TABLE III: Species Found in the Resonance Raman Spectra of Heat-Treated Sodium-Doped PPV Observed with Various Excitation Wavelengths

excitn wavelength, nm	species
514.5	neutral PPV, NBP1
632.8	NP2, NBP2
711.0	NP3, NBP2, NBP3
1064	NP3, NBP3

heat-treated film (Figure 6c) correspond, respectively, to the bands at 1575, 1551, 1316, and 1167 cm^{-1} of $PV3^{\cdot-}$ (Figure 3c). The 1579-, 1345-, 1294-, 1168-, and 1147-cm^{-1} bands (Figure 6c) correspond, respectively, to the bands at 1580, 1346, 1294, 1163, and 1144 cm^{-1} of $PV2^{2-}$ (Figure 4b). In addition, the 1579-, 1510-, 1314-, 1294-, 1214-, and 1168-cm^{-1} bands (Figure 6c) correspond, respectively, to the bands at 1591, 1506, 1319, 1296, 1217, and 1165 cm^{-1} of $PV3^{2-}$ (Figure 4c). These results indicate the existence of NP3, NBP2, and NBP3 in the heat-treated film. The resonance Raman spectrum excited at 740.0 nm (not shown) is close to that excited at 711.0 nm (Figure 6c).

The resonance Raman spectrum excited at 1064 nm (Figure 6d) is also similar to the 711.0-nm-excited spectrum. However, the 1345-cm^{-1} band, which is present in the 711.0-nm-excited spectrum and is considered to be a key band of NBP2, is not found in the 1064-nm-excited spectrum. Accordingly, the 1064-nm-excited spectrum seems to represent NP3 and NBP3. This result is rather strange, since the separation between the absorption maximum of NBP2 and 1064 nm is expected to be smaller than that between the absorption maximum of NP3 and 1064 nm, if the absorption bands of NP3 and NBP2 are assumed to be close to those of $PV3^{\cdot-}$ and $PV2^{2-}$, respectively (see Table I). This may mean that the amount of NBP2 is smaller than that of NP3.

The species detected with various excitation wavelengths are listed in Table III. The heat-treated sodium-doped PPV film contains NP2, NP3, NBP1, NBP2, and NBP3. As compared with the results obtained for the sample before heating (Table II), the short bipolarons (NBP1 and NBP2) are formed at the expense of the shortest polaron (NP1). It is well-known that a bipolaron is more stable than two polarons.[27] The shortest polaron NP1 probably combines with another polaron to form a bipolaron with concomitant migration of the sodium ions. NP2 and NP3 seem to be more stable than NP1 against such a drastic heat treatment.

Concluding Remarks

In the present study, we have demonstrated the potential of resonance Raman spectroscopy in the characterization of self-localized excitations such as polarons and bipolarons existing in doped conducting polymers. Studies on the radical ions and divalent ions of model compounds in general are expected to give useful information which will form a basis for the spectral analysis of doped polymers. We are now extending our studies to PPV treated with concentrated sulfuric acid (p-type doping) and the radical cations of the model compounds. These studies may lead us to a more quantitative understanding of the relationship between electrical conduction and the self-localized excitations.

Registry No. PPV, 26009-24-5; PV1, 18869-29-9; PV2, 140150-05-6; PV3, 140175-16-2; sodium, 7440-23-5; sodium naphthalide, 3481-12-7.

Effect of Charge Distribution within a Droplet on the Electrical Conductivity of Water-in-Oil Microemulsions[†,‡]

Melanija Tomić* and Nikola Kallay

*Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Maruličev trg 19, P.O. Box 163, 41001 Zagreb, Yugoslavia (Received: July 29, 1991; In Final Form: November 19, 1991)

Model calculations of electrostatic energy, free energy, and the average square of charge number of a water-in-oil microemulsion droplet are performed. The system is considered to consist of spherical noninteracting droplets of equal size with charged surfactant heads at the droplet interface and the oppositely charged counterions in the droplet interior. The counterion distribution within a droplet is assumed to be governed by the Poisson–Boltzmann equation. The influence of entropy and association of counterions with charged surfactant heads is also considered. The resulting mathematical expressions and numerical results obtained in this study are compared with those based on the approximation inferring that the Born energy is the only energy contribution responsible for charging the droplet. The results agree well, except for the assumption of extremely strong association.

Introduction

The scope of this article is the electrical conductivity of the water-in-oil microemulsion systems consisting of water droplets with ionic surfactant molecules at the water/oil interface and dispersed in apolar continuous medium. The ionic surfactant partly dissociates, leaving charged heads at the droplet interface and oppositely charged ions (counterions) distributed in the polar medium, i.e., in the droplet interior. Figure 1 presents an example of a spherical water droplet with negatively charged surface and positive counterions. The electrical conductivity of such systems

was recently explained by the finding that droplets are charged themselves and, therefore, migrate in the applied electric field.[1-3] On the average, the droplets are electrically neutral, but there is a certain probability that the numbers of charged surfactant heads and counterions in a droplet are not equal. Several mechanisms of charging were proposed.[4] However, the mechanism itself is out of the scope of this paper, since only the ther-

(1) Eicke, H.-F.; Borkovec, M.; Das-Gupta, B. *J. Phys. Chem.* **1989**, *93*, 314.
(2) Hall, D. G. *J. Phys. Chem.* **1990**, *94*, 429.
(3) Kallay, N.; Chittofrati, A. *J. Phys. Chem.* **1990**, *94*, 4755.
(4) Jada, A.; Lang, J.; Candau, S.-J.; Zana, R. *Colloids Surf.* **1989**, *38*, 251.
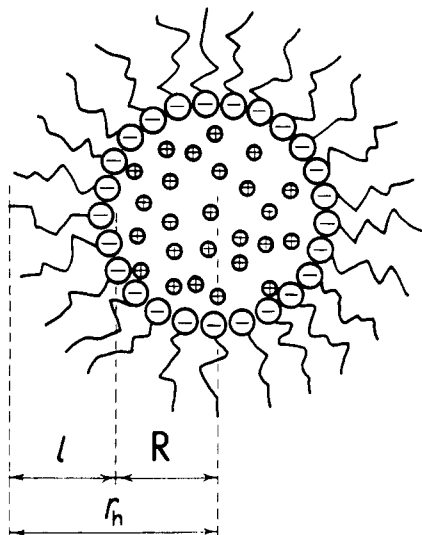
Figure 1. Water-in-oil microemulsion droplet with negatively charged surfactant heads at the interface and positive counterions in the interior. The radius of the water core is denoted by R, the hydrodynamic radius by r_d, and the mean length of surfactant chains by l.

modynamic equilibrium will be considered here.

The electrical conductivity, κ, of a monodisperse system consisting of spherical droplets is proportional to the average square of charge, $\langle z^2 \rangle$, but not to the average charge (which is zero):[1]

$$\kappa = (Ce^2/6\pi\eta r_h)\langle z^2 \rangle \qquad (1)$$

In the above equation, C is the droplet concentration (number in unit volume), e is the proton charge, η is the viscosity of the medium, z is the droplet charge number, and r_h is the hydrodynamic droplet radius, which is larger than R, the radius of the water core (see Figure 1). It is possible to obtain all the quantities in eq 1 experimentally, except for the value of $\langle z^2 \rangle$. In order to calculate this statistical quantity, two approaches have been employed.[1-3] One of them[1] is based on the fluctuation theory, and the other[2] is the standard calculation of mean values using the Boltzmann distribution function. Both approaches use the electrostatic energy of the droplet to obtain $\langle z^2 \rangle$, since the probability of charging a droplet depends on its energy. So far,[1-3] the electrostatic energy was approximated by the Born energy:

$$W_{\text{Born}} = e^2 z^2/8\pi\epsilon_m R \qquad (2)$$

The permittivity of the medium (oil) is denoted by ϵ_m. This approximation ignores the influence of the charge distribution within a droplet. In fact, the electrostatic energy of a system of volume V depends on both charge density and electrostatic potential in that volume:

$$W_{el} = \frac{1}{2}\int_V \rho\phi \, dV + \frac{1}{2}\int_A \sigma\phi \, dA \qquad (3)$$

In the above equation, ρ denotes the volume charge density and σ is the surface charge density, while ϕ is the electrostatic potential (in a volume element dV or at an element of surface area dA) of the electric field of all the charge present in volume V and surface area A. Taking a droplet of radius R as an isolated system (i.e., neglecting droplet interaction), the Born energy, expressed by eq 2, would have been obtained by eq 3 if all the charge lay at the surface of the sphere. The latter assumption on the electrostatic energy of the droplet (i.e., about the charge density and consequent electrostatic potential) resulted in a fairly good interpretation of electrical conductivity of an AOT/isooctane/water microemulsion system.[1-3]

The present study offers more elaborate expressions for the droplet energy, based on eq 3, assuming validity of the Poisson–Boltzmann equation for the droplet interior. In addition, the influence of the entropy and the association of counterions with charged surfactant heads on the total energy of the droplet will be examined. The solution of the Poisson–Boltzmann equation,

obtained by a series expansion of electrostatic potential in the radial coordinate,[5] is used in the present work, because it enables separation of the expression for the electrostatic energy into two terms with the Born energy as one of them. Such an expression makes comparison with approximate Born energy easier. Finally, already existing approaches[1-3] of calculating $\langle z^2 \rangle$ and, hence, the electrical conductivity will be used in order to check the validity of the model and the Born energy approximation. The influence of parameters such as permittivity of the water core and association equilibrium constant will be examined.

Model

(a) Size and Shape. The droplets are assumed to be spherical and equal in size, as is also assumed in deriving eq 1. The radius of the water core, R, or the "inner radius" is assumed to be smaller than the hydrodynamic radius, r_h, or the "outer radius" of the droplet.

(b) Charge Distribution and Electrostatic Energy. Having in mind the above geometrical considerations, the model approximations relating to charge distribution are as follows: all the charge carried by the charged surfactant heads is assumed to be located at the spherical plane of radius R. Furthermore, the surface charge density (σ) is assumed to be homogeneous, although its origin is discrete:

$$\sigma = z_s eN_s/4\pi R^2 \qquad (4)$$

where z_s is the charge number of dissociated surfactant heads (equal in magnitude to the counterion charge number, z_d) and N_s is their number per droplet. This number is not necessarily the same as the aggregation number (the total number of surfactant heads per droplet), because some of them may associate with counterions and form neutral species.

The counterions are allowed to be anywhere in the droplet interior, but not with equal probabilities, since their attraction to the oppositely charged surface can be expected. Their distribution is assumed to be governed by the Poisson–Boltzmann equation:

$$\nabla^2\phi = -\frac{ez_d c_d(0)}{\epsilon_w} \exp[-ez_d(\phi - \phi(0))/kT] \qquad (5)$$

where ϕ is the electrostatic potential and ϵ_w ($=\epsilon_0\epsilon_{r,w}$) is the permittivity of the interior of the sphere. The reference point is chosen at the center of the spherical droplet where the counterion (number) concentration and electrostatic potential are $c_d(0)$ and $\phi(0)$, respectively. The dependence of the charge density on the distance from the center of the sphere, r, is given by

$$\rho(r) = ez_d c_d(0) \exp[-ez_d(\phi(r) - \phi(0))/kT] \qquad (6)$$

Equation 5 is not the Poisson–Boltzmann equation in its usual form; it has only one term on the right-hand side, since only one kind of ion (counterion) is assumed to exist in the droplet interior. The modeling of charge distribution in the microemulsion droplet described by the Poisson–Boltzmann equation and by eq 4 has already been employed in the literature[6,8] for droplets with more than one kind of ion (e.g., neutral electrolyte added to the system causes the existence of co-ions).

The assumption that potential and charge distributions are governed by eqs 5 and 6 introduces approximations inherent to them: discrete counterion charge is described by continuous function $\rho(r)$, the mean electrostatic potential is introduced, and the medium (water) is described as a dielectric of space-independent permittivity.

Both charge density functions, σ (charged surfactant heads) and ρ (counterions), are spherically symmetrical. Choosing the droplet center ($r = 0$) as the origin of the coordinate system, eq 5 reads

(5) Tomić, M. Ph.D. Thesis, University of Zagreb, Zagreb, 1990.
(6) Karpe, P.; Ruckenstein, E. J. Colloid Interface Sci. 1990, 137, 408.
(7) Levine, S.; Robinson, K. J. Phys. Chem. 1972, 76, 876.
(8) Bratko, D.; Luzar, A.; Chen, S. H. J. Chem. Phys. 1988, 89, 545.

$$\frac{d^2\psi}{dx^2} + \frac{2}{x}\frac{d\psi}{dx} = -\exp(-\psi) \tag{7}$$

where x is dimensionless distance

$$x = r(e^2z_d^2c_d(0)/\epsilon_w kT)^{1/2} = \lambda r \tag{8}$$

and ψ dimensionless potential with respect to the center

$$\psi = ez_d(\phi - \phi(0))/kT \tag{9}$$

The Poisson–Boltzmann equation, as presented here, is not in its usual form; there is only one kind of ion whose concentration is governed by it. Consequently, only one exponential term on the right-hand side of eq 7 remains. The electric field at the center of the sphere is equal to zero due to the spherical symmetry of charge distribution. Therefore, the boundary condition to be used in solving eq 6 reads

$$\left.\frac{d\psi}{dx}\right|_{x=0} = 0 \tag{10}$$

The application of eqs 4–10 to the microemulsion droplet system introduces other simplifications, except for those which are already mentioned (continuous charge distribution, space-independent permittivity). The size of ionic species and the interaction of droplets are neglected. Moreover, in the correct treatment of electrostatics, even in a simplified picture like the one described, "image" interactions at the interface of two dielectrics (water/oil) should be considered. In the present work they are neglected, as already commonly accepted.[6-8] Special attention will be paid to the approximation of the space-independent permittivity; different values of this parameter (expected to be lower than bulk water) will be used to examine its influence on the final results.

The Poisson–Boltzmann equation is usually solved by numerical integration[6-10] or by approximation of the initial equation (e.g., linearization of exponential function[7] and expansion in the surface potential[7,10,11]). It has been shown in the first part of this study[5] that a satisfactory solution can be obtained by the expansion of potential in the radial coordinate. The applicability of this method is limited to small droplets with a small number of counterions. In this work, the solution in the form of series expansion in the radial coordinate is used, since it enables separation of the expression for the electrostatic energy into several terms and makes comparison with the already existing approximations (i.e., the Born energy) easier. The dimensionless potential, as expressed in ref 5, reads

$$\psi(r) = \sum_{j=1}^{\infty} b_j(\lambda r)^{2j} \tag{11}$$

where λ is defined by eq 8 and coefficients b_j are numbers independent of the system determined by the recursive relation

$$b_{n+1} = \frac{1}{(2n+2)(2n+3)} \times$$
$$\sum_{\substack{m_1,m_2,\dots,m_n=0 \\ (m_1+2m_2+3m_3\dots+nm_n=n)}}^{n} (-1)^{\sum_{j=1}^{n}m_j+1} \frac{b_1^{m_1}b_2^{m_2}\dots b_n^{m_n}}{m_1!m_2!\dots m_n!} \tag{12}$$

The expression for the electrostatic energy is obtained by substitution of eqs 4, 6, 9, and 11 into eq 3:

$$W_{el} = 2\pi\phi(0)\int_0^R \rho(r)r^2\,dr - \frac{ez_dN_s}{2}\phi(R) +$$
$$2\pi kTc_d(0)\sum_{j=1}^{\infty}b_j\lambda^{2j}\int_0^R \exp(-\sum_{n=1}^{\infty}b_n(\lambda r)^{2n})r^{2j+2}\,dr \tag{13}$$

The first term in the above equation is related to the total number of counterions in the droplet:

$$4\pi\int_0^R \rho(r)r^2\,dr = ez_dN_d \tag{14}$$

The surface potential, $\phi(R)$, is derived by the Gauss theorem, which gives the electric field outside the droplet:

$$E = ez/4\pi\epsilon_m r^2 \tag{15}$$

where ϵ_m is the permittivity of the apolar medium (oil) and ez is the total charge of the droplet. The surface potential reads

$$\phi(R) = ez/4\pi\epsilon_m R \tag{16}$$

so that the potential at the center of the droplet can be written, using eqs 9 and 11, as

$$\phi(0) = \frac{ez}{4\pi\epsilon_m R} - \frac{kT}{ez_d}\sum_{j=1}^{\infty}b_j(\lambda R)^{2j} \tag{17}$$

Substitution of eqs 14, 16, and 17 into 13 yields

$$W_{el} = \frac{e^2z^2}{8\pi\epsilon_m R} - \frac{kTN_d}{2}\sum_{j=1}^{\infty}b_j(\lambda R)^{2j} + 2\pi kTI \tag{18}$$

where I is given by

$$I = c_d(0)\sum_{j=1}^{\infty}b_j\lambda^{2j}\int_0^R \exp(-\sum_{n=1}^{\infty}b_n(\lambda r)^{2n})r^{2j+2}\,dr \tag{19}$$

Evaluation of the above expression is described in the Appendix I. The final expression for the electrostatic energy of the droplet is

$$W_{el} = \frac{e^2z^2}{8\pi\epsilon_m R} + \frac{kT}{\beta}\sum_{j=1}^{\infty}D_j(\lambda R)^{2j} \tag{20}$$

where coefficients D_j are calculated according to

$$D_j = \frac{1}{2j+1}\sum_{i=1}^{j}i(j-i)b_ib_{j-i} \tag{21}$$

and β is given by

$$\beta = e^2z_d^2/8\pi\epsilon_w kTR \tag{22}$$

The first term in eq 20 is equal to the Born energy, given by eq 2, so that the second term may be interpreted as a correction. The magnitude of the correction term will be discussed later.

Equations 14 and I.2 yield the relation between the number of counterions in the droplet and their density at the center, $c_d(0)$, which is an unknown parameter in eq 20 [i.e., in eq 8, which gives the dependency of λ on $c_d(0)$]:

$$N_d = -\frac{1}{\beta}\sum_{j=1}^{\infty}jb_j(\lambda R)^{2j} \tag{23}$$

The above equation gives the explicit dependence of N_d on $c_d(0)$ (i.e., λ, according to eq 8). However, to obtain λ from N_d, it is necessary to solve eq 23 iteratively.

(c) Association of Counterions with Surfactant Heads. The association of counterions with surfactant heads is treated according to the "site binding model", which is commonly accepted for a metal oxide/electrolyte interface.[12] It was applied to micelles[13,14] and recently to water-in-oil microemulsion droplets.[6] According to this model, the equilibrium is described by the following equation:

$$K\exp[-\psi(R)] = N_{as}/N_sc_d(0) \tag{24}$$

where K is the "intrinsic" equilibrium constant and N_{as} is the number of associates at the water/oil interface of a droplet. These neutral species are formed by the association of oppositely charged ions with surfactant heads. The equilibrium depends on the dimensionless potential at the surface, $\psi(R)$, which is, according

(9) Jonsson, B.; Wennerstrom, H. *J. Colloid Interface Sci.* **1981**, *80*, 482.

(10) Tenchov, B. G.; Koynova, R. D.; Raytchev, B. D. *J. Colloid Interface Sci.* **1984**, *102*, 337.

(11) Martynov, G. A. *Kolloidn. Zh.* **1976**, *38*, 1111.

(12) Kallay, N.; Sprycha, R.; Tomić, M.; Žalac, S.; Torbić, Ž. *Croat. Chem. Acta* **1990**, *63*, 467.

(13) Beunen, J. A.; Ruckenstein, E. *J. Colloid Interface Sci.* **1983**, *96*, 469.

(14) Ruckenstein, E.; Beunen, J. A. *Langmuir* **1988**, *4*, 77.

to eq 9, defined as the difference between potentials at the interface, $\phi(R)$, and at the chosen reference point—the center of the sphere, $\phi(0)$, where the counterion concentration is $c_d(0)$.

The ionic size is neglected, as already discussed, so that associates are also placed at the surface of the water core sphere (distance R from the center).

In the interpretation of the experimental data, the "intrinsic" association constant, K, can be treated as an adjustable parameter. One can estimate its value from the dissociation constant in the bulk water or NMR measurements.[6] In order to observe the effect of the association in the droplet on the energy, average square of charge, and electrical conductivity, the values of K will be varied. The absence of association corresponds to $K = 0$.

(d) Entropy. Entropy is calculated according to the thermodynamic theory of polyelectrolytes,[15] which was successfully applied to ionic amphiphile/water systems.[9] The theory provides the following relation for the entropy of the mixing of mobile ions in the cell of volume V in which there is an excess of water:

$$S = -k\sum_j \int_V c_j (\ln (c_j/c^\circ) - 1) \, dV \qquad (25)$$

where c_j is the concentration of species j in the cell and c° is the standard value of concentration. For the systems presently studied, the species are: counterions in the (semi)diffuse layer ($j = d$), oppositely charged surfactant heads ($j = s$), and electrically neutral associates ($j = as$). The assumed charge distribution in the droplet (see eqs 4–6) and the assumption that the associates lie at the surface of the sphere enable us to rewrite eq 25 as

$$S = k(N_d + N_s + N_{as}) - k(N_s \ln (N_s) + N_{as} \ln (N_{as})) -$$
$$4\pi k \int_0^R r^2 c_d(r) \ln (c_d(r)/c^\circ) \, dr \qquad (26)$$

The first three terms (kN_j) in the above equation are the contribution to the entropy due to the presence of species in the cell, the fourth and fifth terms represent the contribution due to the mixing of surface species at the sphere surface, and the sixth term (the integral) describes the entropy of mixing of counterions in the droplet together with the entropy due to space-dependent distribution of counterions within the droplet.

The entropy contribution due to compelling surface species to the surface of the sphere is not included in eq 26. It is assumed to be constant, and its contribution to the free energy will be included in the corresponding standard chemical potentials.

(e) Free Energy and Chemical Potentials. The free energy of the droplet is taken as the sum of the standard free energies of its constituents (products of the standard chemical potential and the number of species j, $\mu_j^\circ N_j$, electrostatic energy of the droplet, W_{el}, entropy contribution, and the interfacial surface energy, F_A):

$$F = \sum_j \mu_j^\circ N_j + W_{el} - TS + F_A \qquad (27)$$

The chemical potential, i.e., the first derivatives of free energy with respect to N_j, is the quantity of interest, rather than the free energy itself. Therefore, terms considered to be independent of small change in N_j (such as interfacial surface energy, F_A) will be omitted. The entropy of a droplet is expressed by eq 26, in which some terms considered to be constant with a change of N_j are already omitted. Substitution of eq 26, eq 18 (the expression for the electrostatic energy), eq 19 (definition of integral I), and eq 6 together with the electrostatic potential (eq 11) into eq 27 yields

$$F = \mu_d^\circ N_d + \mu_s^\circ N_s + \mu_{as}^\circ N_{as} - kT(N_d + N_s + N_{as}) -$$
$$\frac{kTN_d}{2}\sum_{j=1}^{\infty} b_j(\lambda R)^{2j} + \frac{e^2 z^2}{8\pi\epsilon_m R} - 2\pi kTI + kT(N_s \ln (N_s) +$$
$$N_{as} \ln (N_{as}) + N_d \ln (c_d(0)/c^\circ)) \qquad (28)$$

The above equation yields the chemical potential of the three kinds of species present in the droplet. The chemical potential of the associates at the surface is

$$\mu_{as} = \left.\frac{\partial F}{\partial N_{as}}\right|_{T,N_d,N_s} = \mu_{as}^\circ + kT \ln (N_{as}) \qquad (29)$$

Negatively charged surfactant heads have the following chemical potential:

$$\mu_s = \left.\frac{\partial F}{\partial N_s}\right|_{T,N_d,N_{as}} = \mu_s^\circ + kT \ln (N_s) - \frac{e^2 z}{4\pi\epsilon_m R} \qquad (30)$$

Since $c_d(0)$ depends on the number of free counterions and not on the number of charged and associated surface species, it was not necessary to differentiate it in the evaluation of eqs 29 and 30. However, one has to take the derivative of $c_d(0)$ with respect to N_d in evaluating the expression for the chemical potential of counterions:

$$\mu_d = \left.\frac{\partial F}{\partial N_d}\right|_{T,N_s,N_{as}} = \mu_d^\circ + \frac{e^2 z}{4\pi\epsilon_m R} - \frac{kT}{2}\left(1 + \right.$$
$$N_d \frac{\partial}{\partial N_d}\right)\sum_{j=1}^{\infty} b_j(\lambda R)^{2j} + kT\left(-1 + \ln (c_d(0)/c^\circ) + \right.$$
$$\left.\frac{N_d}{c_d(0)}\frac{\partial c_d(0)}{\partial N_d}\right) - 2\pi kT \frac{\partial I}{\partial N_d} \qquad (31)$$

The chemical potential of water molecules will not be considered here because an excess of water in the droplet is assumed. The above assumption is consistent with the Poisson–Boltzmann equation.

(f) Average Square of the Charge Number of the Droplet. For calculation of the average square of the droplet charge number, two methods are applied using the results of the former paragraphs: the charge fluctuation model, introduced by Eicke et al.,[1] and the Boltzmann probability distribution applied to microemulsion droplets by Hall.[2]

(i) Charge Fluctuation Model. According to the definition, the fluctuation of the number of species of kind i, $\delta N_i = N_i - \langle N_i \rangle$, the mean square of the droplet charge number, $\langle z^2 \rangle = \langle (N_d - N_s)^2 \rangle$, is given by

$$\langle z^2 \rangle = \langle (\delta N_d)^2 \rangle + \langle (\delta N_s)^2 \rangle - 2\langle (\delta N_d)(\delta N_s) \rangle \qquad (32)$$

The equality $\langle N_d \rangle = \langle N_s \rangle$, used in evaluation of the above equation, holds because the droplet is neutral on the average ($\langle z \rangle = 0$). The fluctuation theory[16] gives the following relation:

$$\langle \delta N_j \delta N_i \rangle = kT \left.\frac{\partial N_j}{\partial \mu_i}\right|_{T,\mu_{k\neq i}} \qquad (33)$$

In order to obtain partial derivatives $\partial N_j/\partial \mu_i$, one needs to invert the matrix whose elements are $\partial \mu_i/\partial N_j$. Taking indexes as $d = 1$, $s = 2$, the matrix with elements $\partial \mu_i/\partial N_j$ obtained from eqs 30 and 31 reads

$$\mathbf{M} = kT \begin{bmatrix} \alpha + d & -\alpha \\ -\alpha & \alpha + 1/N_s \end{bmatrix} \qquad (34)$$

where α and d are

$$\alpha = e^2/4\pi\epsilon_m RkT \qquad (35)$$

$$d = \frac{2}{c_d(0)}\frac{\partial c_d(0)}{\partial N_d} - \frac{N_d}{(c_d(0))^2}\left(\frac{\partial c_d(0)}{\partial N_d}\right)^2 + \frac{N_d}{c_d(0)}\frac{\partial^2 c_d(0)}{\partial N_d^2} -$$
$$\left(\frac{N_d}{2}\frac{\partial^2}{\partial N_d^2} + \frac{\partial}{\partial N_d}\right)\sum_{j=1}^{\infty} b_j(\lambda R)^{2j} - 2\pi \frac{\partial^2 I}{\partial N_d^2} \qquad (36)$$

Function d is evaluated in Appendix II, and its final form is given by eq II.6.

The determinant of matrix $\mathbf{M}$ is equal to

$$\det (\mathbf{M}) = (kT)^2[(\alpha + d)/N_s + \alpha d] \qquad (37)$$

(15) Marcus, R. A. *J. Chem. Phys.* **1955**, *23*, 1057.

(16) See, e.g.: Everdell, M. H. *Statistical Mechanics and its Chemical Applications*; Academic Press: London, 1975.

Inverse matrix M^{-1} contains elements $\partial N_i / \partial \mu_j$:

$$M^{-1} = \frac{kT}{\det(M)} \begin{bmatrix} \alpha + 1/N_s & \alpha \\ \alpha & \alpha + d \end{bmatrix} \qquad (38)$$

Substitution of the elements of matrix M^{-1} into eq 33, and afterward into eq 32, gives the average square of the charge number of the droplet:

$$\langle z^2 \rangle = [d + 1/N_s]/[(\alpha + d)/N_s + \alpha d] \qquad (39)$$

Furthermore, one takes the average numbers of positive and negative species in the droplet as equal, since the droplet is electrically neutral on the average. Therefore, N_s in the above equation is equal to N_d used in eq 23, i.e.

$$N_d = N_s \qquad (40)$$

Apparently, according to eq 39, $\langle z^2 \rangle$ does not depend on the number of associates (N_{as}), but the latter influences the value of N_s because the total number of surfactant chains ($N^{tot} = N_s + N_{as}$) is constant. It is obvious that higher affinity toward association is accompanied by an increase of N_{as} and a decrease of the number of counterions (N_d), which in turn influences the value of function d.

In the absence of association of charged surfactant heads with the oppositely charged counterions ($K = 0$), $N_s = N_d = N^{tot}$. In such a case, or in the case where the association is negligible, the approximation introduced by Eicke et al.,[1] $\alpha \gg 1/N_s$, is valid. As a consequence, terms originated from the entropical contribution to the free energy ($1/N_d$) in the expression for $\langle z^2 \rangle$ are negligible and $\langle z^2 \rangle = 1/\alpha$. In other words, the more elaborated expression for $\langle z^2 \rangle$, originating from the assumption that the droplet energy depends on the charge distribution within the droplet, does not have to be used unless significant association takes place.

(ii) Boltzmann Probability Distribution. The Boltzmann statistics was applied to the calculation of $\langle z^2 \rangle$ of microemulsion droplets by Hall[2] together with the approximate Born energy approximation, which is proportional to z^2. However, according to eq 20, the electrostatic energy is a sum of two terms: the first is equal to the Born energy, while the second term is a function of the charge distribution within the droplet (only on the counterion distribution at the present model):

$$W_{el}/kT = \alpha z^2/2 + g(N_d) \qquad (41)$$

In the above expression, α is defined by eq 35 and $g(N_d)$ is the second term on the right-hand side of eq 20 divided by kT. Assuming that droplets of different charge differ in energy only due to the electrostatic contribution, the Boltzmann statistics lead to the average value of $(N_d - N_s)^2$:

$$\langle z^2 \rangle = \frac{\sum\limits_{N_d=0}^{\infty} e^{-g(N_d)} \sum\limits_{N_s=0}^{\infty} (N_d - N_s)^2 \exp\left[-\frac{\alpha}{2}(N_d - N_s)^2\right]}{\sum\limits_{N_d=0}^{\infty} e^{-g(N_d)} \sum\limits_{N_s=0}^{\infty} \exp\left[-\frac{\alpha}{2}(N_d - N_s)^2\right]} \qquad (42)$$

The above expression can be reduced to the one used by Hall,[2] i.e., to the expression independent of function g, with the following assumptions: (1) function g increases slowly with the increase of N_d so that $\exp(-g(N_d)) \ll \sum_{N_d=0}^{\infty} \exp(-g(-N_d))$ (for $N_d = 0$, 1, 2, ...). (2) $\exp(-x) \ll 1$ for $x > 9\alpha/2$. Accordingly, the approximate relation for $\langle z^2 \rangle$ reads

$$\langle z^2 \rangle = \frac{2(e^{-(\alpha/2)} + 4e^{-2\alpha} + 9e^{-(9\alpha/2)})}{1 + 2(e^{-(\alpha/2)} + e^{-2\alpha} + e^{-(9\alpha/2)})} \qquad (43)$$

Results and Discussion

The expressions developed in the former paragraph are used to examine the influence of the model and the parameters, such as the association equilibrium constant and water core permittivity, on the numerical results. Special attention is paid to electrostatic
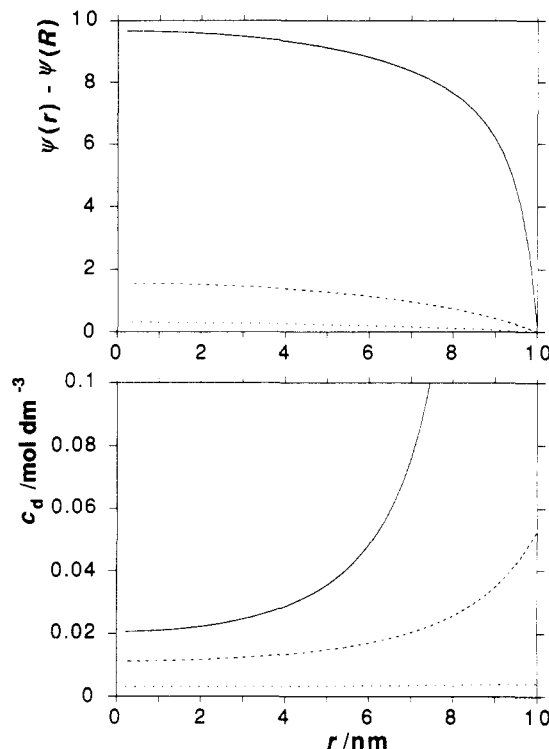

Figure 2. Dependence of the dimensionless potential with respect to the surface potential (upper) and counterion concentration (lower) on the distance from the droplet center. Different values of the intrinsic association equilibrium constant were used: solid line, $K = 0$ (no association); dashed line, $K = 10^{-24}$ m³; dotted line, $K = 10^{-22}$ m³. Other parameters: $z_s = -1$, $z_d = +1$, $R = 10$ nm, $\epsilon_w = 78.54\epsilon_0$, $A_s = 55$ Å², $T = 298$ K.

energy and the average square of the droplet charge number.

Choice of Parameters. The parameters used in calculations are chosen to match the system AOT/isooctane/water, because that microemulsion system is well described in the literature.[1-4,6,8,17] In this system, counterions (sodium ions) are of charge number $z_d = +1$, while the surface of the water core is negatively charged by ionic surfactant heads of charge number $z_s = -1$.

The average surface area occupied per surfactant head, A_s, is assumed to be independent of the droplet size. This assumption was found[18] to be a good approximation for droplets whose water core radius is larger than 4 nm. By use of the value $A_s = 55$ Å², corresponding to the AOT/water/isooctane system,[6] the average number of surfactant molecules per droplet was calculated, for the whole range of droplet sizes, from

$$N^{tot} = 4\pi R^2/A_s \qquad (44)$$

In order to examine the effect of association, the intrinsic association equilibrium constant, K, is varied in the calculations. The unit of this parameter, defined by eq 24, is meters cubed, but its value can be also expressed in "molar" units. For example, $K = 10^{-27}$ m³ corresponds to $K = 0.6022$ dm³ mol⁻¹.

In most of the calculations, the permittivity of the water core is taken to be equal to the one of the bulk water at 25 °C; $\epsilon_w = 78.54\epsilon_0$. In order to examine the influence of this parameter on the charge distribution, its value will be decreased to $1.96\epsilon_0$. In that case, $\epsilon_w = \epsilon_m$ and neglectance of the image interactions is fully justified.

The following values of the parameters of continuous phase (isooctane) are used:[1] at 298 K the permittivity is $1.96\epsilon_0$, density 0.68 g/cm³, and viscosity 4.7×10^{-4} Pa s.

Potential and Charge Distribution within a Droplet. Association of counterions with charged surfactant heads plays an important

(17) Kotlarchyk, M.; Chen, S.-H.; Huang, J. S. *J. Phys. Chem.* **1982**, *86*, 3273. Carlstrom, G.; Halle, B. *J. Phys. Chem.* **1989**, *93*, 3287. Zulauf, M.; Eicke, H.-F. *J. Phys. Chem.* **1979**, *83*, 480.

(18) Biais, J.; Bothorel, P.; Clin, B.; Lalanne, P. *J. Colloid Interface Sci.* **1981**, *80*, 136.
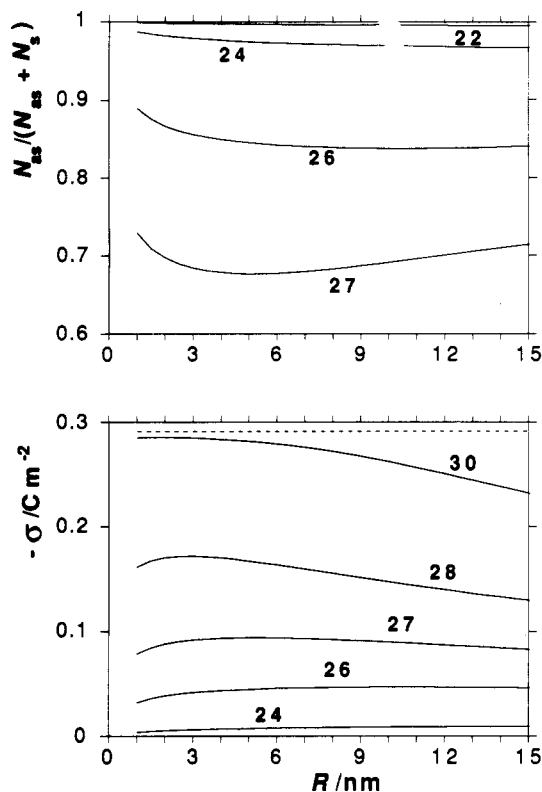
Figure 3. Fraction of surfactant molecules associated with counterions (upper) and surface charge density (lower) as a function of the water core radius. Numbers associated with lines indicate the value of $-\log (K/m^3)$ used in calculations. Other parameters: $z_s = -1$, $z_d = +1$, $\epsilon_w = 78.54\epsilon_0$, $A_s = 55$ Å^2, $T = 298$ K.

Figure 4. Electrostatic energy (lower, solid lines) and the energy of charging (upper, solid lines) as a function of water core radius. The latter quantity is the difference between the electrostatic energy and the energy of a droplet with net charge equal to zero. Numbers associated with lines denote the corresponding droplet charge number, z. For comparison, the Born energies are also presented (dashed lines). Other parameters: $z_s = -1$, $z_d = +1$, $\epsilon_w = 78.54\epsilon_0$, $\epsilon_m = 1.96\epsilon_0$, $A_s = 55$ Å^2, $T = 298$ K.

role in describing the droplet equilibrium. The upper part of Figure 2 shows the effect of association (whose extent is varied through the change of intrinsic association equilibrium constant) on the difference of dimensionless electrostatic potentials in the droplet and at the surface, $\psi(r) - \psi(R)$. The absence of association corresponds to $K = 0$. In this case, the difference of dimensionless potentials at the center and surface of the droplet $\psi(0) - \psi(R)$ = 9.75 [in terms of electrostatic potentials $\phi(0) - \phi(R) = 250$ mV]. One can hardly expect such a large potential drop within 10 nm, so that, on the basis of this model, it can be concluded that association of charged surfactant heads with counterions takes place.

An example of the dependence of the counterion concentration on the distance from the droplet center for several values of K is given in the lower part of Figure 2.

The described model for charge distribution and association of counterions with charged surfactant heads was already used in order to predict the equilibrium charge and potential distribution within a droplet containing ionic species other than just counterions.[6] Special attention was paid to the effect of permittivity. The present model yields similar results: a significant increase of the absolute value of potential drop with decreasing the value of permittivity.

Surface Charge Density. With no association taking place and the assumption of constant surface area per molecule of surfactant, A_s, the surface charge density, σ, is independent of the inner droplet radius and, according to this model, equal to $-e/A_s$. Taking A_s = 55 Å^2, the surface charge density is $\sigma = -0.29$ C m^{-2}. This value is indicated by the straight dashed line in the lower part of Figure 3 showing the surface charge density as a function of the droplet water core radius. The effect of association affinity is examined by using different values of the association equilibrium constant. In the case of association ($K > 0$), the absolute value of σ depends on the droplet size and is lower in magnitude than 0.29 C m^{-2}. Obviously, according to this model, the association of counterions with charged surfactant heads influences significantly the surface charge density of droplets. The calculated
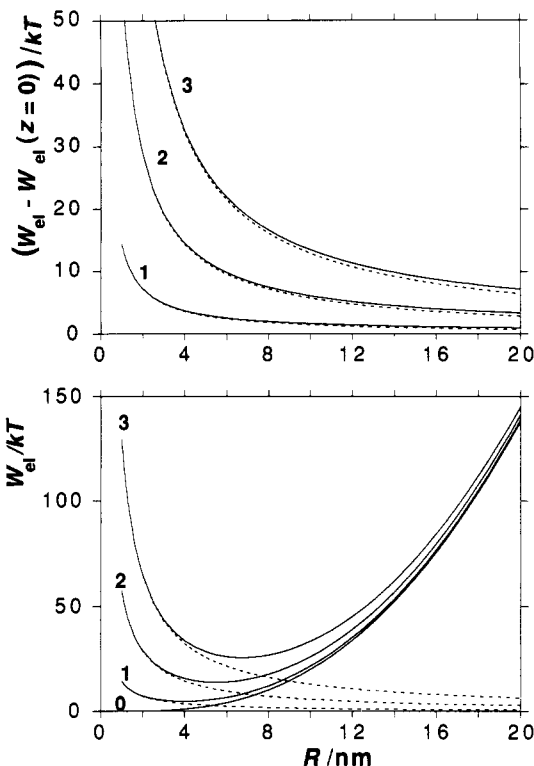
equilibrium values have the same order of magnitude as the surface charge density of metal oxides.[19]

The upper part of Figure 3 displays the same results expressed as a fraction of associates. With $K = 10^{-27}$ m^3 (=0.6022 dm^3 mol^{-1}), about 70% of the surfactant heads are associated with counterions. Experiments with the AOT/water/isooctane microemulsion droplets containing co-ions (neutral electrolyte added) showed that 72% of Na$^+$ ions is bound to the surface. On the basis of this result, Karpe and Ruckenstein[6] estimated $K = 5.56 \times 10^{-28}$ m^3, which is in agreement with the present result ($K = 10^{-27}$ m^3 corresponds to about 70% of associates). Since the presence of co-ions could weaken the attraction between positive counterions and negatively charged surfactant heads, and the systems considered in the present study contain only one kind of charged species in the droplet interior (counterions and no co-ions), one can assume that the fraction of associates in reality is higher than 72%, i.e., $K > 10^{-27}$ m^3.

Electrostatic Energy of a Droplet. Electrostatic energy of the droplet, W_{el}, as predicted by the present model in eq 20, is calculated for several numbers of positive and negative species in the droplet. The droplet charge number z can be obtained in several ways; $N_d = \langle N^{tot} \rangle + i$ and $N_s = \langle N^{tot} \rangle + i - z$, where i = ..., -2, -1, 0, 1, 2, ...

The results are shown in Figure 4. The lower part of Figure 4 gives the electrostatic energy as a function of the radius of the water core, R, for droplet charge numbers $z = 0, 1, 2, 3$. The deviation from the mean value of the total number of surfactant molecules per droplet (calculated from eq 44) is taken as less than four molecules ($-3 \leq i \leq +3$) and the electrostatic energies calculated for the same droplet charge number, but a different number of charged species, are not distinguishable by the width of the lines. Dashed lines in Figure 4 are Born energies for the same droplet charge numbers. Obviously, the Born energy is a

(19) *Adsorption of Inorganics at Solid/Liquid Interfaces*; Anderson, M. A., Rubin, E. J., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1981.
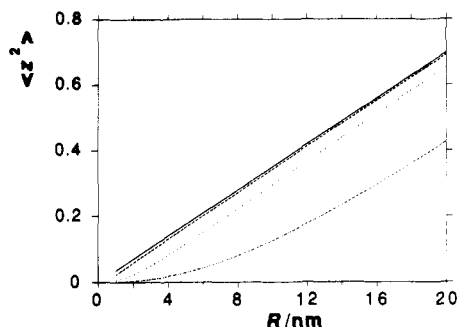
Figure 5. Average square of droplet charge number as a function of water core radius, as obtained by the charge fluctuation model. The solid line is an approximate solution of eq 39, $\langle z^2 \rangle = 1/\alpha$; the dashed line is the solution of eq 39 with $K = 10^{-22}$ m^3, the dotted line with $K = 10^{-20}$ m^3, and the dash–dotted line with $K = 10^{-18}$ m^3. Other parameters are the same as in Figure 4.

Figure 6. Average square of droplet charge number as a function of water core radius obtained by the Boltzmann distribution (solid line) and charge fluctuation model (dashed line). Both solutions are approximate; the influence of charge distribution within a droplet is neglected. Parameters used in calculation: $z_s = -1$, $z_d = +1$, $\epsilon_m = 1.96\epsilon_0$, $T = 298$ K.

good approximation to the present model for small droplets ($R \leq 4$ nm); i.e., the influence of the charge distribution within the droplet is negligible for small droplets. This finding could answer the criticism of the use of the Poisson–Boltzmann equation for evaluating the energy of small droplets, despite the fact that this equation is more realistic for larger droplets.

The contribution of the charge distribution to the total electrostatic energy for particles larger than 6 nm is higher than the Born energy (contribution due to the net charge). However, the difference between electrostatic energies of electrically charged and neutral droplets (charging energy) is practically the same as the Born energy. This finding is demonstrated in the upper part of Figure 4, and it indicates the applicability of the Born energy as the energy of the charging process in the whole region of droplet sizes.

Average Square of the Charge Number and the Electrical Conductivity. The average square of the charge number is calculated according to the charge fluctuation model (eq 39) and also on the basis of the Boltzmann distribution function (eq 42).

(i) Charge Fluctuation Model. The average square of the charge number of droplets of different sizes (water core radii) is calculated according to eq 39. The results for several values of K are shown in Figure 5. The straight line is the function $\langle z^2 \rangle = 1/\alpha$, i.e., the approximate solution of eq 39. This relation was also obtained by Eicke et al.[1] on the assumption that the Born energy is the only relevant energy contribution in calculating $\langle z^2 \rangle$ by the charge fluctuation model. Figure 5 shows that the values of $\langle z^2 \rangle$ approach $1/\alpha$ if the degree of association (i.e., intrinsic association constant) decreases. The values of $\langle z^2 \rangle$ calculated for $K = 10^{-22}$ m^3 (in that case the degree of association, according to the present model, is higher than 99%, as shown in Figure 3) are already close to $1/\alpha$. The values of $\langle z^2 \rangle$ calculated for $K < 10^{-24}$ m^3 are so close to $1/\alpha$ that they cannot be resolved by separate lines. Obviously, an increase of the association degree decreases the average number of charged species, which makes entropy-originated terms (proportional to $1/N_s$) in eq 39 significant, as already mentioned in the discussion of eq 39.

Except for the dependence of $\langle z^2 \rangle$ on the choice of K, the influence of another model parameter, the permittivity of the droplet interior, is examined. As already discussed, ϵ_w is assumed to be space independent in the droplet interior. Although the charge and potential distribution in the droplet interior depend significantly on the choice of ϵ_w (as shown in ref 6 and confirmed by this work), the values of $\langle z^2 \rangle$ for different values of ϵ_w, calculated by using fixed values of K ($\leq 10^{-22}$ m^3) and R (in the range from 1 to 20 nm), do not show a significant deviation from $1/\alpha$. The permittivity of the polar interior is varied from the bulk value of isooctane to water, for which ϵ_w is equal to $1.96\epsilon_0$ and $78.54\epsilon_0$, respectively. The highest observed deviation in $\langle z^2 \rangle$, calculated with different permittivities and association equilibrium constants, (for $K < 10^{-22}$ m^3) is 0.005; i.e., the highest observed deviation is only 1%. Therefore, it can be concluded that $\langle z^2 \rangle = 1/\alpha$ is a good approximation with respect to the present model, which takes
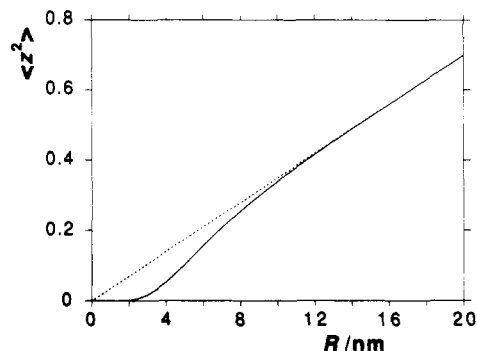
into account the charge distribution, association, and entropy effects. Only in the case when the association is so strong that more than 99% of surfactant heads are associated with counterions ($K > 10^{-22}$ m^3), i.e., when the number of charged species is significantly reduced, does the entropy effect on $\langle z^2 \rangle$ become important and $\langle z^2 \rangle$ is lesser than $1/\alpha$.

It might be of interest to analyze the impact of the obtained values of $\langle z^2 \rangle$ on the possible charge numbers of microemulsion droplets. Assuming $\langle z \rangle = 0$, equal probabilities of the existence of droplets with charge numbers $+z$ and $-z$, and continuous charge distribution, such an analysis can be performed by means of the Gauss probability function. This choice is also confirmed by the fact that the Born energy is proportional to the square of the charge. The Gaussian distribution says that 68% of droplets have charge numbers ranging from $-\langle z^2 \rangle^{1/2}$ to $\langle z^2 \rangle^{1/2}$, and 99% of them between $-2.6\langle z^2 \rangle^{1/2}$ and $+2.6\langle z^2 \rangle^{1/2}$. For example, the system containing relatively large microemulsion droplets of the inner radius $R = 20$ nm whose $\langle z^2 \rangle = 0.7$ has, accordingly, 68% of droplets whose absolute value of the charge number does not exceed 0.84, and only 1% of droplets can be expected to have a charge number larger than 2.17. The system containing droplets of the inner radius $R = 6$ nm and $\langle z^2 \rangle = 0.2$ can be expected to have 68% of droplets with the absolute value of the charge number less than 0.45 and 99% of them less than 1.16. After applying such a simple analysis, based on continuous probability, on microemulsion droplets, which in fact can have only discrete charge numbers, one can hardly expect the existence of droplets of charge number three or higher.

(ii) Boltzmann Distribution. The average square of the charge number, calculated by the Boltzmann distribution function using eq 43, is compared with the results obtained by the charge fluctuation model in Figure 6. Both solutions are obtained by assuming that no association takes place. The results of the two methods perfectly agree for relatively large droplets ($R > 12$ nm). The values obtained by the Boltzmann distribution for smaller particles are lower than those obtained by the charge fluctuation model. This result was explained by the fact that the charge fluctuation model does not respect the discreteness of the net droplet charge ($z = 0, \pm 1, \pm 2, ...$), while the Boltzmann distribution does.[2] Unfortunately, measurements of electrical conductivity of the AOT/isooctane/water system cannot be used to distinguish between these two approaches, since both could fit the experimental data.[2,3]

While $\langle z^2 \rangle$ obtained by eq 43 (presented in Figure 6) ignores the influence of the charge distribution, the use of eq 42 enables an insight into its effects. Figure 7 is a comparison of the two approaches giving slightly different results. The assumption that no association takes place ($K = 0$) results in $\langle z^2 \rangle$ higher than the one calculated on the basis of the Born energy approximation. Increase of the association extent (i.e., association equilibrium constant, K) enables the condition $\exp(-g(N_d)) \ll \sum_{N_d=0}^{\infty} \exp(-g(N_d))$ to be satisfied and, therefore, as already discussed, the results approach those obtained by eq 43.
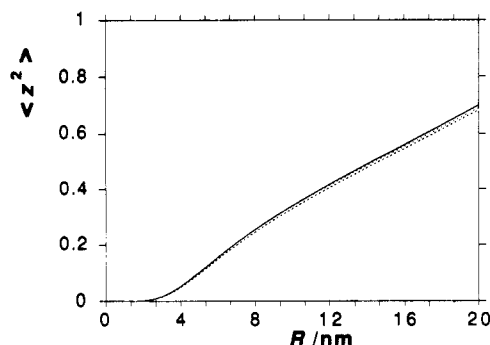
Figure 7. Average square of droplet charge number as a function of water core radius obtained by the Boltzmann probability distribution. The solid line is the solution of eq 43 where the influence of the charge distribution is neglected; the dashed and dotted lines are the solutions of eq 42 with $K = 0$ and $K = 10^{-24}$ m^3, respectively. Other parameters are the same as in Figure 4.

However, the differences in $\langle z^2 \rangle$ obtained in these ways are so small that it is hard to expect the accuracy of experimental methods (e.g., electrical conductivity can be calculated by eq 1) to be high enough to confirm the choice of a particular method of calculation of $\langle z^2 \rangle$.

Although the Boltzmann statistics and the charge fluctuation model give opposite trends for $\langle z^2 \rangle$ with an increase of the association extent (compare Figures 5 and 7), the differences are not significant, except for a very strong association in the case of the application of the charge fluctuation model. For relatively small droplets ($R < 8$ nm), the difference in the values of $\langle z^2 \rangle$ calculated by these two approaches becomes significant (Figure 6). This difference depends solely on the approach (the charge fluctuation model or the Boltzmann statistics), but not on the model chosen for the charge distribution, nor on the values of the association constant and the water core permittivity. This discrepancy was assigned to the effect of discreteness of charge, which was respected in the Boltzmann statistics (expressed by sums, not integrals) and ignored in the charge fluctuation model.[2] The average square of the droplet charge number, obtained by the Boltzmann probability distribution, was used to calculate the electrical conductivity (eq 1 with $r_h = R$), and the results fitted well the experiments on the AOT/water/isooctane microemulsion system.[2] However, the same experimental results[1] were also fitted well[3] by the charge fluctuation model (eq 1 with $r_h = R + l$) with one adjustable parameter, the mean length of surfactant chains, l. The same approach (i.e., taking $r_h = R + l$) with the Boltzmann distribution function does not enable such a good fit of the mentioned experimental results.[20]

Conclusions

The present model of the water-in-oil microemulsion droplet results in the expression for the droplet electrostatic energy, which can be separated into two terms: the first depends on the net charge of the droplet (Born energy), and the second depends on the charge distribution within a droplet (obtained from the Poisson-Boltzmann equation). The second term is not a mere correction of the first one; it is significant for large droplets. While the absolute value of the energy depends on the choice of the model, the difference between charged and electrically neutral droplets (energy of charging) is close to the Born energy in the whole region of droplet sizes. This finding suggests that the calculation of statistical quantities (as the average square of the charge number) will not be heavily influenced by the effect of charge distribution within the droplet.

The average square of the droplet charge number, $\langle z^2 \rangle$, which is proportional to the microemulsion conductivity, is decreased in the case of strong association of counterions (>99%) with

(20) Kallay, N.; Tomić, M.; Chittofrati, A. *J. Colloid Polym. Sci.*, in press.
(21) See, e.g.: Korn, G. A.; Korn, T. M. *Mathematical Handbook for Scientists and Engineers*; McGraw-Hill: New York, 1961.
(22) Bratko, D.; Woodward, C. E.; Luzar, A. *J. Chem. Phys.* **1991**, *95*, 5318.

charged surfactant heads. This decrease is due to the entropy effect. The permittivity of water core, ϵ_w, does not influence $\langle z^2 \rangle$ and thus the electrical conductivity. This is of importance because ϵ_w is, in principle, unknown. However, both parameters, the association equilibrium constant and the water core permittivity, influence the (absolute) value of the droplet energy, which is important in consideration of the microemulsion formation and chemical reactions taking place within droplets.

According to the analysis conducted here, the Born energy is a good approximation for the interpretation of the electrical conductivity of water-in-oil microemulsions. The only remaining problem is the choice of the statistical model; the Boltzmann distribution should better describe the discrete nature of the net droplet charge, while the charge fluctuation fits better the available experimental data when proper size parameters are used.

The above problems do not exist for large droplets ($R > 12$ nm), which enables accurate interpretation in this region.

Note Added in Proof. After the completion of this work, another interpretation of the charge fluctuation in water-in-oil microemulsion droplets using the assumption of counter- and co-ions present in the droplet interior was published by Bratko et al.[22] These authors used linear response/Poisson-Boltzmann approximation and grand canonical ensemble Monte Carlo simulation in order to obtain $\langle z^2 \rangle$. The former gave results identical to those of the charge fluctuation model with association of counterions and charged surfactant heads neglected, while the latter approach gave results similar to those obtained by the Boltzmann probability distribution in the present work.

While the present paper deals with droplets containing only two charged species (counterions and charged surfactant heads), an analogous analysis could have been performed on systems with added neutral electrolyte (co-ions also present), which would require the application of the appropriate form of the Poisson-Boltzmann equation. The usual form of this equation implies the assumption of equal referent concentrations of counterions and co-ions. Such an assumption may not take into account the possible deviation from electrical neutrality of a droplet.

Appendix I

The integral defined by eq 19 is solved by the use of the Gauss theorem:

$$4\pi r^2 E(r) = \frac{4\pi}{\epsilon_w} \int_0^r \rho(r') r'^2 \, dr' \tag{I.1}$$

The electric field can be written as

$$E = -\frac{d\phi}{dr} = -\frac{2kT}{ez_d} \sum_{j=1}^{\infty} j b_j \lambda^{2j} r^{2j-1} \tag{I.2}$$

Substituting eqs I.2 and eq 6 into I.1 and taking the derivative of the whole equation with respect to r yields

$$\exp(-\sum_{j=1}^{\infty} b_j (\lambda r)^{2j}) = -\frac{2\epsilon_w kT}{e^2 z_d^2 c_d(0) r^2} \sum_{n=1}^{\infty} n(2n+1) b_n (\lambda r)^{2n} \tag{I.3}$$

Equation 19 and I.3 give the expression for I, which contains a simple integral:

$$I = -\frac{2\epsilon_w kT}{e^2 z_d^2} \sum_{n=1}^{\infty} \sum_{j=1}^{\infty} j(2j+1) b_n b_j \lambda^{2n+2j} \int_0^R r^{2n+2j} \, dr \tag{I.4}$$

whose solution is

$$I = -\frac{2\epsilon_w kTR}{e^2 z_d^2} \sum_{n=1}^{\infty} \sum_{j=1}^{\infty} \frac{j(2j+1)}{2n+2j+1} b_n b_j (\lambda R)^{2n+2j} \tag{I.5}$$

Using the identity $2j + 1 = (2j + 2n + 1) - 2n$ and the expression for the total number of counterions in the droplet (eq 23) yields

$$I = \frac{2\epsilon_w kTR}{e^2 z_d^2} \left[\beta N_d \sum_{n=1}^{\infty} b_n (\lambda R)^{2n} + 2 \sum_{n=1}^{\infty} \sum_{j=1}^{\infty} \frac{nj}{2j+2n+1} b_n b_j (\lambda R)^{2n+2j} \right] \tag{I.6}$$

Applying the rule about the product of indefinite sums[21] on the above equation gives

$$I = \frac{1}{4\pi}N_d\sum_{n=1}^{\infty}b_n(\lambda R)^{2n} + \frac{1}{2\pi\beta}\sum_{n=1}^{\infty}D_n(\lambda R)^{2n} \qquad (I.7)$$

where the coefficients D_n are system independent:

$$D_n = \frac{1}{2n+1}\sum_{j=1}^{n}j(n-j)b_jb_{n-j} \qquad (I.8)$$

Appendix II

Taking the derivative of eq 23 with respect to N_d (λ depends on $c_d(0)$ according to eq 8) yields the expression for the partial derivative of the counterion concentration in the droplet center with respect to the counterion number:

$$\frac{\partial c_d(0)}{\partial N_d} = -\frac{\beta c_d(0)}{\Sigma_2} \qquad (II.1)$$

and the second derivative

$$\frac{\partial^2 c_d(0)}{\partial N_d^2} = \frac{\beta^2 c_d(0)}{\Sigma_2^2} - \frac{\beta^2 c_d(0)\Sigma_3}{\Sigma_2^3} \qquad (II.2)$$

where

$$\Sigma_n = \sum_{j=1}^{\infty}j^n b_j(\lambda R)^{2j}; \quad n = 2, 3 \qquad (II.3)$$

The last term in eq 36 is obtained by taking the second derivative of eq I.6 and substituting eq 23:

$$2\pi\frac{\partial^2 I}{\partial N_d^2} = \frac{3\beta^2 N_d}{2\Sigma_2} + \frac{\beta^3 N_d^2\Sigma_3}{2\Sigma_2^3} + \frac{\beta}{\Sigma_2^2}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\frac{ij(i+j)}{2j+2i+1}b_ib_j(\lambda R)^{2i+2j}\left(i+j-\frac{\Sigma_3}{\Sigma_2}\right) \qquad (II.4)$$

Substitution of eqs II.1, II.2, and II.4 into eq 36 gives

$$d = -\frac{\beta}{\Sigma_2}(2+3\beta N_d) - \frac{\beta^2 N_d\Sigma_3}{\Sigma_2^3}(1+\beta N_d) + \frac{\beta}{\Sigma_2^3}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}\frac{ijk^2(i+j)(k-i-j)}{2j+2i+1}b_ib_jb_k(\lambda R)^{2i+2j+2k} \qquad (II.5)$$

It is possible to simplify the calculation of the triple sum in the above equation by applying the rule about the product of indefinite sums,[21] so that the final expression for d reads

$$d = -\frac{\beta}{\Sigma_2}(2+3\beta N_d) - \frac{\beta^2 N_d\Sigma_3}{\Sigma_2^3}(1+\beta N_d) + \frac{\beta}{\Sigma_2^3}\sum_{m=1}^{\infty}B_m(\lambda R)^{2m} \qquad (II.6)$$

where coefficients B_m are calculated from the coefficients b_j:

$$B_m = \sum_{i=1}^{m}\sum_{j=1}^{i}\frac{ij(i-j)(m-i)^2(m-2i)}{2i+1}b_{i-j}b_{m-i}b_j \qquad (II.7)$$

Glossary

A	surface area
A_s	average surface area occupied per surfactant molecule
b_j	coefficients in the series expansion of eq 11 defined by eq 12
B_j	coefficients in the series expansion of eq II.6
c_d	(number) concentration of counterions in diffuse layer
c°	standard value of concentration of counterions
C	number of droplets per unit volume
d	function defined by eqs 36 and II.6
D_i	coefficients in the series of eq 20
e	proton charge
E	electric field
F	free energy
F_A	interfacial surface energy
g	energy contribution due to the counterion distribution used in eq 41
I	function defined by eqs 19 and I.6
k	the Boltzmann constant
K	intrinsic association constant
l	mean length of surfactant chains
$\mathbf{M}$	matrix with elements $\partial\mu_i/\partial N_j$
N_{as}	number of associates at the droplet interface
N_d	number of counterions in the droplet water core
N_s	number of dissociated surfactant heads at the droplet interface
r	radial coordinate
r_h	hydrodynamic droplet radius
R	radius of the water core
S	entropy
T	(thermodynamic) temperature
V	volume
W_{el}	electrostatic energy
x	dimensionless distance defined by eq 8
z	charge number of the droplet
z_d	counterion charge number
z_s	charge number of dissociated surfactant head
α	constant defined by eq 35
β	constant defined by eq 22
ϵ_0	permittivity of the vacuum
ϵ_m	permittivity of the oil medium
ϵ_w	permittivity of the water core
η	viscosity of the medium
κ	electrical conductivity
λ	inverse distance defined by eq 8
μ_{as}	chemical potential of associates
μ_d	chemical potential of counterions
μ_s	chemical potential of charged surfactant heads
μ_i°	standard chemical potential of species i (i = as, d, s)
ρ	charge density
σ	surface charge density
Σ_n	(n = 2, 3) sum defined by eq II.3
ϕ	electrostatic potential
ψ	dimensionless potential defined by eq 9