W + S)/(W + S + O) = c_w$ were varied, while keeping the droplet radius $R_1 \cong 4.2$ nm (as determined from quasi-elastic light scattering [14]) constant throughout the measurements, that is, $W/S = 1$. The experiments

were performed slightly above room temperature, $T = 310 \pm 0.1$ K. Conductivity measurements were carried out with a plate condenser-type glass cell equipped with two rectangular Pt-electrodes of $5 \text{ mm} \times 10 \text{ mm}$ and a gap width of 2 mm. Conductance was determined by an auto-balancing bridge (Radiometer, Copenhagen, type CDM 83) between $2 \times 10^{-8} \Omega^{-1}$ and $1.3 \Omega^{-1}$ at 73 Hz and 50 kHz, respectively.

3. Percolation model

The occurrence of a phase transition in the microemulsion is suggested by the behaviour of the conductivity as shown in the inset of Fig. 2. Qualitatively, it reminds one of the magnetization curve of a ferromagnet: below/above some critical value a measurable quantity vanishes while above/below this value it starts to increase with a nonzero slope. A simple model is set up, based on the percolation of nanodroplets, in order to explain the tent-shaped dependence of the conductivity on the droplet concentration. Our knowledge of the structure of the microemulsion is condensed into the following assumptions.

- (i) Throughout the concentration range studied here, the monomers, i.e. the individual nanodroplets constitute the *basic units* for the process of transport.
- (ii) The electrolyte dissolved in the water core of the droplets provides the charges on the monomers. There is a *fixed number* of neutral, positively and negatively charged droplets when the measurement of the conductivity is performed. In the actual experiment, about every other of the droplets is charged as follows from thermodynamics [4].
- (iii) Each nanodroplet carries *at most one* (positive or negative) charge.
- (iv) Any number of monomers may form an *aggregate*, including possibly a system-spanning cluster. The equilibrium between aggregates of different size is *dynamic*: for given temperature T and concentration δc_w , the distribution over all possible sizes is well-defined only when averaged over some time interval.
- (v) The charge on the droplets does *not* influence the formation of aggregates. This is reasonable since the Debye radius L_D (being a measure for the scale of polarization effects) is much smaller than the radius R_1 of a monomer.
- (vi) The total *charge of an aggregate* is solely due to the charges of the monomeric droplets which form it.
- (vii) The conductivity of the sample results from the *motion of charged aggregates* through the dielectric medium with viscosity η , while the ions of the electrolyte are not able to travel as such through the oil. The Stokes transport of the aggregates has a preferred sense of direction which is provided by the weak external electric field.

In a first step, a general expression for the conductivity of a microemulsion will be derived. It depends on the size distribution of the aggregates which, in turn, is a function of the concentration δc_w . In a second step, the actual behaviour of the conductivity will be determined under the assumption that the distribution of the aggregates over the sizes is governed by percolation theory.

When dispersed in a medium with viscosity η , spherical objects with radius R and charge $q = ze$ (with e the elementary unit of charge and z the valency) give rise to a conductivity σ_0 given by

$$\sigma_0 = \frac{q^2}{6\pi\eta R}. \quad (1)$$

The various contributions to the total conductivity of the microemulsion stem from differently sized aggregates carrying different amounts of charge. Consider first an aggregate which consists of s monomers. Its valency $z_{s,k} = k$ is determined by the charges of the monomers which form it and, therefore, takes on values between $\pm s$. Denote the probability for $z_{s,k}$ charges on an s -aggregate by p_k^s ; then the s -aggregates contribute an amount

$$\sigma_s = \frac{e^2}{6\pi\eta R_s} \sum_{k=0}^s z_{s,k}^2 p_k^s \equiv \frac{q_{\text{eff},s}^2}{6\pi\eta R_s}, \quad s = 1, 2, \dots, \quad (2)$$

to the conductivity, where $R_s \propto s^\rho$ is the hydrodynamic radius of an s -aggregate, with $\rho = \frac{1}{3}$ for perfect spherical aggregation. The second equality simply says that the conductivity σ_s associated with s -aggregates can *effectively* be taken into account by a charge $q_{\text{eff},s} = e(\sum_{k=0}^s z_{s,k}^2 p_k^s)^{1/2}$. The distribution p_k^s of valencies $z_{s,k}$ on s -mers follows from combinatorics: as shown in Appendix A, one has

$$q_{\text{eff},s}^2 = 2\alpha s e^2, \quad (3)$$

if a fraction 2α of the monomers is charged and the remaining fraction $(1 - 2\alpha)$ is neutral. It is important to note that the charge $q_{\text{eff},s}^2$ is linear in the number of constituents, s . Thus, the charge associated with s -aggregates grows faster with s than the radius R_s .

The total conductivity $\delta\sigma$ of the microemulsion is obtained by summing over all contributions σ_s multiplied with the probability P_s which governs the distribution of s -aggregates:

$$\delta\sigma = \sum_{s=1}^{\infty} \sigma_s P_s = \frac{1}{6\pi\eta} \sum_{s=1}^{\infty} \frac{q_{\text{eff},s}^2}{R_s} P_s. \quad (4)$$

If only one type of the aggregates of size s_0 is present, $P_s = \delta_{s,s_0}$, all with the same charge, $q_{s,k_0} = k_0 e$, corresponding to $p_k^s = \delta_{kk_0}$, one obtains $\delta\sigma = e^2 k_0^2 / (6\pi\eta R_{s_0})$, agreeing with Eq. (1). Using Eq. (3), the total conductivity is found to be given by

$$\delta\sigma = \frac{\alpha e^2}{3\pi\eta} \sum_{s=1}^{\infty} P_s s^{1-\rho} \equiv \frac{\alpha e^2}{3\pi\eta} \langle s^{1-\rho} \rangle; \quad (5)$$

it is thus proportional to the $(1 - \rho)$ th moment of the size distribution P_s of the aggregates.

The link to percolation theory [15] is now established by claiming that the concentration δc_w of nanodroplets in the microemulsion plays the same role as does the

occupation probability p of a site in three-dimensional percolation:

$$\delta c_w \sim p. \quad (6)$$

Then the distribution P_s of aggregates must be identified with the cluster numbers,

$$P_s \sim n_s, \quad (7)$$

the dependence of which on the occupation probability p follows from percolation theory. Therefore, the conductivity is seen to be proportional to the $(1 - \rho)$ th moment of the cluster numbers:

$$\delta\sigma(\delta c_w) \propto M_{1-\rho}(\delta c_w), \quad (8)$$

thus being a well-defined function of the concentration. This relation is the central result of the approach presented here.

Since $\rho = 0.4$ at the critical concentration, one immediately obtains an upper bound for the conductivity:

$$\delta\sigma \propto M_{0.6} < M_1 = \delta c_w - \mathcal{P}, \quad (9)$$

the last equality in Eq. (9) following from a relation being generally valid in percolation theory: $\sum_{s=1}^{\infty} n_s s = p - \mathcal{P}$. It relates the cluster numbers n_s with the probability $\mathcal{P}(p)$ that a given site is connected to the infinite cluster, also known as cluster strength. It is zero below a critical concentration p^* , while it strongly increases for concentrations p above p^* .

For the microemulsion, it follows from Eq. (9) that the conductivity $\delta\sigma$ increases (almost) linearly with the concentration if $\delta c_w < \delta c_w^*$, since no system spanning cluster has formed yet, $\mathcal{P} = 0$. Above δc_w^* , the conductivity strongly decreases because there is an infinite cluster, $\mathcal{P} > 0$: the monomers attached to the infinite cluster can no longer contribute to the charge transport. The increase of available carriers due to larger values of the concentration δc_w does by no means compensate for the resulting decrease of the overall conductivity. An important aspect of Eq. (9) is that the conductivity does *not* diverge at δc_w^* which would clearly contradict the measured values for $\sigma(\delta c_w)$ in Fig. 1; the exponentially fast decrease of the cluster numbers n_s as a function of s suppresses the linear increase of σ_s , Eq. (3). If, however, the conductivity were given by a moment M_k with $k \geq 1.2$ instead of $k \simeq 0.6$, a divergence would have been encountered.

Thus, the overall behaviour of $\delta\sigma(\delta c_w)$ is compatible with its upper bound, Eq. (9), at least in the concentration range studied here, that is, for values of δc_w not much larger than the critical one, δc_w^* . Nevertheless, it is not reasonable to conclude that the first moment M_1 (instead of $M_{1-\rho}$) indeed approximates well the conductivity $\delta\sigma$. The exponent for the strength of the infinite cluster \mathcal{P} near the critical concentration is known to have the value $\beta = 0.4$, which, however, does *not* agree with the almost *linear* increase of the order parameter as shown in the inset of Fig. 2. In general, the

non-analytic part of the k th moment is given by

$$M_k(\delta c_w) \propto |\delta c_w^* - \delta c_w|^{(\tau-1-k)/\sigma}, \quad (10)$$

with universal exponents $\tau=2.2$ and $\sigma=0.45$ [15]. If $k=0.6$ is used here, better agreement with the observed linear dependence of the order parameter \mathcal{P} on δc_w near δc_w^* results:

$$\delta \sigma(\delta c_w) \propto M_{0.6} \propto (\delta c_w^* - \delta c_w)^{1.3}, \quad \delta c_w > \delta c_w^*. \quad (11)$$

A strictly linear increase would follow for $k=\frac{3}{4}$, corresponding to $\rho \sim \frac{1}{4}$. This clearly does not agree with $\rho=\frac{1}{3}$ describing the nonfractal growth of large clusters in three dimensions. However, it is not obvious whether one can indeed identify the typical radius of aggregates above δc_w^* with the effective hydrodynamic radius R_s as it has been done in the present derivation.

4. Conclusions

A simple percolation model of aggregating nanodroplets has been shown to qualitatively describe conductometric measurements in the L_2 phase of the nonionic microemulsion. However, no attempt was made to determine quantitatively the measured conductivity. It is worthwhile to point out that there are *no* freely adjustable parameters in this approach. In this way, independent evidence is provided for a system-spanning cluster the existence of which had been indicated earlier from viscosity measurements.

This result suggests to modify the phase diagram of the microemulsion as follows. The mechanism described here is expected to work also for different temperatures, as long as one remains in the L_2 phase (cf. Fig. 1). Thus, a system-spanning cluster should as well form for temperatures slightly above and below $T=310$ K. Consequently, a *line* (shown dashed) of critical concentrations $\delta c_w^*(T)$ will exist, defined by the maximum values of the conductivity $\sigma(\delta c_w)$. The formation of large aggregates is probably hampered for higher temperatures leading to a positive slope of the critical line as a function of concentration. Therefore, we suggest a division of the L_2 phase into two distinct regions, L_2^- and L_2^+ , corresponding to the nonexistence and existence, respectively, of a system-spanning cluster in the microemulsion. This modification of the phase diagram conforms with the experience that microemulsions are highly complicated systems depending sensitively on slight variations of parameters such as temperature or the concentration of their constituents.

Appendix A

Suppose a fraction α_0 of all isolated droplets are neutral and the remaining monomers (fraction $1-\alpha_0$) either carry a single positive charge, α_+ , or a single negative charge,

α_- . One has $\alpha_0 + 2\alpha = 1$, since from electro-neutrality it follows that $\alpha_+ = \alpha_- (\equiv \alpha)$. It will be shown now that by random association of s monomers the effective (squared) charge of these aggregates is given by

$$q_{\text{eff},s}^2 = 2\alpha s e^2 \quad (12)$$

with $0 \leq \alpha \leq 1/2$.

For simplicity, consider the case $\alpha = \frac{1}{2}$ first, i.e., there are only charged droplets, $\alpha_0 = 0$. The probability p_k^s to encounter an aggregate with valency $z_{s,k} = k$, $k = -s, -s+1, \dots, s$, follows from combinatorics as

$$P_{k=s-2m}^s = \frac{1}{2^s} \binom{s}{m}, \quad m = 0, 1, \dots, s. \quad (13)$$

Formally, this is easily seen from the equality

$$\frac{1}{2^s} (x + x^{-1})^s = \frac{1}{2^s} \sum_{m=0}^s \binom{s}{m} x^{s-2m}, \quad (14)$$

where x is a continuous variable. Associating a positive (negative) charge with each positive (negative) power of x when multiplying out the left hand side, the coefficient of the term x^{s-2m} is proportional to the number of combinations giving a total charge $s - 2m \equiv k$. The advantage of Eq. (14) is that one can use it to calculate arbitrary moments of the distribution defined by p_k^s . The vanishing of the first moment,

$$\sum_{k=-s}^s z_{s,k} p_k^s = \sum_{m=0}^s (2s - m) P_{2s-m}^s = 0, \quad (15)$$

follows immediately from taking the first derivative of Eq. (14) with respect to x , multiplying by x and evaluating both sides for $x = 1$:

$$\langle k \rangle = \sum_{k=-s}^s k p_k^s = \frac{1}{2^s} [x \partial_x (x + x^{-1})^s]_{x=1} = 0, \quad (16)$$

where $\partial_x \equiv d/dx$. Similarly, the second moment is found from appropriate differentiations and evaluation at $x = 1$:

$$q_{\text{eff},s}^2 = \sum_{k=-s}^s q_{s,k}^2 p_k^s = e^2 \left[\sum_{m=0}^s (2s - m)^2 P_{2s-m}^s x^{s-2m} \right]_{x=1} \quad (17)$$

$$= \frac{e^2}{2^s} [(x \partial_x)^2 (x + x^{-1})^s]_{x=1} = s e^2, \quad (18)$$

in agreement with Eq. (12) for $\alpha = \frac{1}{2}$.

When neutral droplets are present, $\alpha_0 \neq 0$, a similar line of reasoning can be used starting from the relation

$$\frac{1}{3^s} (\alpha_0 x^0 + \alpha (x + x^{-1}))^s = \frac{1}{3^s} \sum_{k_0+k_++k_-=s} \binom{s}{k_0, k_+, k_-} \alpha_0^{k_0} \alpha^{k_++k_-} x^{k_+-k_-}, \quad (19)$$

where the sum is over all integers k_0 and k_{\pm} being positive or zero; the binomials are replaced by the trinomial coefficients. When collecting all factors multiplying the powers $x^{k_+ - k_-}$ with $k = k_+ - k_-$ fixed, one obtains the probability $p_k^s(\alpha)$ to have an s -aggregate with total charge $q_{s,k} = ek$. It reads explicitly

$$p_k^s(\alpha) = \frac{1}{3^s} \sum_{k_0=0}^s \binom{s}{k_0, (s-k_0+k)/2, (s-k_0-k)/2} \alpha_0^{k_0} \alpha^{s-k_0} \quad (20)$$

$$= \frac{s!}{3^s} \sum_{k_0=0(1)}^{s-k} \left[k_0! \left(\frac{1}{2}(s-k_0+k)! \right) ((s-k_0-k)!) \right]^{-1} \alpha_0^{k_0} \alpha^{s-k_0}, \quad (21)$$

where k_0 is summed over even (odd) values only, if $(s-k)$ is even (odd). The moments of this distribution can be obtained by arguments identical to those given above. Electro-neutrality is again fulfilled, and the effective charge of s -aggregates is calculated as

$$q_{\text{eff},s}^2 = \frac{e^2}{3^s} [(x\partial_x)^2 (\alpha_0 x^0 + \alpha(x+x^{-1}))^s]_{x=1} = 2\alpha s e^2, \quad (22)$$

as has been claimed above.

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