Model for the Conductivity of Ionic Mixtures in the Mean Spherical Approximation. 2. Surfactant Solutions

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We recently obtained analytic expressions for the concentration dependence of the conductance of a mixture with three simple ionic species. These expressions are available at concentrations up to 1 equiv of solute per liter of solution. The success of our description is based on the use of the mean spherical approximation (MSA). It yields explicit formulas in terms of the MSA inverse screening length Γ and the dynamical Debye−Falkenhagen length. We present here results obtained for ionic surfactant systems where, above the critical micellar concentration (cmc), three charged species are present in the solution. From the accuracy of the results one may infer that the size and the charge of ionic micelles above the cmc could be determined using conductivity experiments.

1. Introduction

The concentration dependence of the transport coefficients of electrolytes is one of the oldest ongoing problems in physical chemistry. In the early papers of Onsager *et al.* in 1926[1] and in 1932[2] the limiting laws for the conductance were given, and in 1957 Onsager *et al.*[3] made an attempt to extend the validity of the conductivity limiting law to higher concentrations. They used the Debye−Hückel equilibrium pair distribution functions available at that time,[4] and their results were limited to concentrations below 0.01 M in water.

Later Quint and Viallard[5,6] were able to extend this limit to 0.1 M, by introducing finite ionic size corrections (extended limiting law). This change allowed them to improve, by a factor of 10, the range of validity of the Onsager−Kim treatment with respect to concentration.

This example shows the necessity of an accurate description of equilibrium properties in order to compute nonequilibrium phenomena such as electrical conductance. It is crucial to use satisfying equilibrium pair distribution functions up to concentrations as high as 1 M in order to describe transport properties up to these concentrations.

We have recently proposed a linear response theory in which Onsager's continuity equations were combined with the MSA equilibrium correlation functions, using the Green's response functions formalism. We use a primitive model description, where the solvent effects are averaged out. This approach was applied to different transport phenomena of electrolyte solutions in the range 0−1 M.[7−9] The treatment was extended to associated electrolytes for conductance and self-diffusion,[10,11] using a chemical model of association. We also extended the theory to the conductance of electrolytes with three simple ionic species where each size of ion was taken into account individually.

The main interest of our mathematical treatment is to lead to relatively simple analytical formulas. These were tested using conductivity experiments of NaCl/KCl[6,12] and NaCl/MgCl$_2$[13] mixtures in water; the agreement between theory and experiment was found satisfactory.[14] In the present paper we apply our theoretical approach to ionic micellar systems. Below the

critical micelle concentration (cmc), two ionic species are present, and above the cmc, three ionic species: monomer surfactant, counterions, and micelles. Thus the chemical system is equivalent to a three-ion species solution.

2. Theoretical Background

The theoretical treatment was given in a previous article;[14] therefore we shall only present the essential steps of our calculation. The two most important phenomena that explain the nonideal behavior of ion conductivity are the relaxation and the hydrodynamic forces. The first correction was introduced by Debye.[4,15] It describes the electric interionic forces that appear when the electric equilibrium state of a charged solution is perturbed. The relaxation force is given by[16,17]

$$\delta \mathbf{k}_i = -\sum_j n_j \int_0^\infty \nabla(V_{ij}^{Cb} + V_{ij}^*)h_{ij}' \, d\mathbf{r} \tag{1}$$

where h_{ij}' is the first-order perturbation of the total pair distribution function, V_{ij}^{Cb} is the Coulomb potential, and V_{ij}^* is the hard sphere potential given by

$$V_{ij}^* = \begin{cases} \infty & \text{if } r < \sigma_{ij} \\ 0 & \text{if } r \geq \sigma_{ij} \end{cases} \tag{2}$$

where σ_{ij} is the sum of the radii of the two ions i and j, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, i.e. the closest approach between the ion i and the ion j. n_j is the numerical concentration of the species j. Using the hydrodynamic continuity equations[18] in the stationary approximation, the linear response theory and the mean spherical approximation for the description of the equilibrium part h_{ij}°,[19,20] we were able to give the relaxation forces acting on the ions. As three ion species are present, we must take into account three forces. Moreover, we assume that the external electric field $\mathbf{E}$ is along the axis z, and so the relevant value is the projection of these forces along z.

$$\delta \mathbf{k}_1^{rel}|_z = \frac{C_1 E}{3n_1} \sum_{l=1}^{3} \{L_{2l} f_{12}(G_{2l}(\kappa_+) - G_{2l}(\kappa_-)) \times$$
$$L_{1l}(G_{1l}(\kappa_+)(f_{11} - \kappa_+^2) + G_{1l}(\kappa_-)(\kappa_-^2 - f_{11}))\} \tag{3}$$

$$\delta \mathbf{k}_2^{\text{rel}}|_z = \frac{C_1 E}{3 n_2} \sum_{l=1}^{3} \{ L_{1l} f_{21} (G_{1l}(\kappa_+) - G_{1l}(\kappa_-)) \times$$
$$L_{2l} (G_{2l}(\kappa_+)(f_{21} - \kappa_+^2) + G_{2l}(\kappa_-)(\kappa_-^2 - f_{21})) \} \quad (4)$$

$$\delta \mathbf{k}_3^{\text{rel}}|_z = \frac{C_1 E}{3 n_3} \sum_{l=1}^{3} \{ L_{1l} (G_{1l}(\kappa_+)(\kappa_+^2 - (f_{11} + f_{21})) +$$
$$G_{1l}(\kappa_-)((f_{11} + f_{21}) - \kappa_-^2)) \times L_{2l} (G_{2l}(\kappa_+)(\kappa_+^2 -$$
$$(f_{12} + f_{22})) + G_{2l}(\kappa_-)((f_{12} + f_{22}) - \kappa_-^2)) \} \quad (5)$$

where

$$C_1 = 1/(\epsilon_0 \epsilon_r k_B T (\kappa_-^2 - \kappa_+^2)) \quad (6)$$

ϵ_r is the relative dielectric constant of the solvent, and ϵ_0, that of the vacuum. k_B is Boltzmann's constant, and T is the absolute temperature. κ_- and κ_+ are the roots of the determinant of the system eqs 7 and 8.

$$\Delta Y_j - \kappa^2 \bar{\omega} (Y_j \sum_{l=1}^{3} (t_l/b_{lj}) - t_j \sum_{l=1}^{3} (Y_l/b_{lj})) = T_j \quad (7)$$

$$\sum_{j=1}^{3} Y_j = 0 \quad (8)$$

where

$$Y_i = n_i e_i \Delta \psi_i' \quad (9)$$

$$t_i = n_i e_i^2 \omega_i / (\sum_{l=1}^{3} n_l e_l^2 \omega_l) \quad (10)$$

$$\kappa^2 = \frac{1}{\epsilon_0 \epsilon_r} \sum_{l=1}^{3} n_l e_l^2 \quad (11)$$

$$b_{kj} = \omega_k + \omega_j \quad (12)$$

$$T_j = \frac{1}{\epsilon_0 \epsilon_r} \sum_{l=1}^{3} \left[\frac{a_l}{b_{lj}} (\mathbf{k}_l \omega_l - \mathbf{k}_j \omega_j) \nabla (a_j h_{jl}^\circ) \right] \quad (13)$$

$$a_i = n_i e_i \quad (14)$$

$$\bar{\omega} = \sum_{i=1}^{3} n_i e_i^2 \omega_i / \sum_{i=1}^{3} n_i e_i^2 \quad (15)$$

$$\omega_i = D_i^\circ / (k_B T) \quad (16)$$

$$\mathbf{k}_j = e_j \mathbf{E} \quad (17)$$

where e_j is the charge of the species j. Furthermore

$$L_{jl} = \frac{e_l D_l^\circ - e_j D_j^\circ}{D_l^\circ + D_j^\circ} n_l e_l n_j e_j \quad (18)$$

where D_j° is the diffusion coefficient at infinite dilution of the species j and

$$f_{11} = (\kappa^2 \bar{\omega} / (\omega_2 + \omega_3))(1 + t_1(\omega_3 - \omega_1)/(\omega_1 + \omega_2)) \quad (19)$$

$$f_{12} = -\kappa^2 \bar{\omega} t_1 ((1/b_{13}) - (1/b_{12})) \quad (20)$$

$$f_{21} = -\kappa^2 \bar{\omega} t_2 ((1/b_{23}) - (1/b_{12})) \quad (21)$$

$$f_{22} = (\kappa^2 \bar{\omega} / (\omega_1 + \omega_3))(1 + t_2(\omega_3 - \omega_2)/(\omega_1 + \omega_2)) \quad (22)$$

and

$$G_{ij}(\kappa) = G_{ji}(\kappa) = e_i e_j \sinh(\kappa \sigma_{ij}) \exp(\kappa \sigma_{ij}) / \{ \sigma_{ij} 4 \pi \epsilon_0 \epsilon_r k_B T (1 +$$
$$\Gamma \sigma_i)(1 + \Gamma \sigma_j)[\kappa^2 + 2\Gamma \kappa + 2\Gamma^2 (1 - (1/\alpha^2) \sum_{k=1}^{3} n_k a_k^2$$
$$\exp(-\kappa \sigma_k))] \} \quad (23)$$

For the very asymmetric case we use the individual ionic radii to calculate Γ using the equations of Blum et al.[19,20]

$$4\Gamma^2 = \frac{e^2}{\epsilon_0 \epsilon_r k_B T} \sum_{i=1}^{3} n_i \left(\left(z_i - \frac{\pi}{2\Delta} P_n \sigma_i^2 \right) / (1 + \Gamma \sigma_i) \right)^2 \quad (24)$$

where

$$P_n = (1/\Omega) \sum_{k=1}^{3} (n_k \sigma_k z_k / (1 + \Gamma \sigma_k)) \quad (25)$$

$$\Omega = 1 + (\pi/2\Delta) \sum_{k=1}^{3} (n_k \sigma_k^3 / (1 + \Gamma \sigma_k)) \quad (26)$$

$$\Delta = 1 - (\pi/6) \sum_{k=1}^{3} n_k \sigma_k^3 \quad (27)$$

$$a_k \approx e^2 z_k / (\epsilon_0 \epsilon_r k_B T 2 \Gamma (1 + \Gamma \sigma_k)) \quad (28)$$

Concerning the second correction, the hydrodynamic one, we used the Oseen's tensor to find the correction to the velocity of each ionic species

$$\delta \mathbf{v}_i^{\text{hyd}} = -\sum_{j=1}^{2} n_j \int_{\mathbf{r}} h_{ij}^\circ(\mathbf{r}) \, \mathscr{T}(\mathbf{r}) \, \mathbf{k}_j \, d\mathbf{r} \quad (29)$$

The calculus was made by Bernard et al.[21] The result is

$$\delta \mathbf{v}_i^{\text{hyd}} = -\frac{e_i \mathbf{E}}{3 \pi \eta_0} \left(\frac{\Gamma}{1 + \Gamma \sigma_i} + \frac{\pi}{2\Delta z_i} \frac{P_n \sigma_i}{(1 + \Gamma \sigma_i)} + \frac{\pi}{z_i} \sum_j n_j z_j \sigma_{ij}^2 \right) \quad (30)$$

where the sum must be extended to the three ionic species.

Finally, we were able to give an expression of the specific conductance where the two interionic forces are taken into account

$$\chi_{\text{sp}}(\Omega^{-1} \text{ cm}^{-1}) =$$
$$\frac{10 e^2 N_A}{k_B T} \sum_{i=1}^{3} c_i D_i^\circ z_i^2 (1 + (\delta v_i^{\text{hyd}}/v_i^\circ))(1 + (\delta k_i^{\text{rel}}/k_i)) \quad (31)$$

where c_i is the molar concentration for the component i and v_i° is its velocity at infinite dilution (without ionic strength correction).

$$v_i^\circ = e_i E D_i^\circ / (k_B T) \quad (32)$$

We express now the conductance as the specific conductivity χ_{sp} divided by the total monomer concentration c_{mon}^t (molar conductivity).

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$$\Lambda(\text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}) = 1000\chi_{\text{sp}}/c_{\text{mon}}^{\text{t}} \qquad (33)$$

3. Results and Discussion

Our theory was first tested with the experimental results for two mixtures of simple salts: NaCl/KCl and NaCl/MgCl$_2$ in water.[14] The agreement with experiment[6,12,13] is very good in a large concentration domain (not shown here). At low concentrations the theory converges to the limiting law, and at high concentrations (about 1 M) experimental results are very well reproduced. The only fitting parameter that appears in the theory is, in this case, the individual closest approach distance σ_i. As there are three species, there are three parameters. It was found that an exellent agreement between theory and experiment was observed by increasing the crystal ionic radii by about 10%. No other salt solution was tested because no other experimental results were available in the literature for electrolyte mixtures at high concentrations.

An interesting application is the description of the conductivity of charged micellar systems. It is well-known that surfactants in water form aggregates above a critical micelle concentration (cmc). In the case of ionic surfactants, below the cmc, the solution consists of surfactant monomer ions and their counterions. Above the cmc, there is an effective loss of ionic charges through ion condensation onto the micellar surface. Three types of charged species may be then considered in the solution: the surfactant monomer, the free counterions not bound to the micellar particles, and the micelles. The consequence of the formation of micelles is a sudden change of slope of the conductivity versus surfactant concentration curve. This change is taken as the cmc. Up to now, theories used for the description of the behavior of the surfactant solutions were not adequate since they had to be restricted to the small concentrations domain (usually below 0.005 M). In the present investigation we extended this concentration domain for the ionic mixtures both below and above the cmc.

Concerning micellar systems, the unknown parameters are as follows: the effective radius of the micelle, the critical micellar concentration (cmc), the apparent charge of the micelle (Z^{app}), the aggregation number (n_{agr}), the micellar diffusion coefficient at infinite dilution (D_{mic}°), and the monomer diffusion coefficient at infinite dilution (D_{mon}°). Most of these parameters are available for some micellar systems using various sophisticated experimental methods.

Conductivity experiments and our theoretical approach could be used to determine one or more of these parameters, offering a test of our equations. We used one cationic surfactant, dodecyltrimethylammonium bromide (DTABr from Eastman Kodak was purified by repeated recrystallization in ethanol), and three anionic surfactants, sodium dodecyl sulfate (SDS), sodium octyl sulfate (SOctylS), and sodium octanoate (SOctan 99% from Aldrich), which was used as received. The surfactants used in this investigation were 1-1 electrolytes, so that below the cmc the monomer concentration was equal to the counterion concentration. Above the cmc, any additional surfactant was considered to be incorporated in the micelles, as required by the pseudophase model of micelle formation. Experimentally, however, the monomer concentration c_{mon} is known to decrease somewhat with surfactant concentration above the cmc. In our treatment we assume that as micelles are formed, the monomer concentration remains constant, whereas a fraction of the counterions will condense onto the micelles. This simplification should have a negligible effect on our results.

If n_{agg} is the micelle aggregation number and Z^{app} the apparent charge of the micelle, the concentrations of the vari-

TABLE 1: Parameters Used for the Theoretical Calculations of the Conductivity of Micellar Systems[g]

surfactant	cmc (M)	Z^{app}	n_{agg}	D_{mic}° ($\times 10^{-10}$ m^2 s^{-1})	D_{mon}° ($\times 10^{-10}$ m^2 s^{-1})	exptl ref
DTABr	0.016[a]	+18[a]	60[a]	1.15[a]	4.5[f]	N$_E$[b]
SDS	0.0081[c]	−18[c]	70[c]	1.15[d]	6.0[d]	23
SOctylS	0.135[c]	−10[c]	24[c]	2.2[f]	7.8[f]	26
SOctan	0.4[e]	−7[f]	15[e]	2.0[e]	6.0[e]	N$_E$[b]

[a] From ref 22. [b] N$_E$: Personnal experiments. [c] From ref 25. [d] From ref 24. [e] From ref 28. [f] Result obtained through a fitting procedure. [g] Exptl ref: references of the conductance experimental data. cmc: critical micellar concentration. Z^{app}: apparent charge of micelles. n_{agg}: aggregation numbers. D_{mic}°: micellar diffusion coefficients of micelles just above the cmc. D_{mon}°: monomer diffusion coefficients at infinite dilution.

ous constituents are

$$c_{\text{mon}} = \text{cmc}$$

$$c_{\text{mic}} = (c_{\text{mon}}^{\text{t}} - \text{cmc})/n_{\text{agg}}$$

$$c_{\text{counterion}} = \text{cmc} + |Z^{\text{app}}|c_{\text{mic}}$$

where $c_{\text{counterion}}$ is the counterion concentration, c_{mic} is the micellar concentration, and $c_{\text{mon}}^{\text{t}}$ is the total monomer concentration.

The hydrodynamic micellar and surfactant monomer radii were estimated from the Nernst−Einstein equation using the approximation of a perfect sticking. The values of all the parameters used are found in Table 1 and in the pertinent figure captions.

The conductivity experiments were performed using a Wayne−Kerr bridge, Model 6425 A. The conductivity cells (Philipps) had platinized electrodes. They were calibrated using standard KCl solutions. The concentration was varied volumetrically by increasing the surfactant concentration using calibrated Gilson syringes. The conductance results had an uncertainty on the order of 1%. Higher precision measurements were not necessary for our purposes. The solutions were thermostated in a water-bath at 25 ± 0.02 °C. The resistances were measured at various frequencies and were extrapolated to zero frequency by linear resistance versus inverse frequency plots.

Figure 1 shows a comparison between theory and experiment for the cationic surfactant (DTABr). The experimental results are very reasonably reproduced. We had no value for D_{mon}° for that system. All the other parameters were taken from Walrand *et al.*[22] They were deduced from quasi-elastic light-diffusion experiments.

Figure 2 presents the same comparison for the anionic surfactant, SDS. The experimental results were taken from the literature.[23] We observe again a very good agreement between theory and experiment. No adjustable parameter was necessary here since the D° values for monomers and micelles were available from Lindman *et al.*[24] These data had been obtained from Fourier transform proton NMR experiments (^{1}H FT NMR) and tracer-diffusion.

Figure 3 presents the results obtained for sodium octyl sulfate. This surfactant has a high cmc (∼0.135 M). The agreement between our theory and experiment[26] is satisfactory below the cmc. Above the cmc, experimental and calculated values diverge rapidly.

The effect of changing the values of the different parameters that have to be introduced in the theory is interesting. Small variations have little consequence on the shape of the curves. The largest effect arises from changes in the aggregation number. Experimentally it has been shown[27] that for SDS the
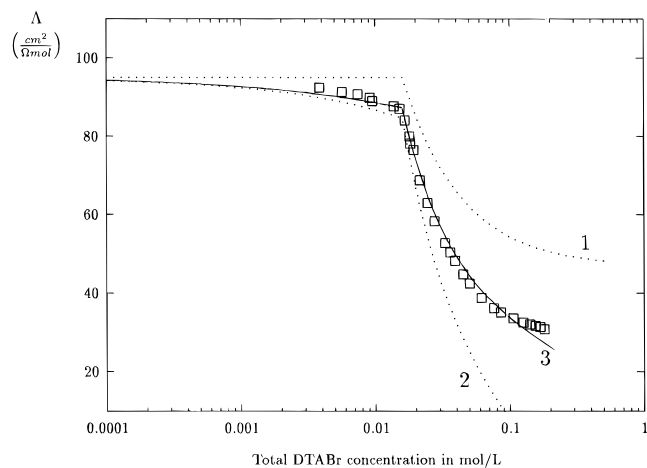
Figure 1. Conductance of dodecyltrimethylammonium bromide (DTABr) as a function of total monomer concentration: ($\square$) experimental data; (1) ideal case; (2) limiting law (Onsager); (3) our results (MSA). Parameters: $r_{mon}^{hyd} = 5.4$ Å, $r_{Br^-} = 1.1 \times 1.97$ Å, $r_{mic}^{hyd} = 21.3$ Å, $D_{mon}^{\circ} = 4.5 \times 10^{-10}$ m^2 s^{-1}, $D_{Br^-}^{\circ} = 2.079 \times 10^{-9}$ m^2 s^{-1}, $D_{mic}^{\circ} = 1.15 \times 10^{-10}$ m^2 s^{-1}.[22] Aggregation number of the micelles $n_{agg} = 60$.[22] Apparent charge $Z^{app} = +18$.[22]
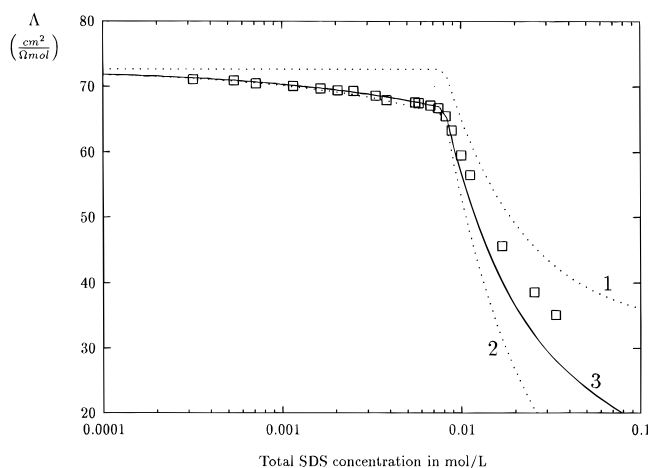
Figure 2. Conductance of sodium dodecyl sulfate (SDS) as a function of total monomer concentration: ($\square$): experimental data;[23] (1) ideal case; (2) limiting law (Onsager); (3) our results (MSA). Parameters: $r_{mon}^{hyd} = 4.1$ Å, $r_{Na^+} = 1.1 \times 0.97$ Å, $r_{mic}^{hyd} = 21.3$ Å, $D_{mon}^{\circ} = 6.0 \times 10^{-10}$ m^2 s^{-1},[24] $D_{Na^+}^{\circ} = 1.333 \times 10^{-9}$ m^2 s^{-1}, $D_{mic}^{\circ} = 1.15 \times 10^{-10}$ m^2 s^{-1}.[24] Aggregation number of the micelles $n_{agg} = 70$.[25] Apparent charge $Z^{app} = -18$.[25]

aggregation number varies from approximately 70 at the cmc to 150 at 0.1 M. We find, theoretically, that at this concentration the conductance decreases from 18.3 cm^2 Ω^{-1} mol^{-1} for an aggregation number of 70 to 12 cm^2 Ω^{-1} mol^{-1} for $n_{agg} = 150$. As all other parameters remaining unchanged, the increase of n_{agg} reflects the decrease of the micelle concentration. Experimentally it is observed that n_{agg} varies less with concentration for cationic micelles than for anionic ones. Not surprisingly, therefore, our calculation is better for the former than for the latter system.

Finally, Figure 4 presents an attempt to apply our model to surfactants with higher cmc. Unfortunaly, the conductivity of sodium octanoate (SOctan) versus total monomer concentration does not show clearly a break at the cmc, and the curve looks very much like those obtained for simple salts in water. The same remark applies to SOctylS. Concerning the sodium octanoate, even if we know that there is a cmc, the reproduction of experimental data would imply choosing an aggregation number lower than 15 and an apparent charge closer to zero.
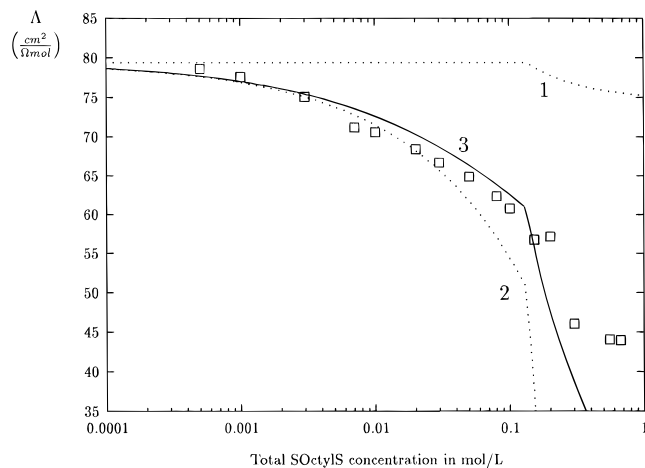

Figure 3. Conductance of sodium octyl sulfate as a function of total monomer concentration: ($\square$) experimental data;[26] (1) ideal case; (2) limiting law (Onsager); (3) our results (MSA). Parameters: $r_{mon}^{hyd} = 3.1$ Å, $r_{Na^+} = 1.1 \times 0.97$ Å, $r_{mic}^{hyd} = 11.15$ Å, $D_{mon}^{\circ} = 7.8 \times 10^{-10}$ m^2 s^{-1}, $D_{Na^+}^{\circ} = 1.333 \times 10^{-9}$ m^2 s^{-1}, $D_{micelle}^{\circ} = 2.2 \times 10^{-10}$ m^2 s^{-1}. Aggregation number of the micelles $n_{agg} = 24$.[25] Apparent charge $Z^{app} = -10$.
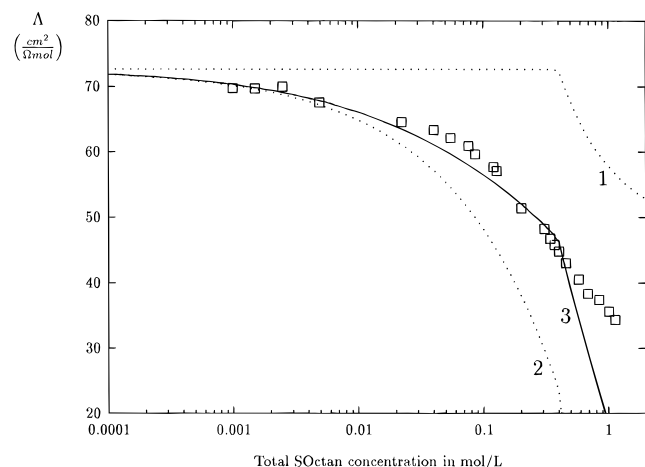

Figure 4. Conductance of sodium octanoate as a function of total monomer concentration (SOctan): ($\square$) experimental data; (1) ideal case; (2) limiting law (Onsager); (3) our results (MSA). Parameters: $r_{mon}^{hyd} = 4$ Å, $r_{Na^+} = 1.1 \times 0.97$ Å, $r_{mic}^{hyd} = 12.3$ Å, $D_{mon}^{\circ} = 6.0 \times 10^{-10}$ m^2 s^{-1},[28] $D_{Na^+}^{\circ} = 1.333 \times 10^{-9}$ m^2 s^{-1}, $D_{micelle}^{\circ} = 2.0 \times 10^{-10}$ m^2 s^{-1}.[28] Aggregation number of the micelles $n_{agg} = 15$.[28] Apparent charge $Z^{app} = -7$.
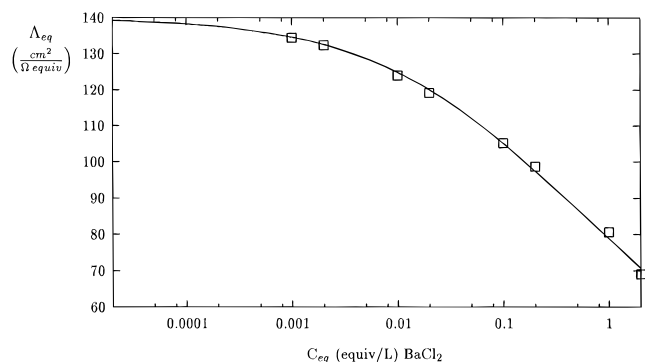

Figure 5. Equivalent conductivity of BaCl$_2$: ($\square$) experimental points at 25 °C;[29] (full line) results obtained with our theoretical treatment.

The conductivity behavior of this last system looks like those of simple salts. As a comparison, Figure 5 presents the results obtained for a 2-1 salt in water: BaCl$_2$.

Direct application of the theory developed for three simple ions to ionic micellar solutions stresses the following points.

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(i) Our description, albeit restricted, is reasonable provided that it is applied to low volume fractions and/or large cmc's and that the interactions between surfactant and counterion are predominant. (ii) At the highest surfactant volume fractions, the structure of the micellar system changes (increase in micellar size, transition from spherical to cylindrical symmetry). Micelle/micelle interactions and micelle/counterion interactions become important, and our approach departs too much from reality.

This latter point is known and has been addressed before.[30,31] However, a correct description of the system implies not only improvements by taking into considerations the hard sphere terms but also the variation of the charge, of the aggregation number, and consequently of the radius of the micelle. If such changes can be made, then a better description of the effect of ionic strength may be envisaged. As it stands today, our theory satisfactorily describes the concentration domain below and slightly above the cmc. An obvious application of our calculation would be the determination of the surfactant diffusion coefficient below the cmc and, at or slightly above the cmc, the evaluation of the micelle diffusion coefficient, the aggregation number, or the apparent charge. The latter quantity is generally obtained, using conductance versus concentration plots, as recalled above, from the ratio of the slopes below and above the cmc. This evaluation implies an ideal situation (no interaction). Using these same experimental quantities, our approach should enable one to give an analytical expression for a more realistic calculation of the apparent micellar charge.

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