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Fluctuation mechanism of the dielectric polarization of water-in-oil microemulsions with ionic surfactant

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A statistical model is proposed to describe the dielectric polarization of ionic microemulsions at a region far below percolation in which the microemulsions consist of spherical single droplets with water in the central core surrounded by a layer of surfactant molecules. The model describes the effect of temperature and dispersed phase content on the behavior of the dielectric polarization of ionic water-in-oil microemulsions and explains the experimentally observed increase of the static dielectric permittivity as a function of temperature. The microemulsions formed with surfactant sodium bis(2-ethylhexyl) sulfosuccinate have been analyzed with the help of this model. The systems are considered to consist of nanometer-sized spherical noninteracting water droplets of equal size with negatively charged head groups, staying at the interface, and positive counterions, distributed in the electrical diffuse double layer of the droplet interior. It is shown that the droplet polarizability is proportional to the mean-square fluctuation dipole moment of the droplet. This mean-square dipole moment and the corresponding value of the dielectric increment depend on the equilibrium distribution of counterions within a diffuse double layer. The density distribution of ions is determined by the degree of the dissociation of the ionic surfactant. The relationship between the dielectric permittivity, the constant of dissociation of surfactant, the content of the dispersed phase, and the temperature has been ascertained.
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I. INTRODUCTION

The microemulsions formed with the surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT), water, and oil are widely investigated systems, the dynamics, phase behavior, and structure of which are well known [1–5]. In the L_2 phase these microemulsions can consist of nanometer-sized spherical droplets with water in the central core surrounded by a layer of surfactant molecules over a wide temperature range. The droplets are fairly monodisperse, with size polydispersity of the order of 10%, and the size depends only weakly on temperature [6]. The surfactant molecules have their hydrophilic head groups facing the water and their hydrophobic tails oriented towards the continuous oil phase. Molecules of AOT can dissociate into anions containing negatively charged head groups SO_3^- staying at the interface and positive counterions Na^+ distributed in the droplet interior.

In our prior research [7–9], the dielectric relaxation, electric conductivity, and diffusion properties of the ionic microemulsions were investigated in the broad temperature region. In particular, it was shown that ionic microemulsions start to exhibit percolation behavior that is manifested by a rapid increase in the static dielectric permittivity ε and electrical conductivity σ when the temperature reaches the percolation onset T_{on}. The appearance of the percolation reveals that in the region $T > T_{\text{on}}$ the droplets form transient clusters. When the system approaches the percolation threshold T_p, the characteristic size of such clusters increases, leading to the observed increase of σ and ε. We defined [7] *the percolation onset* as the temperature at which the microemulsion starts to display a scaling behavior for conductivity and dielectric permittivity (because of the coupling of droplets and formation of fractal clusters) and *the percolation threshold* as the temperature corresponding to the formation of the first infinite cluster of droplets.

Below the percolation onset, both the conductivity σ and static dielectric permittivity ε of the microemulsions also increase as a function of the volume fraction of droplets φ and/or temperature T. However, this increase is not particularly significant, as it is within the percolation region [5–7,10,11].

It was shown [12,13] that the increase of the conductivity of ionic microemulsions versus temperature and volume fraction of droplets below the percolation onset ($T < T_{\text{on}}$) can be described by the charge fluctuation model. In this model, the conductivity is explained by the migration of charged aqueous noninteracting droplets in the electric field. The droplets acquire charges owing to the fluctuating exchange of charged surfactant heads at the droplet interface and the oppositely charged counterions in the droplet interior. The conductivity is then proportional to the temperature and volume fraction $\sigma \sim \varphi T$.

Unlike the mechanism of temperature increase of conductivity below the percolation onset, the temperature behavior of the static dielectric permittivity of ionic microemulsions below percolation has been puzzling. Since the static dielectric permittivity of liquids ε is proportional to the macroscopic mean-square dipole moment $\langle M^2 \rangle$ of the system unit volume and inversely proportional to the temperature $\varepsilon(T \sim \langle M^2 \rangle / T$ [14]), the value of the mean-square dipole moment of a droplet must grow faster than the linear function of temperature in order to provide the experimentally monitored temperature increase of the dielectric permittivity. In particular, the observed behavior of ε has been explained in terms of aggregation of the microemulsion droplets [15]. In contrast, we have recently shown that the experimentally observed temperature increase of the dielectric polarization and the macroscopic mean-square dipole moment $\langle M^2\rangle$ in the microemulsions in the nonpercolating region is not related to the aggregation [16]. The experimental temperature behavior of ε is related to the temperature dependence of $\langle M^2\rangle$ of noninteracting and therefore nonaggregating droplets dispersed in oil. This dipole moment is associated with movements of ions and it is modulated by the temperature dependence of the dissociation of the ionic surfactant.

The contribution of ion movements to the total dielectric polarization has been taken into account in the analysis of the static [17] and dynamic [18] dielectric properties of ionic microemulsions consisting of noninteracting and therefore nonaggregating droplets dispersed in oil. These theoretical models are based on the use of the Poisson-Boltzmann equation describing the distribution of the counterions in the electric double layer [18] and on the analysis of ion fluxes caused by the potential and concentration gradients [17]. The temperature behavior of static dielectric permittivity of water-in-oil microemulsions with ionic surfactant below percolation has not been analyzed in [17] and [18]. This behavior of ε has been explained in our paper [16] in terms of the model of the fluctuation dipole moment.

Despite being a big step forward in the understanding of the dielectric behavior observed in ionic microemulsions, the practical utility of these models is restricted since the results were obtained only numerically and cannot be presented in terms of simple analytical relationships. The purpose of this paper is to develop further the model of the fluctuation mechanism of dielectric polarization. We will elaborate a statistical approach based on the determination of the average droplet polarization following the Boltzmann distribution function. The analytical solution of the Poisson-Boltzmann equation will be used for a calculation of the mean-square dipole moment of a droplet. This approach enables us to present the dielectric parameters of ionic microemulsions as functions of both the temperature and composition of the system. The various types of approximate relationships will be derived for the mean-square dipole moment of a droplet and for the dielectric permittivity.

II. MODEL OF DIELECTRIC POLARIZATION OF IONIC MICROEMULSIONS

A. Static dielectric constant of ionic microemulsions

We can calculate the dielectric permittivity of an ionic microemulsion in a general way from its description by treating it as a monodispersed system consisting of spherical water droplets dispersed in the oil medium. In this way the system is considered as a homogeneous specimen consisting of a number of charges and/or dipoles, each of which is described in terms of its displacement from the position of its lowest energy level. The dielectric permittivity ε of the system can be derived [14] in terms of the dielectric polarization P and/or the total electric dipole moment M of some macroscopic volume V in the presence of the macroscopic electric field E as

$$\varepsilon-1=\frac{4\pi P}{E}=\frac{4\pi M}{VE}. \tag{1}$$

In the case of ionic microemulsions the total electric dipole moment M can be represented as a sum of the two contributions associated with the moment M_E due to displacements of mobile ions in the diffuse double layer and the moment M_{mix} due to all other displacements in the mixture. We note that M_{mix} is related to the contributions from various processes of polarization in the microemulsion that are treated as a heterogeneous system composed of various components. Thus, for the calculation of M_{mix} the interfacial polarization mechanism has to be taken into account. A reorientation of AOT and free and bound water molecules should also contribute in the dielectric polarization of the system.

Equation (1) can be specialized by separating the contribution to ε due to the processes of polarization of components and treating them on a macroscopic basis in terms of the dielectric permittivity $\varepsilon_{\text{mix}}=1+4\pi M_{\text{mix}}/VE$. Hence Eq. (1) becomes

$$\varepsilon-\varepsilon_{\text{mix}}=\frac{4\pi M_E}{VE}. \tag{2}$$

The dielectric permittivity due to the polarization of heterogeneous system ε_{mix} can be taken into account by the model of interfacial polarization. Since each droplet consists of a water core surrounded with a surfactant layer in a continuous phase made of oil, the effect of the interfacial polarization can be accurately regarded by using a Maxwell-Wagner mixture formula (one-shell model [19]).

A component of the total dipole moment due to ions M_E is a projection of the average macroscopic dipole moment $\mathbf{M}$ of the volume V in the direction of the macroscopic field $\mathbf{E}$. Since $\mathbf{M}=\sum_i\boldsymbol{\mu}_i$, where $\boldsymbol{\mu}_i$ is the dipole moment of the ith droplet due to the distribution of charges in the droplet, and if θ_i is the angle between $\boldsymbol{\mu}_i$ and $\mathbf{E}$, then M_E can be given by

$$M_E=\frac{\langle\Sigma_i^N(\boldsymbol{\mu}_i\cdot\mathbf{E})\rangle}{E}=\sum_i^N\langle\mu_i\cos\theta_i\rangle \tag{3}$$

For the identical water droplets dispersed in nonpolar oil medium, one has $M_E=N\mu_E$, where N is the number of droplets in the volume V and μ_E represents the average value of the projection of the dipole moment of a droplet in the direction of the macroscopic electric field $\mathbf{E}$. By using the averaging procedure with the Boltzmann distribution function similar to that in [14] for calculation of μ_E, we obtain

$$\mu_E=\frac{\langle\mu^2\rangle}{3k_BT}E_d, \tag{4}$$

where $\langle\mu^2\rangle$ is the mean-square dipole moment of a droplet in the equilibrium in the absence of the electric field, E_d is the electric field inside the droplet, T is the temperature, and k_B is the Boltzmann constant.

The electric field inside a droplet due to outside sources E_d can be calculated from the electrostatic principles [14] as a field inside the sphere (water core of the droplet) inserted in the other sphere selected in the specimen (volume V). It reads

$$E_d\approx\frac{3\varepsilon}{2\varepsilon+\varepsilon_{\text{mix}}}\frac{3\varepsilon}{2\varepsilon+\varepsilon_w}E, \tag{5}$$

where ε_w is the dielectric permittivity of water. In this approach we neglected the contribution of the thin surfactant film surrounding the water core. As it is commonly accepted [14], the electric fields due to the charges in the volume V are considered to be negligibly small in comparison to the value of the macroscopic field E.

Hence, inserting Eq. (4) into Eq. (2) and using Eq. (5) leads to the equation for obtaining the dielectric permittivity of ionic microemulsions ε,

$$\frac{(\varepsilon-\varepsilon_{\text{mix}})(2\varepsilon+\varepsilon_{\text{mix}})(2\varepsilon+\varepsilon_w)}{\varepsilon^2}=\frac{12\pi N_0\langle\mu^2\rangle}{k_BT}, \tag{6}$$

where $N_0=N/V$ is the concentration of droplets. On the assumption of the spherical shape and monodispersed droplets, N_0 can be replaced in favor of the volume fraction of the droplets φ by using the relation $\varphi=V_dN_0$, where $V_d=\frac{4}{3}\pi R_d^3$ (R_d is the radius of the surfactant-coated water droplet), as

$$\frac{(\varepsilon-\varepsilon_{\text{mix}})(2\varepsilon+\varepsilon_{\text{mix}})(2\varepsilon+\varepsilon_w)}{\varepsilon^2}=\frac{9\varphi\langle\mu^2\rangle}{R_d^3k_BT}. \tag{7}$$

Relation (7) establishes a dependence of the dielectric permittivity of a microemulsion on the temperature T, volume fraction of droplets φ, and apparent dipole moment of a droplet $\mu_a=(\langle\mu^2\rangle)^{1/2}$.

B. Fluctuating dipole moment of a droplet

For a calculation of the mean-square dipole moment of a droplet $\langle\mu^2\rangle$, the theoretical development is carried out within the framework of the following assumptions. (a) The droplets are considered as identical and the interaction of the droplets is neglected. (b) A nanodroplet contains N_a surfactant molecules, N_s of which are dissociated. For electroneutrality the numbers of the negatively charged surfactant molecules N and the number of positively charged counterions N^+ are equal, i.e., $N^+=N^-=N_s$. (c) The ions are treated as point charges. (d) The average spatial distribution of counterions inside the droplets is continuous and governed by the Boltzmann distribution law. (e) All the negatively charged surfactant molecules are assumed to be located in the interface at the spherical plane of radius R_w, corresponding to the radius of the droplet water pool. The simplifications considered in the present work are commonly used in similar problems for the description of electrostatics of ionic microemulsions [17,20,21].

In the model we describe a single droplet in the spherical coordinate system shown in Fig. 1. The dipole moment of a single droplet is given by

$$\mu=e\sum_{i=1}^{N_s}(\mathbf{r}_i^+-\mathbf{r}_i^-), \tag{8}$$

where $\mathbf{r}_i^+$ and $\mathbf{r}_i^-$ are the radius vectors of the positively charged counterion and negatively charged surfactant head, respectively, and e is the magnitude of the ion charge.

The quantity of interest is the mean-square dipole moment $\langle\mu^2\rangle$ of a droplet. It can be expressed in terms of the mean-squared fluctuations of the dipole moment μ by

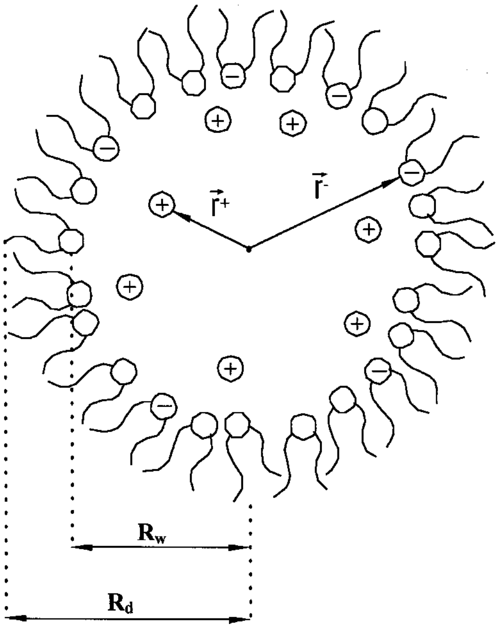

FIG. 1. Schematic picture of the spherical water-surfactant droplet. The reference point is chosen at the center of the droplet. The ith ion-counterion pair is represented by radius vectors of ion and counterion $\mathbf{r}_i^+$ and $\mathbf{r}_i^-$.

$$\langle\mu^2\rangle=\langle(\Delta\mu)^2\rangle+\langle\mu\rangle^2, \tag{9}$$

where $\langle(\Delta\mu)^2\rangle=\langle(\mu-\langle\mu\rangle)^2\rangle$.

As it was mentioned above, the mean-square dipole moment of a droplet $\langle\mu^2\rangle$ is calculated in the equilibrium state in the absence of the electric field. Indeed, since the right-hand side of Eq. (4) is already proportional to the electric field, $\langle\mu^2\rangle$ cannot be a function of E_d. In this case the calculation of the electric polarization is retained in the framework of the linear theory by the electric field. Thus, in zeroth order of the electric field one can assume a spherical symmetry of the distribution of charges within a droplet. That means $\langle\mu\rangle=0$. Hence the apparent dipole moment in the system has a fluctuating nature, i.e.,

$$\langle\mu^2\rangle\approx\langle(\Delta\mu)^2\rangle. \tag{10}$$

In order to calculate the value of $\langle\mu^2\rangle$, we square the left- and right-hand sides of Eq. (8) and average the result by the ensemble of the realizations of random positions of ions. Then, retaining the main terms in the quadratic form, we obtain

$$\langle(\Delta\mu)^2\rangle\approx e^2\sum_{i=1}^{N_s}[\langle(\mathbf{r}_i^+)^2\rangle+\langle(\mathbf{r}_i^-)^2\rangle]. \tag{11}$$

It is easy to show that approximation (11) can be used when the following correlation coefficients are small:

$$Q_{i,j}^{\pm,\pm}=\frac{\langle\mathbf{r}_i^\pm\mathbf{r}_j^\pm\rangle}{\sqrt{\langle(\mathbf{r}_i^\pm)^2\rangle\langle(\mathbf{r}_j^\pm)^2\rangle}}\ll 1 \quad \text{for } i\neq j, \tag{12}$$

$$Q_{i,i}^{+,-}=\frac{\langle\mathbf{r}_i^+\mathbf{r}_i^-\rangle}{\sqrt{\langle(\mathbf{r}_i^+)^2\rangle\langle(\mathbf{r}_i^-)^2\rangle}}\ll 1. \tag{13}$$

The justification of inequalities (12) and (13) is given in the Appendix. It is performed on the basis of the asymptotic analysis of the Bogolyubov equation [22,23] for the two-particle coordinate distribution function.

A calculation of the terms $\langle(\mathbf{r}_i^+)^2\rangle$ and $\langle(\mathbf{r}_i^-)^2\rangle$ entering Eq. (11) can be performed using the one-particle distribution functions $W_1^+(\mathbf{r}^+)$ and $W_1^-(\mathbf{r}^-)$ that are proportional to the ion density

$$W_1^+(\mathbf{r}^+)=W_1^+(|\mathbf{r}^+|)=\frac{1}{N_s}\,c(r), \tag{14}$$

$$W_1^-(\mathbf{r}^-)=\frac{1}{4\pi R_w^2}\,\delta(|\mathbf{r}^-|-R_w), \tag{15}$$

where R_w is the radius of the water core, $c(r)$ is the density of the counterions at the distance $r=|\mathbf{r}^+|$ from the center of the droplet, and N_s is the total number of the counterions in the droplet interior:

$$N_s=4\pi\int_0^{R_w} r^2 c(r)\,dr. \tag{16}$$

By taking into account Eqs. (14) and (15), Eq. (11) reads

$$\langle(\Delta\mu)^2\rangle=e^2\left\{4\pi\int_0^{R_w} r^4 c(r)\,dr+N_sR_w^2\right\}. \tag{17}$$

According to Eq. (10), relation (17) allows us to calculate the apparent dipole moment $\mu_a=[\langle(\Delta\mu)^2\rangle]^{1/2}$ of a droplet.

C. Counterion density distribution

The distribution of the counterions in the droplet interior is assumed [17,20,21,25] to be governed by the Poisson equation

$$\Delta\Psi=-\frac{4\pi e c(r)}{\varepsilon_w}, \tag{18}$$

where Ψ is the electrostatic potential and ε_w is the dielectric permittivity of the water core. The dependence of the charge density $c(r)$ on the distance from the center of the water core r is given by

$$c(r)=c_0 e^{-e[\Psi(r)-\Psi(0)]/k_BT}. \tag{19}$$

Here the reference point is chosen at the center $(r=0)$ of the spherical droplet, where the counterion density is c_0 and the electric potential is $\Psi(0)$. The modeling of the charge distribution in the microemulsion droplet was employed in the literature for positive charges inside the water pool [17,20] as well as for droplets with more than one kind of ion [21].

By using Eq. (19), Eq. (18) reads in the Poisson-Boltzmann form [20]

$$\psi''+\frac{2}{x}\,\psi'=-e^{-\psi}, \tag{20}$$

with the boundary conditions

$$\psi(0)=0 \tag{21}$$

and

$$\psi'(0)=0, \tag{22}$$

where ψ and x are the dimensionless potential $\psi=e[\Psi-\Psi(0)]/k_BT$ with respect to the center and the dimensionless distance $x=r/l_D$, respectively. Here the characteristic thickness of the counterion layer near the surface of the water core

$$l_D=\left(\frac{\varepsilon_w k_BT}{4\pi e^2 c_0}\right)^{1/2} \tag{23}$$

is the Debye screening length.

We look for the solution of the Poisson-Boltzmann equation (20) in the form of a logarithm of a power series

$$\psi(x)=-\ln\sum_{j=0}^{\infty} a_j x^{2j}, \tag{24}$$

where the coefficients a_j are to be found. By substituting Eq. (24) into Eq. (19), we obtain a simple relationship for the charge density

$$c(x)=c_0\sum_{j=0}^{\infty} a_j x^{2j}. \tag{25}$$

Differentiating Eq. (24) and substituting the corresponding series for ψ and the derivatives ψ' and ψ'' in Eq. (20), we then obtain the recurrence formula for a_j,

$$2\sum_{m,n}^{\infty} a_n a_m m[2(n-m)-1]\delta_{m,j-1}$$
$$=-\sum_{q,p,k}^{\infty} a_q a_p a_k \delta_{k,j-1-p-q}. \tag{26}$$

In order to satisfy the boundary condition (21) we set $a_0=1$. Then, for the next few coefficients we obtain $a_1=\frac{1}{6}$, $a_2=\frac{1}{45},\ldots$. We note here that, as a matter of fact, the number of terms of the series in recurrence formula (26) is finite due to the Kronecker symbol.

The convergence of the power series in Eqs. (24) and (25) is dependent on the value of x being considered. In order to determine the values of x at which the series converges, we use the ratio test [24], which states that the series converges when the limit of $|a_{j+1}/a_j|x^2<1$ as $j\rightarrow\infty$. Hence the interval of convergence of Eqs. (24) and (25) in our case is given by

$$0<x<\lim_{j\rightarrow\infty} L_j, \tag{27}$$

where $L_j=(a_j/a_{j+1})^{1/2}$. The numerical calculation of the parameter L_j as a function of the serial number j is shown in Fig. 2. One can see that the value of L_j increases and approaches the value of approximately 3.27 in the limit of large j. Hence, when applying Eq. (24) to the calculation of the dielectric properties of ionic microemulsions, one has to bear in mind that the domain of variance of x is the interval (27), i.e., $0<x<3.27$.

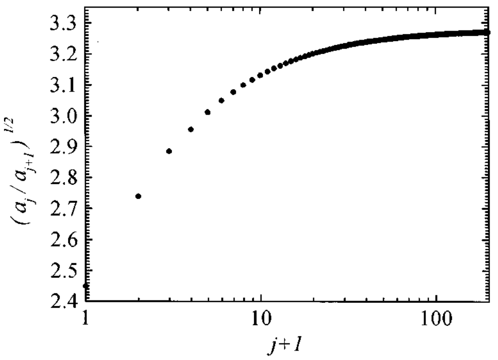

FIG. 2. Dependence of the parameter $L_j=(a_j/a_{j+1})^{1/2}$ on serial number j for the series in Eqs. (24) and (25).

D. Calculation of the fluctuation dipole moment of a droplet and the dielectric permittivity of ionic microemulsions

Equation (25) describes the distribution of the counterions in the droplet interior and can be substituted in Eq. (17) for the calculation of the mean-square dipole moment of a droplet. The total number of the counterions in the droplet interior N_s entering Eq. (17) can be obtained by substituting Eq. (25) into Eq. (16) and integrating it term by term, namely,

$$N_s=4\pi l_D^3 c_0\sum_{j=0}^{\infty}\frac{a_j}{2j+3}x_R^{2j+3}, \tag{28}$$

where $x_R=R_w/l_D$. Furthermore, using Eqs. (17), (25), and (28), we obtain the relationship for the mean-square dipole moment $\langle\mu^2\rangle$ of a droplet as

$$\langle\mu^2\rangle=4\varepsilon_w k_B T R_w^3\sum_{j=0}^{\infty}\frac{a_j(j+2)}{(2j+3)(2j+5)}x_R^{2(j+1)}. \tag{29}$$

In order to find the counterion density at the center of a droplet c_0 entering Eq. (23) for the Debye length l_D, the counterion concentration $c(r)$ must be related to the dissociation of the surfactant molecules in the water core of the droplet. The dissociation of the surfactant molecules is described by the equilibrium relation [20,21]

$$K_s(T)=c_0 e^{-\psi(x_R)}\frac{N_s}{N_a-N_s}, \tag{30}$$

where N_a is the micelle aggregation number, i.e., the number of surfactant molecules per droplet, N_s of which are dissociated, K_s is the equilibrium dissociation constant of the surfactant, and $\psi(x_R)$ is the dimensionless electrical potential near the surface of the water core (i.e., at $r=R_w$). Substituting $\psi(x_R)$ in Eq. (30) with the power series given by Eq. (24), we obtain

$$K_s(T)=\frac{c_0N_s}{N_a-N_s}\sum_{j=0}^{\infty}a_j x_R^{2j}. \tag{31}$$

The system of coupled equations (28), (29), and (31), along with the recurrence formula for a_j [Eq. (26)] and Eq. (23) for l_D, constitutes the model describing the temperature and geometry dependence of the mean-square dipole moment of the droplet $\langle\mu^2\rangle$. Furthermore, by inserting the calculated values of the mean-square dipole moment into Eq. (7), we obtain the equation

$$\frac{(\varepsilon-\varepsilon_{\mathrm{mix}})(2\varepsilon+\varepsilon_{\mathrm{mix}})(2\varepsilon+\varepsilon_w)}{\varepsilon^2}=36\varphi\varepsilon_w\left(\frac{R_w}{R_d}\right)^3\sum_{j=0}^{\infty}\frac{a_j(j+2)}{(2j+3)(2j+5)}x_R^{2(j+1)}. \tag{32}$$

This enables us to calculate the values of the dielectric permittivity ε of the system.

E. Approximate relationships for the fluctuation dipole moment of a droplet and the dielectric permittivity of ionic microemulsions

An adequate approximate relationship for the calculation of the mean-square dipole moment $\langle\mu^2\rangle$ in the case of a small droplet and/or the small dissociation of surfactant ($R_w\leqslant l_D$) can be obtained in the first approximation by taking into account the first term ($j=0$) only, in the series of the expressions (28), (29), and (31). In this approximation, by using the relationship $x_R=R_w/l_D$ and taking into account Eq. (23), we obtain for the mean-square dipole moment

$$\langle\mu^2\rangle\approx\frac{8\varepsilon_w k_B T R_w^5}{15 l_D}=\frac{32}{15}\pi e^2 c_0 R_w^5. \tag{33}$$

An approximate relationship for the counterion density at the droplet center c_0 can be obtained by using Eqs. (28) and (31) in the first approximation, which reads

$$c_0\approx\left(\frac{3K_s}{R_wA_s}\right)^{1/2}, \tag{34}$$

where $A_s=4\pi R_w^2/N_a$ is the average area (cm^2/molecule) on the surface of a water core associated with one surfactant molecule. After combining Eqs. (33) and (34), the mean-square fluctuation dipole moment of a droplet becomes

$$\langle\mu^2\rangle\approx\frac{32\sqrt{3}}{15}\pi e^2\left(\frac{R_w^9K_s}{A_s}\right)^{1/2}. \tag{35}$$

By substituting Eq. (35) in Eq. (7), we obtain an approximate relationship for the dielectric permittivity of the system,

$$\frac{(\varepsilon-\varepsilon_{\mathrm{mix}})(2\varepsilon+\varepsilon_{\mathrm{mix}})(2\varepsilon+\varepsilon_w)}{\varepsilon^2}=\frac{96\sqrt{3}\pi\varphi e^2}{5R_d^3k_BT}\left(\frac{R_w^9K_s}{A_s}\right)^{1/2}. \tag{36}$$

In order to obtain a more tractable relationship for ε, further simplifications can be made when taking into account the relative magnitudes of ε, $\varepsilon_{\mathrm{mix}}$, and ε_w. For $\varepsilon_w\approx78$ and $\varepsilon\sim\varepsilon_{\mathrm{mix}}\ll\varepsilon_w$, we approximate $2\varepsilon+\varepsilon_w$ by ε_w and $2\varepsilon+\varepsilon_{\mathrm{mix}}$ by 3ε to obtain

$$\varepsilon\approx\frac{\varepsilon_{\mathrm{mix}}}{1-X}, \tag{37}$$

where

$$X=\frac{32\sqrt{3}\pi\varphi e^2}{5R_d^3k_BT\varepsilon_w}\left(\frac{R_w^9K_s}{A_s}\right)^{1/2}. \qquad (38)$$

It is easy to show that $X\ll 1$ in the case of small droplet concentrations; thus an approximate relationship for ε is

$$\varepsilon\approx\varepsilon_{\text{mix}}(1+X). \qquad (39)$$

In order to explain the experimental temperature behavior of the dielectric permittivity of the system we have to consider the temperature behavior of the dissociation constant of the surfactant K_s, which has an Arrhenius behavior [25]

$$K_s(T)=A\exp\left(-\frac{\Delta H}{k_BT}\right), \qquad (40)$$

where ΔH is the apparent activation energy of the dissociation of the surfactant in the water pool of a droplet and A is the pre-exponential factor. It is easy to show that the dielectric permittivity of microemulsions obtained from Eq. (37) or (39) for the Arrhenius behavior of the dissociation constant is a growing function of temperature in the temperature range of $T<\Delta H/2k_B$, which is always fulfilled in the measured temperature interval for any reasonable value of the activation energy.

III. EXAMINATION OF THE MODEL

It is naturally of interest to examine the model developed and to determine the electrical characteristics of the studied microemulsions. We have taken the experimental data [16] obtained for the ternary sodium bis(2-ethylhexyl) sulfosuccinate–water–oil (decane) microemulsions, with compositions of (1.9:2.4:93.7), (5.9:7.1:87.0), (11.7:14.2:74.1), and (17.5:21.3:61.2) for AOT:water:decane, respectively. All compositions are represented as percent by volume. In order to keep the radius of all the droplets fixed at 48 Å the molar ratio of water to surfactant has the value of $W=[\text{water}]/[\text{AOT}]=26.3$ for all the microemulsions.

Dielectric measurements in [16] were carried out by means of the Dipole TDS Ltd. time domain dielectric spectroscopy system TDS-2. All samples were measured in a temperature range much inferior to that of the percolation region. Hence, for each microemulsion the measurements were started at 2 °C and continued until the temperature reached the onset of the percolation region T_{on}.

For numerical evaluations of the model developed we have to set the values of the parameters matching the studied systems. The value of the dielectric permittivity of water was assumed to be equal to that of the bulk water at the corresponding temperature throughout all the calculations, as $\varepsilon_w=87.74-0.400\,08t+9.398\times10^{-4}t^2-1.41\times10^{-6}t^3$ [26,27], where t is the temperature in degrees Celsius. The value of 2 for the dielectric permittivity of decane was adopted in the present calculations. The effective value of 8.5 was used [28] for the dielectric permittivity of AOT. The value of ε_{mix} was calculated by using the one-shell model [19]. The aggregation number N_a was estimated to be 244 molecules per droplet. The value of $A_s=65$ Å^2 for the average area on the surface of the water core associated with one AOT molecule was adopted [15].

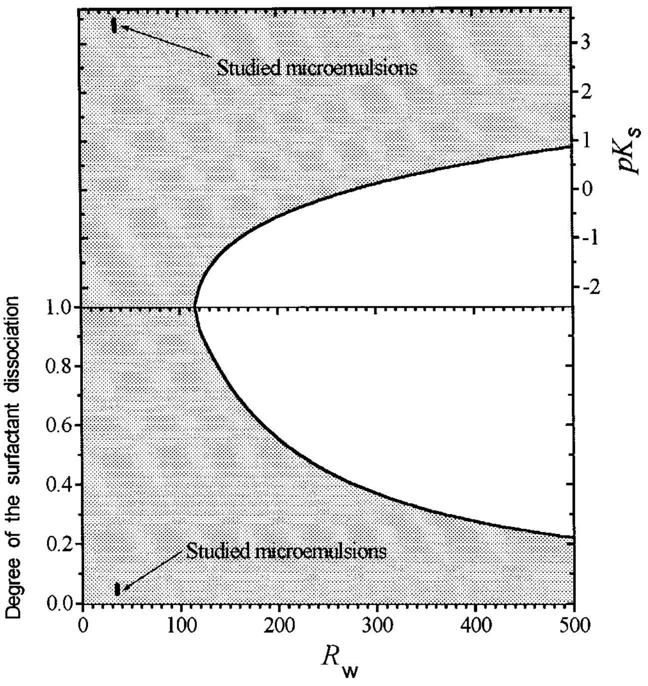

FIG. 3. $pK_s-(R_w)_{\max}$ and $\alpha-(R_w)_{\max}$ diagrams of the validity of the series solution (24).

We have to bear in mind that the model developed can be applied within the special ranges of the droplet radius and ionic dissociations of the surfactant only. On the one hand, the droplets cannot be too small. The high-frequency dielectric measurements showed [29,30] that the radius of the water core must be larger than 15 Å (the water to surfactant ratio $W>10$) to ensure that a core of ''free'' water exists. On the other hand, the droplets cannot be too large. One can see that condition (27), which determines the range of the applicability of the analytical solution (24) of Poisson-Boltzmann equation (20), is always fulfilled if $R_w/l_D<3.27$, i.e., the radius of the water core R_w cannot exceed the value of $3.27l_D$. It is convenient to characterize the value of the Debye radius l_D by the strength of the electrolyte in the droplet interior pK_s ($pK_s\equiv-\log_{10}K_s$) and/or by the degree of dissociation of surfactant $\alpha=N_s/N_a$. Thus a maximal value for the permitted radius of the water core $(R_w)_{\max}=3.27l_D$ will also depend on pK_s or α. The $pK_s-(R_w)_{\max}$ and $\alpha-(R_w)_{\max}$ diagrams depicted in Fig. 3 show the domain of the validity of the solution (24). One can see that if the droplet radius does not exceed 110 Å, the solution obtained can be applicable at any values of pK_s and α. The average radius of the water core R_w is related to W by a semiempirical relation [7,31] $R_w=(1.25W+2.7)$ Å. In the case of our microemulsions studied, R_w and the surfactant-coated water droplet R_d (the AOT chain length is 12.4 Å) are estimated to be 35.6 and 48 Å, respectively. Thus the solution (24) can be applied for the characterization of the microemulsions.

Regarding K_s of AOT surfactant, little is known and we did not find any reliable experimental data for it in the literature. Thus K_s can be considered as an adjustable parameter of the theory, which can be calculated from the inverse problem, i.e., we can determine K_s from the knowledge of experimentally measured dielectric permittivity of the micro-

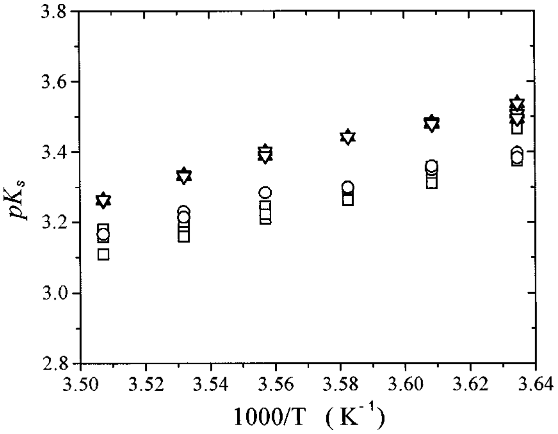

FIG. 4. Arrhenius plot of pK_s values ($pK_s \equiv -\log_{10} K_s$, where K_s is the equilibrium dissociation constant) of AOT surfactant for the studied AOT-water-decane microemulsions for various volume fractions φ of the dispersed phase: 0.043 (□), 0.13 (○), 0.26 (△), and 0.39 (▽).

emulsions studied. The equilibrium dissociation constant K_s can be calculated by using Eqs. (23), (31), and (32) or, in the case of small droplets and/or small dissociation of surfactant, by the approximate equation (36). The activation energy of the dissociation ΔH of AOT surfactant can be calculated from the Arrhenius plot [Eq. (40)] of pK_s values for various volume fractions φ of the dispersed phase. Figure 4 shows the effect of temperature on the dissociation of surfactant in microemulsions. For all the studied AOT-water-decane microemulsions the magnitude of pK_s, calculated on the basis of the equations (23), (31), and (32) for various volume fractions φ of the dispersed phase, does not depend on φ within a degree of accuracy better than 7%. This confirms the initial assumptions of the model that droplets in the system can be considered as noninteracting for such concentrations of droplets.

It is relevant to note that the values obtained for K_s (or pK_s) are indeed somewhat different from those elsewhere reported [21,25]. This could be due to fact that the estimation of the pK_s values in Refs. [21,25] was based on a NMR spectroscopic investigation [32] of the AOT-water-isooctane microemulsions containing coions (neutral electrolyte added). It was estimated for such microemulsions that about 28% of the Na^+ ions are bound to the interior surface of the droplets. On the basis of this result the value of pK_s was found to be 0.475 [21]. However, as it was noted in [20], the presence of co-ions could weaken the attraction between positive counterions and negatively charged surfactant heads. Thus, in the systems considered in the present study, in which only one kind of charged species is in the droplet interior, one can assume that the dissociation should be lower than 28%, i.e., $pK_s > 0.475$. Hence our data for K_s do not contradict the data in the literature. The energy activation obtained from Fig. 4 has the value of 39 kJ/mol. This rather high activation energy level indicates a strong interaction of Na^+ with the SO_3^- group of AOT molecules at the interface.

We note here that the model was developed for the special case in which coordinate correlations of different ions are negligible [see Eqs. (12) and (13)]. It is shown in the Appendix that these conditions are fulfilled if the ratio of the Bjerrum length l_B to the characteristic scale of the screening of electrostatic field is small. For our systems l_B was estimated to be 8 Å, whereas the screening scale is the Debye length l_D determined by Eq. (23). An estimate of the value of l_B was obtained by taking into account a distinction of the water permittivity near the ion [19] from the bulk value of ε_w. We found that the value of l_D decreases weakly from 34 to 28 Å as the temperature increases between 2 °C and 10 °C. One can see that the ratio $l_B/l_D \sim 0.3$, which means that the model developed can be applied for calculation of the mean-square dipole moment of a droplet.

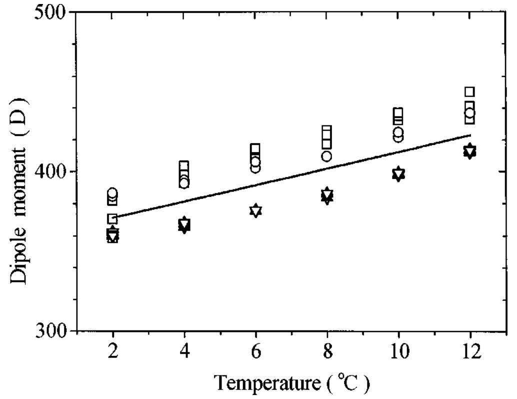

FIG. 5. Temperature dependence of the experimental and calculated on the basis of Eq. (29) macroscopic apparent dipole moments of a droplet of the AOT-water-decane microemulsions. The experimental values of the dipole moment are shown for various volume fractions φ of the dispersed phase: 0.043 (□), 0.13 (○), 0.26 (△), and 0.39 (▽). The calculated values are shown by the solid line.

Figure 5 compares the values of the experimental apparent dipole moment μ_a of the studied microemulsions, obtained from Eq. (7), together with the theoretical values obtained on the basis of Eq. (29). One can see that the apparent dipole moment $\mu_a = (\langle \mu^2 \rangle)^{1/2}$ of the microemulsions studied increases versus temperature. Figure 6 shows the deviation of the dipole moment of the droplet calculated on the basis of the formula (29) from the corresponding value obtained from the approximate formula (35) versus the dimensionless drop-

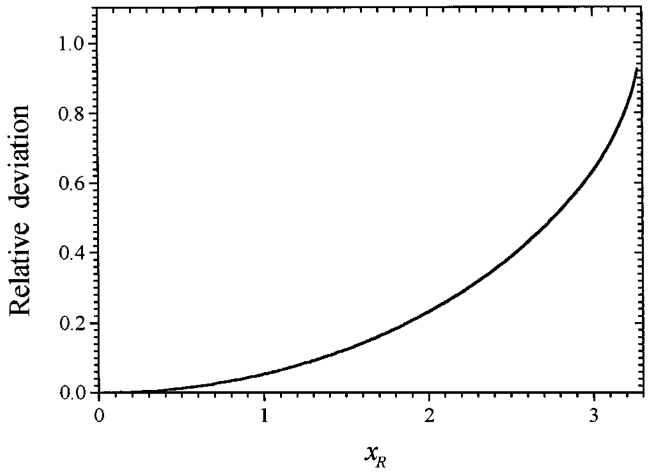

FIG. 6. Relative deviation of the dipole moment of the droplet calculated on the basis of formula (29) from the corresponding value obtained from the approximate formula (35) versus the dimensionless droplet radius.

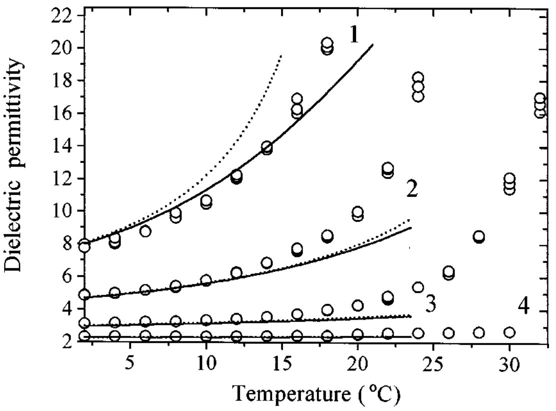

FIG. 7. Experimental (○) and calculated static dielectric permittivity versus temperature for the AOT-water-decane microemulsions for various volume fractions φ of the dispersed phase: 0.39 (curve 1), 0.26 (curve 2), 0.13 (curve 3), and 0.043 (curve 4). The calculations were performed by using formula (32) (solid line) and approximate formula (37) (dash line).

let radius x_R. Since the discrepancy between the values obtained from formulas (29) and (35) for the microemulsions studied ($x_R \sim 1.05-1.25$) is less than 8%, it can be concluded that the first approximation considered is sufficient for an accurate numerical description of the dipole moment of the droplet of the microemulsions studied.

IV. CONCLUSION

In conclusion, let us briefly discuss the dielectric permittivity of the microemulsions studied. Figure 7 shows the temperature dependences of the experimental dielectric permittivity and the results of the calculations on the basis of the model developed performed by using Eqs. (32) and (37), respectively. The difference between the values of ε obtained from Eqs. (32) and (37) can only be observed at high φ. The calculated values of ε concur well with the experimental data in the region far below the onset of percolation ($T<T_{\text{on}}$), where the assumptions of the model are fulfilled. At the temperatures close to the percolation onset T_{on} and beyond it, deviations of the theoretical values from the experimental data are observed. These deviations indicate the structural changes in the system that appear at percolation.

As a final comment, we note that the model considered does not take into account the droplet size polydispersity in the system. However, the effect of the polydispersity on the dielectric permittivity of ionic microemulsions can be estimated by using Eqs. (37) and (38) and the literature data for the size polydispersity index [6]. Indeed, it is easy to show that in the assumption of the weak dependence of the dissociation constant on the droplet radius and in the case of the small droplet concentrations, i.e., $X \ll 1$, the effect of polydispersity on the dielectric permittivity can be estimated by a formula

$$\frac{\Delta\varepsilon}{\varepsilon} \approx 1.5\,\frac{X}{1-X}\,\frac{\Delta R}{R} \approx 1.5X\,\frac{\Delta R}{R}, \tag{41}$$

where $\Delta\varepsilon$ and ΔR are the deviations of dielectric permittivity and droplet radius from their mean values, respectively. Ricka, Borkovec, and Hofmeier [6] recommended a value of $\Delta R/R \sim 0.1$ for the polydispersity of AOT-water-oil microemulsions. Thus, within the considered temperature interval $T \sim 275-280$ °K and the range of the volume fractions of the dispersed phase $\varphi \sim 0.043-0.39$, the influence of polydispersity on the dielectric permittivity is rather small: $\Delta\varepsilon/\varepsilon \sim 3-7\,\%$.

ACKNOWLEDGMENTS

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APPENDIX: ESTIMATION OF THE COEFFICIENTS $Q_{i,j}^{\pm,\pm}$ OF ION COORDINATE CORRELATIONS

The coordinate correlation coefficients of ions should be calculated by using the two-particle coordinate distribution function W_2, which in the general case can be found from the Bogolyubov equation [23]. However, it is not necessary to solve the Bogolyubov equation for corroboration of inequalities (12) and (13). The restriction imposed by Eqs. (12) and (13) on the system parameters can be obtained by means of the asymptotic analysis of W_2.

The ion correlations in a droplet are characterized by three length scales: the radius of the water core of the droplet R_w, the Debye screening length l_D, and the Bjerrum length l_B (l_B is the distance between two ions at which kT is comparable to the potential energy of Coulomb interaction $e^2/\varepsilon_w l_B$). If $l_D \ll R_w$, then the scale of screening in the system is determined by the Debye length, whereas in the case of $l_D \gg R_w$, the actual screening scale is R_w. It is known [23] that if the ratio of the Bjerrum length l_B to the screening scale is small ($\gamma = l_B/\min\{l_D,R\} \ll 1$), then a solution of the Bogolyubov equation can be constructed in the form of power series in the parameter γ. For the two-particle coordinate distribution function it reads

$$W_2 = W_2^{(0)} + \gamma W_2^{(1)} + \gamma^2 W_2^{(2)} + \cdots\,. \tag{A1}$$

Since the term $W_2^{(0)}$ is the constant, it does not give a contribution to the coordinate correlations $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$ of the two ions i and j. Hence $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle \sim \gamma \int\int W_2^{(1)} (\mathbf{r}_i \cdot \mathbf{r}_j) d^3\mathbf{r}_i d^3\mathbf{r}_j = O(\gamma)$ because the double integral is bounded. On the other hand, one can show that the main term of the asymptotic expansion of $\langle \mathbf{r}_i^2 \rangle$ in the parameter γ is $\langle \mathbf{r}_i^2 \rangle = O(1)$. Thus, for $\gamma \ll 1$, the coordinate correlation coefficients of a pair of ions [inequalities (12) and (13)] are of the order of γ:

$$Q_{i,j} = \frac{\langle \mathbf{r}_i \mathbf{r}_j \rangle}{\sqrt{\langle \mathbf{r}_i^2 \rangle \langle \mathbf{r}_j^2 \rangle}} = O(\gamma). \tag{A2}$$

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