Determining the Radius and the Apparent Charge of a Micelle from Electrical Conductivity Measurements by Using a Transport Theory: Explicit Equations for Practical Use

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Received: May 15, 2006

We propose here a procedure which combines experiments and simple analytical formulas that allows us to determine good estimations of the size and charge of ionic micelles above the critical micellar concentration (cmc). First, the conductivity of *n*-tetradecyltrimethylammonium bromide and chloride (TTABr and TTACl, respectively) aqueous solutions was measured at 25 °C, before and above their cmc. Then, an analytical expression for the concentration dependence of the conductance of an ionic mixture with three species (monomers, micelles, and counterions) was developed and applied to the analysis of the experiments. The theoretical calculations use the mean spherical approximation (MSA) to describe equilibrium properties. Here, we propose new expressions for the electrical conductivity, adapted to the case of electrolytes that are dissymmetric in size, and applicable up to a total surfactant concentration of 0.1 mol L^{-1}. Moreover, we show that they are good approximations of the corresponding numerical results obtained from Brownian dynamics simulations. Since the analytical formulas given in the present paper involve a small number of unknown parameters, they allow one to derive the size and charge of macroions in solution from conductivity measurements.

I. Introduction

Charge-stabilized colloidal suspensions contain large macroion particles (diameters in the range of 1–100 nm), their counterions (which are usually small and weakly charged), and a possibly added electrolyte, whose concentration strongly influences the stability of the whole system. The attractive Coulomb interaction that appears between macroions and ions of opposite charges leads to an ionic condensation that decreases the charge of nanoparticles. In such systems, both the effective charge and the radius of dispersed particles are the key parameters that control the stability and the structural properties of the suspension.

The charge or the ζ potential of colloidal particles may be determined by many experimental tools, such as electrophoresis, dielectric spectroscopy, acoustophoresis, or electrical conductivity.[1,2] Among these quantities, electrical conductivity is the one for which experimental determinations are the oldest and the most precise. If the temperature of the experimental cell is correctly controlled, one is usually able to measure the electrical conductivity with a relative precision lower than 0.1%. Nevertheless, in all cases, experimental results must be interpreted by way of adequate theoretical models that link the measured signal to the investigated parameter, either the apparent charge or the radius of particles, for example. Most of these models are adapted to the description of suspensions in which the length scales relative to the nanoparticles and the ions of the supporting electrolyte are very different. For example, a very recent study of Cuquejo et al.[3] provides analytical formulas for the electrical conductivity of concentrated colloidal suspensions with thin double layers, that is, in the limit $\kappa a > 1$, with a being the radius of the macroion and κ being the double-layer thickness. These expressions allow for determining the ζ potential from

experimental results. For dispersions containing colloidal particles with a nanometric size (a radius smaller than 10 nm), only few experimental and theoretical tools are available. First, because of their small size, nanoparticles are difficult to detect with optical devices, and, second, the usual approximations of theoretical models, which neglect the size of small ions, become irrelevant. Recently, some of us proposed to determine the effective charge of spherical magnetic nanoparticles and of platelike particles (Laponite particles) by using both electrical conductivity and acoustophoresis experiments.[4] The results were interpreted by using an analytical transport theory. Here we show how this theory can be adapted to the case of micellar solutions to deduce the effective charge and the radius of micelles from the experimental conductivity.

The theoretical description of the electrical conductivity that is used here is based on Onsager's continuity equations. It treats the solution in the framework of the primitive model, which assumes that the solvent is a continuous medium and that ions are charged hard spheres. Indeed, the early papers of Onsager et al.,[5,6] which gave the well-known limiting laws for electrical conductance, described ions as point charges and were only able to quantitatively account for the experimental behavior of simple electrolyte solutions in the very dilute range. The validity of these laws was extended to higher concentrations[7] by using the Debye–Hückel pair distribution functions[8] and also by taking into account finite size corrections.[9] Nevertheless, latter models were valid only for concentrations lower than 0.1 mol/L for 1–1 electrolytes. The use of equilibrium correlation functions calculated in the mean spherical approximation (MSA) took a big step forward because the theory, still analytically solvable, allowed one to describe several transport phenomena of electrolyte solutions up to molar concentrations.[10–13] In the case of the electrical conductivity, this treatment was next extended to solutions containing three different ionic species,[14,15] each

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J. Phys. Chem. B, Vol. 110, No. 31, 2006 **15543**

one being described by its charge, its individual size, and its diffusion coefficient at infinite dilution.

In the present paper, we propose to determine the effective charge and the radius of ionic micellar species by using the following strategy: (i) the electrical conductivity of a micellar solution before and above the critical micellar concentration (cmc) is precisely measured, and (ii) analytical formulas for the conductivity are used to fit the effective charge and the radius of the micellar species from latter experiments. For this purpose, we have adapted the transport theory based on the MSA equations given in ref 15 to better account for the high dissymmetry in size between macroions and small ions. Moreover, we have checked the validity of these new equations by computing the conductivity of the same system from numerical simulations based on the continuous solvent model. The principle of these Brownian dynamics simulations may be found in refs 16 and 17. Finally, it should be noted that we aim to provide explicit analytical expressions of the electrical conductivity that may be used practically for any solution of asymmetrical electrolytes containing three different ionic species.

The experimental systems consist of solutions of *n*-tetradecyltrimethylammonium bromide and chloride (TTABr and TTACl, respectively) in water. These ionic surfactants are known to form spherical micelles that keep a spherical shape for moderate concentrations.[8] Here, we may then study the influence of the nature of the counterion on the effective charge of the micelle.

The paper is organized as follows. We begin with an Experimental Section, which gives the procedure used to measure the electrical conductivity. Then, the theoretical treatment of the electrical conductivity is presented in detail: we derive new analytical formulas that are particularly adapted to solutions containing asymmetrical electrolytes, and all formulas are explicitly given. Section IV contains the results, including experiments, analytical calculations, and numerical simulations. The paper ends with a concluding discussion.

II. Experimental Determination of the Electrical Conductivity

The conductivity experiments were performed using a Wayne−Kerr bridge, 6425 A. The conductivity cell had bright platinum electrodes. It was calibrated using standard KCl solutions. The cell constant was found to be equal to 0.1792 ± 0.0003 cm^{-1}. This value was checked several times and did not change between the beginning and the end of the measurements. The TTABr (336.41 g/mol) from Fulka was recrystallized in ethanol and then dried in ether. The TTACl (291.95 g/mol) from TCI-EP was used as received. The conductivity cell was thermostated in a water bath at 25.0 ± 0.1 °C. All the solutions were made up by weight. The molarities of the solutions were then assumed to be equal to their molalities, as the densities of the involved solutions are very close to that of pure water (the maximum density correction leads to an error less than 0.2%[19]). Indeed, the maximum molalities of TTABr and TTACl solutions are 0.02 and 0.05 mol/kg, respectively, which correspond to very low volume fractions (0.75 and 1.4%). The resistances of the solutions were measured at various frequencies (10, 5, 2, and 1 kHz) and were extrapolated to zero frequency by linear regressions of the resistance versus inverse frequency plots, as usual.[20] The conductance results have a relative uncertainty evaluated at 0.5%.

III. Analytical Expressions of the Electrical Conductivity

The calculation of the electrical conductivity is based on the assumption that the dominant forces that determine the deviations from the ideal behavior (i.e., without any interactions between ions) are the relaxation and electrophoretic forces.[21] The first one appears when the ionic equilibrium distribution is perturbed by some external force: in that case, electrostatic forces appear, which tend to restore the equilibrium distribution of ions. This effect is called the *relaxation effect*. On the other hand, when external forces are applied on the solution, the different ions have different drift velocities. Hydrodynamic interactions, mediated by the solvent, tend to equalize these velocities: this effect is called the *electrophoretic effect*. As far as the electrical conductivity is involved, the electrophoretic effect is greater than the relaxation effect, and it strongly decreases the conductivity with respect to the infinite dilution.

In the framework of the transport theory, the expression of the electrical conductivity of an ionic solution is the following,[6] in international units:

$$\chi = \frac{e^2}{k_B T}\sum_{i=1}^{3} n_i D_i^o z_i^2 \left(1 + \frac{\delta v_i^{hyd}}{v_i^o}\right)\left(1 + \frac{\delta k_i^{rel}}{k_i}\right) \tag{1}$$

where n_i is the number density of species i, e is the elementary charge, k_B is the Boltzmann constant, T is the temperature, z_i is the valency of species i, and D_i^o is its diffusion coefficient at infinite dilution. δv_i^{hyd} is the electrophoretic correction (also called hydrodynamic correction) on the velocity of species i, δk_i^{rel} is the relaxation correction on the electric force $k_i = z_i e E$ acting on species i, with E being the external applied electric field, and v_i^o is the velocity of species i at infinite dilution:

$$v_i^o = \frac{z_i e E D_i^o}{k_B T} \tag{2}$$

Some of us have already proposed expressions of the relaxation and the electrophoretic corrections in ref 14, which allowed us to account for the experimental conductivity[22,23] of two mixtures of simple electrolyte solutions (NaCl/KCl and NaCl/MgCl$_2$) up to a total concentration of 1 mol/L and of several micellar solutions.[15,17] At low concentrations, the theory converges to the limiting law. Here, we propose a new expression for the conductivity, which is adapted to solutions containing ions that are asymmetrical in size. Indeed, the electrophoretic correction is now evaluated at a higher order than in previous studies, by calculating more precisely the terms that involve the asymmetry in size. Moreover, we give explicit expressions of the three relaxation corrections, corresponding to the three ionic species, which are necessary if one wants to implement the calculation. The equations are of easier use than those given in previous papers. The electrophoretic correction is derived in section III-A, and the relaxation correction is given in section III-B.

A. Calculation of the Electrophoretic Correction Applied on Species *i*. The electrophoretic contribution arises from hydrodynamic interactions between ions mediated by the solvent and translates as[12]

$$\delta v_i^{hyd} = -\sum_{j=1}^{3} n_j \int_r h_{ij}^0(r)\ \mathcal{T}_{ij}(r)\ k_j\ dr \tag{3}$$

where $\mathscr{T}_{ij}(\mathbf{r})$ is the diffusion tensor, which accounts for the influence of the velocity of species j on the velocity of species i. Here, we propose to model hydrodynamic interactions by using the Rotne−Prager tensor,[24] which is a truncated expansion of the pair mobility tensor between two moving spheres with stick boundary conditions.[25,26] This expression contains contributions proportional to $1/r^3$, with r being the distance between particles, and involves the hard sphere diameters of particles i and j, σ_i and σ_j (see section III-B):

$$\mathscr{T}(\mathbf{r}) = \frac{1}{8\pi\eta_o r}\left[\left(\mathscr{I} + \frac{\mathbf{r} \otimes \mathbf{r}}{r^2}\right) - \frac{\sigma_i^2 + \sigma_j^2}{4r^2}\left(\frac{\mathbf{r} \otimes \mathbf{r}}{r^2} - \frac{\mathscr{I}}{3}\right)\right] \tag{4}$$

where η_o is the viscosity of the pure solvent, and $\mathscr{I}$ is the identity matrix.

In previous papers, an approximate evaluation of the electrophoretic contribution was deduced from the expression of the excess internal energy in the MSA,[27,28] since the same integrals appear in both the internal energy (with a Coulomb potential) and the hydrodynamic contribution. As a consequence, some terms, related to the size dissymmetry of the charged species, which cancel when involved in the internal energy, were neglected in the evaluation of the hydrodynamic contribution. The magnitude of these contributions is negligible in the case of simple electrolytes, but may become high in the case of asymmetrical electrolytes, especially at high volume fractions. Now, we obtain

$$\delta\mathbf{v}_i^{\text{hyd}} = -\frac{e\mathbf{E}}{3\pi\eta_o}\left(\mathscr{V}_i' + \frac{\pi}{4}\sum_j n_j z_j \sigma_j^2 - \frac{\pi}{6}\sum_j n_j \sigma_j^3 \mathscr{V}_j'\right) \tag{5}$$

where the two last terms take into account the asymmetry in the size of the ionic species and hard sphere interactions, and with

$$\mathscr{V}_i' = \frac{\Gamma z_i}{1 + \Gamma\sigma_i} + \frac{\pi}{2}\frac{P_n \sigma_i}{\Delta(1 + \Gamma\sigma_i)} \tag{6}$$

where Γ is given in a recursive way by[27,29]

$$4\Gamma^2 = \frac{e^2}{\epsilon_o \epsilon_r k_B T}\sum_{i=1}^{3} n_i\left(\left(z_i - \frac{\pi}{2\Delta}P_n \sigma_i^2\right)/(1 + \Gamma\sigma_i)\right)^2 \tag{7}$$

where

$$P_n = (1/\Omega)\sum_{k=1}^{3}(n_k \sigma_k z_k/(1 + \Gamma\sigma_k)) \tag{8}$$

$$\Omega = 1 + (\pi/2\Delta)\sum_{k=1}^{3}(n_k \sigma_k^3/(1 + \Gamma\sigma_k)) \tag{9}$$

$$\Delta = 1 - (\pi/6)\sum_{k=1}^{3} n_k \sigma_k^3 \tag{10}$$

with ϵ_0 being the permittivity of vacuum and ϵ_r being the relative permittivity of the solvent. Finally, the hydrodynamic correction involved in eq 1 is obtained by dividing $\delta\mathbf{v}_i^{\text{hyd}}$ by v_i^o.

B. Calculation of the Relaxation Correction Applied on Species i. The relaxation force $\delta\mathbf{k}_i$ is given by[30,31]

$$\delta\mathbf{k}_i = -\sum_j n_j \int_0^\infty \nabla(V_{ij}^{\text{Cb}} + V_{ij}^{\text{HS}})h_{ij}'d\mathbf{r} \tag{11}$$

where h_{ij}' is the perturbation of the total pair distribution function due to the external applied electric field, V_{ij}^{Cb} is the Coulomb potential, and V_{ij}^{HS} is the hard sphere potential:

$$V_{ij}^{\text{HS}} = \begin{cases} \infty & \text{if } r < \sigma_{ij} \\ 0 & \text{if } r \geq \sigma_{ij} \end{cases} \tag{12}$$

with σ_{ij} being the closest approach distance between ions i and j: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. If we assume that the external applied electric field is directed along the z-axis ($\mathbf{E} = E\mathbf{z}$), the projection of the relaxation forces along $\mathbf{z}$ applied on species j is given by

$$\delta\mathbf{k}_j^{\text{rel}})_z = \frac{\kappa^2 \mathscr{C}_1 E}{3n_j}\sum_{l=1}^{3} L_{jl}[G_{jl}(\kappa_+)(m_j - q_+) + G_{jl}(\kappa_-)(q_- - m_j)] - t_j\sum_{k=1}^{3} m_k L_{kl}[G_{kl}(\kappa_+) - G_{kl}(\kappa_-)] \tag{13}$$

where $\kappa^2 = \sum_l n_l e_l^2/(\epsilon_o \epsilon_r k_B T)$ is the square of the Debye screening parameter, with $e_i = z_i e$,

$$G_{ij}(x) = G_{ji}(x) =$$

$$\frac{A_{ij}\sinh(x\sigma_{ij})\exp(-x\sigma_{ij})}{x^2 + 2\Gamma x + 2\Gamma^2\left(1 - \frac{1}{\alpha^2}\sum_k n_k a_k^2 \exp(-x\sigma_k)\right)} \tag{14}$$

with

$$A_{ij} = \frac{e_i e_j}{4\pi\epsilon_o \epsilon_r k_B T \sigma_{ij}(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)} \tag{15}$$

with

$$a_k \approx \frac{z_k}{(1 + \Gamma\sigma_k)} \tag{16}$$

and

$$\alpha^2 = \sum_k n_k a_k^2 \tag{17}$$

The quantities involved in the previous equations are as follows:

$$L_{il} = \frac{e_l D_l^o - e_i D_i^o}{D_l^o + D_i^o} n_l e_l n_i e_i \tag{18}$$

$$\mathscr{C}_1 = \frac{1}{\epsilon_o \epsilon_r k_B T(\kappa_-^2 - \kappa_+^2)} \tag{19}$$

with

$$\kappa_+^2 = \kappa^2 q_+ = \frac{\tilde{B} + \sqrt{\tilde{B}^2 - 4\tilde{C}}}{2} \quad \kappa_-^2 = \kappa^2 q_- = \frac{\tilde{B} - \sqrt{\tilde{B}^2 - 4\tilde{C}}}{2} \tag{20}$$

where $\tilde{B}$ and $\tilde{C}$ are two positive real values:

$$\tilde{B} = \kappa^2[(1 - t_1)m_1 + (1 - t_2)m_2 + (1 - t_3)m_3] \tag{21}$$

$$\tilde{C} = \kappa^4[t_1 m_2 m_3 + t_2 m_1 m_3 + t_3 m_1 m_2] \tag{22}$$

with

$$m_1 = \bar{\omega}/(\omega_2 + \omega_3) \qquad (23)$$

$$m_2 = \bar{\omega}/(\omega_1 + \omega_3) \qquad (24)$$

$$m_3 = \bar{\omega}/(\omega_1 + \omega_2) \qquad (25)$$

and

$$\bar{\omega} = \sum_l n_l e_l^2 \omega_l / \sum_l n_l e_l^2 \qquad (26)$$

is a mean mobility,

$$\omega_i = D_i^o/k_B T$$

is the individual mobility of species i, and

$$t_i = \frac{n_i e_i^2 \omega_i}{\sum_l n_l e_l^2 \omega_l}$$

is the transport number at infinite dilution.

IV. Results and Discussion

The experimental molar electrical conductivities of aqueous solutions of TTABr and TTACl are given in Tables 1 and 2 as functions of the total molality of the surfactant. Here the molar conductivity is defined by the conductivity χ divided by the total monomer molar concentration c_{mon}^t:

$$\Lambda = \frac{\chi}{c_{mon}^t} \qquad (27)$$

Several independent series of measurements have been performed, which have led to results very close to each other. Here, the molality of the surfactant (in moles per kilogram) has been assumed to be equal to the molarity (in moles per liter), since the density correction are small for both systems in the concentration range under study. As expected, the electrical conductivity varies strongly at the cmc, when some surfactants

TABLE 1: Experimental Molar Electrical Conductivity (Λ/S cm^2 mol^{-1}), of TTABr Solutions at 298.15 K as a Function of the Total Monomer Molality (C_{mon}^t/mol kg^{-1})^a

C_{mon}^t	Λ	C_{mon}^t	Λ	C_{mon}^t	Λ	C_{mon}^t	Λ
0.01266	44.18	0.00380	92.26	0.00976	50.14	0.01990	36.09
0.00950	51.42	0.00362	93.73	0.00652	64.27	0.01488	40.74
0.00761	58.67	0.00346	94.33	0.00435	84.65	0.01173	45.71
0.00634	66.37	0.00331	94.67	0.00187	95.30	0.00977	50.42
0.00476	80.17	0.00317	94.81	0.00127	95.95		
0.00423	86.86	0.00272	95.25	0.00084	96.33		
0.00400	89.87						

^{a}Three independent series of measurements are given.

aggregate to form micellar species. The experimental results lead to cmc = 3.8 10^{-3} mol L^{-1} for TTABr and to cmc = 5.5 10^{-3} mol L^{-1} for TTACl, which is in the range of the literature values.[32−37]

For concentrations higher than the cmc, the solution consists of

(i) spherical macroions (the micellar species) formed by the association of n_{agg} monomers. The micelle radius $a_{micelle}$ is linked via the Stokes law to the self-diffusion coefficient at infinite dilution $D_{micelle}^o$ and has an apparent charge, Z_{app}, due to the partial condensation of counterions on the micelle surface.

(ii) small monovalent counterions of radius a_{ion} and of self-diffusion coefficient at infinite dilution D_{ion}^o,

(iii) monovalent coions (the free surfactant ions) of hydro-dynamic radius a_{mon} deduced via the Stokes law from the self-diffusion coefficient at infinite dilution D_{mon}^o.

In the following, Z_{app} and n_{agg} are supposed to remain constant. Thus, for the solutions above the cmc, the concentrations of the various constituents are

$$c_{mon} = cmc$$

$$c_{mic} = \frac{c_{mon}^t - cmc}{n_{agg}}$$

$$c_{counterion} = cmc + |Z_{app}|c_{mic}$$

where $c_{counterion}$ is the concentration of free counterions, c_{mic} is the micellar concentration, and c_{mon}^t is the total monomer concentration. This last quantity is known from experiments. It should be noted that previous relations that give the concentrations of the three species rely on the pseudo-phase model of micelle formation; that is, above the cmc, any additional surfactant is supposed to be incorporated in a micelle. Even if the concentration of free monomers c_{mon} is known to decrease slightly when the total concentration of surfactant increases above the cmc, we assume here that this effect is negligible.

Since the radii and the self-diffusion coefficients at infinite dilution are well-known,[13] the unknown parameters reduce to n_{agg}, Z_{app}, $a_{micelle}$, and a_{mon}. Some previous studies of the same micellar solutions gave n_{agg}[18,32,33,36,38−41] so that Z_{app}, $a_{micelle}$, and a_{mon} may be fitted from experiments. In the range below the cmc, the MSA-transport theory is used to fit the radius of the free surfactant ion. For both micellar solutions, we obtain $a_{mon} = 4.4 \ 10^{-10}$ m and the corresponding self-diffusion at infinite dilution $D_{mon}^o = (k_B T/6\pi\eta a_{mon}) = 5.47 \ 10^{-10}$ m^2 s^{-1}. Then these parameters are introduced in the MSA-transport equations above the cmc to fit the radius of the micellar species together with its apparent charge. More precisely, because the size of the particles is known to have a slight influence on the electrical conductivity in the low concentration range, the radius of the micellar species is fitted to account for the experimental conductivity at high concentrations. On the other hand, the charge of ions slightly influences the electrical conductivity in
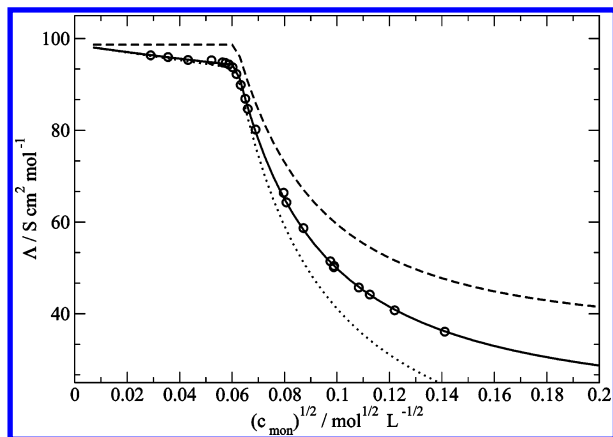
TABLE 2: Experimental Molar Electrical Conductivity (Λ/S cm^2 mol^{-1}) of TTACl Solutions at 298.15 K as a Function of the Total Monomer Molality (C_{mon}^t/mol kg^{-1})^a

	C_{mon}^t	Λ	C_{mon}^t	Λ	C_{mon}^t	Λ	C_{mon}^t	Λ	C_{mon}^t	Λ
	0.01146	60.73	0.01504	53.45	0.05176	37.60	0.01549	53.20	0.00184	93.71
	0.00860	70.63	0.01196	59.33	0.03381	41.06	0.01033	64.25	0.00110	94.42
	0.00574	87.95	0.00997	65.01	0.01997	48.08	0.00618	85.01	0.00061	94.97
	0.00344	92.31	0.00749	76.04	0.01099	62.00	0.00344	92.62		
	0.00191	93.41	0.00600	85.72						
	0.00132	94.20								

^{a} Five independent series of measurements are given.

Figure 1. Molar electrical conductivity of TTABr solutions at 298.15 K as a function of the square root of the total monomer concentration: experimental data (circles), MSA-transport calculations (solid line), ideal case, i.e., without any interactions (dashed line), and Onsager limiting laws (dotted line). $D^\circ_{Br^-} = 2.079 \ 10^{-9} \ m^2 \ s^{-1}$, $D^\circ_{mon} = 5.47 \ 10^{-10} \ m^2 \ s^{-1}$, $D^\circ_{mic} = 1.0 \ 10^{-10} \ m^2 \ s^{-1}$, $a_{Br^-} = 1.97 \ 10^{-10} \ m$, $a_{mon} = 4.4 \ 10^{-10} \ m$, $a_{mic} = 24.5 \ 10^{-10} \ m$, $Z_{app} = 19$, $n_{agg} = 80$, cmc $= 3.8 \ 10^{-3} \ mol \ L^{-1}$.
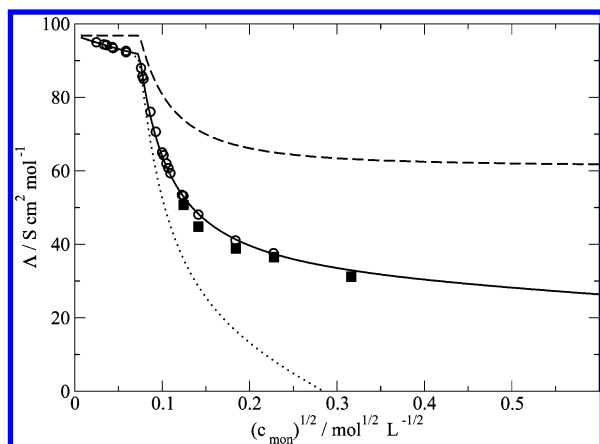

Figure 2. Molar electrical conductivity of TTACl solutions at 298.15 K as a function of the square root of the total monomer concentration: experimental data (circles), MSA-transport calculations (solid line), simulation results (squares), ideal case, i.e., without any interactions (dashed line), and Onsager limiting laws (dotted line). $D^\circ_{Cl^-} = 2.032 \ 10^{-9} \ m^2 \ s^{-1}$, $D^\circ_{mon} = 5.47 \ 10^{-10} \ m^2 \ s^{-1}$, $D^\circ_{mic} = 1.2 \ 10^{-10} \ m^2 \ s^{-1}$, $a_{Cl^-} = 1.81 \ 10^{-10} \ m$, $a_{mon} = 4.4 \ 10^{-10} \ m$, $a_{mic} = 20.4 \ 10^{-10} \ m$, $Z_{app} = 22$, $n_{agg} = 66$, cmc $= 5.5 \ 10^{-3} \ mol \ L^{-1}$.

TABLE 3: Parameters of TTABr and TTACl Aqueous Solutions at 298.15 K

	cmc (mol L^{-1})	n_{agg}	Z_{app}	a_{mic} (10^{-10} m)	D°_{mic} (10^{-10} m^2 s^{-1})	a_{mon} (10^{-10} m)	D°_{mon} (10^{-10} m^2 s^{-1})
TTABr	3.8×10^{-3}	80	19	24.5	1.0	4.4	5.47
TTACl	5.5×10^{-3}	66	22	20.4	1.2	4.4	5.47

the high concentration range, so that the effective charge of the micellar species is fitted to account for the experimental conductivity at concentrations near the cmc. It should be noted that the parameter that mostly influences the shape of the analytical curves is the aggregation number, which, in the present study, has been taken from the literature.[18,36,38,40] Figures 1 and 2 give the experimental molar conductivity together with the results of the analytical calculations. The values of all the involved parameters are collected in Table 3. Moreover, Figure 2 presents the results of Brownian dynamics simulations, which have been performed with the same parameters used in the analytical calculations, by including 10 micellar species in the simulation boxes together with the adequate number of coun-

terions and monomers. Simulations take into account hydrodynamic interactions, which are evaluated by using the Rotne−Prager tensor, as it was done in the transport theory. Both theoretical results are in good agreement. Last, the parameters used to model the micellar solutions (cmc, Z_{app}, and n_{agg}) are consistent with the known specificity of the chloride and bromide counterions: the degree of counterion binding is higher for the bromide ion than it is for the chloride ion. This result is in good agreement with other results of the literature.[41,42] Finally, it should be noted that the difference between the present analytical expression of the conductivity and the one given in previous papers[14,15] becomes noticeable above volume fractions larger than 0.5%.

V. Conclusion

We have shown how the MSA-transport theory allows one to deduce the effective charge and the radius of micellar species from experimental determinations of the electrical conductivity. Explicit expressions of the electrophoretic effect and of the relaxation effect were given, which may be used to evaluate the conductivity of any solution of asymmetrical electrolytes in a moderate concentration range. Then the radius and the apparent charge of the macroions, which are usually difficult to obtain from direct measurements, may be deduced from the experimental conductivity. Nevertheless, as far as micellar solutions are concerned, the use of the transport theory relies on two hypotheses: (i) The volume fraction must be moderate, so that both the treatment of the hydrodynamic interactions and the MSA remain valid. (ii) The structure of the micellar species is supposed to be the same all along the concentration range under study. This is not always the case, as an increase in the micellar size or a transition from the spherical to the cylindrical symmetry may be observed for some systems. A better description of the system would imply accounting for the variation of the charge, of the aggregation number, and, consequently, of the radius of the micelle with the concentration. Nevertheless, as it stands today, our theory satisfactorily describes the concentration domain below and moderately above the cmc.

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