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New perspectives in the transport of electrolyte solutions

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Abstract: We recently obtained simple expressions for the variation with concentration of the transport coefficients of electrolytes in aqueous solution, namely: self-diffusion, conductance of two simple ionic species, conductance of three simple ionic species and micellar systems. The Fuoss-Onsager continuity equations were solved using modern equilibrium pair distribution functions such as the MSA (mean spherical approximation) leading to explicit expressions for the variation of the transport coefficients with concentration. These expressions are in good agreement with the experimental values for both unassociated and associated electrolytes and micellar solutions.

1 Introduction

The variation of transport coefficients of electrolytes with concentration is one of the oldest subjects in physical chemistry, since in 1926 [1] and in 1932 [2] the limiting laws in $\sqrt{C}$ of variation of conductance with the concentration C for single electrolytes were given by Onsager *et al.*.
In 1945 Onsager [3] gave also the limiting laws for self-diffusion in single electrolytes and in 1957 for electrolyte mixtures [4]. Acoustophoresis was originally described by Debye in 1933 [5]. The extension of the conductivity description to higher concentrations was made by Onsager *et al.* [4] in 1957, using the Debye-Hückel equilibrium pair distribution functions available at this time [6]. The self-diffusion was also treated at the same level [7].
Ebeling *et al.* [8] used the MSA (mean spherical approximation) with the restricted primitive model to describe the variation of conductance with concentration, with approximate pair distribution functions in the calculation of the relaxation contribution.
Recently an approach was proposed in which Onsager's continuity equations were combined with MSA equilibrium correlation functions, using a Green's functions formalism. This treatment is a primitive model theory, where the solvent effects are averaged out. This yields concentration independant potentials, generally valid in the 0-1 M concentration range. This approach was applied to self-diffusion coefficients [9], acoustophoresis [10], conductance [11] of two simple ionic species [11] of unassociated electrolytes. An extension to associated electrolyte were made for conductance and self-diffusion coefficients [12], using a chemical model of association. We also propose a model for conductance in electrolyte mixtures in the case of three simple ionic species and micellar systems.
The purpose of the present paper is to summarize the main features of this approach within the MSA only, emphazing on the resulting explicit expressions more than on the techniques of their derivation.

2 General Theory

The most important effects in the non-ideal transport of electrolytes are the relaxation and electrophoretic effects. The first effect was first introduced by Debye [6].
When the equilibrium state is perturbed in a charged solution, electric interionic forces appear, which tend to restore the electric equilibrium of the ions.

The other effect, the hydrodynamic correction, was intiated by Onsager (2,3). This effect consists in the mutual deceleration of the ions by the mean of the solvent, when they have different velocities, tending to equalize those velocities.

The electrophoretic effect can be evaluated by means of the Navier-Stokes equations (13); the relaxation effect requires the evaluation of the electrostatic drag of the ions by their surroundings and the time lag of this effect known as the *Debye relaxation time.*

The basic equations of the relaxation effect are the hydrodynamic continuity equations

$$-\partial f_{ij}/\partial t = \nabla_1(f_{ij}v_{ij}) + \nabla_2(f_{ji}v_{ji}) \tag{1}$$

where v_{ij} is the velocity of an ion j in the vicinity of an ion i and f_{ij} is the two–particle density, related to the pair distribution function $g_{ij}(r,t)$

$$f_{ij}(r,t) = \rho_i\rho_j g_{ij}(r,t) \tag{2}$$

The pair distribution function is related to the total distribution function $h_{ij}(r,t)$

$$g_{ij}(r,t) = 1 + h_{ij}(r,t) \tag{3}$$

In the linear response theory, the total pair distribution is expressed as the sum of an equilibrium part (superscript ^{0}) and a part that is proportional to the external perturbation (superscript $'$).

$$h_{ij}(r,t) = h^o_{ij}(r) + h'_{ij}(r,t) \tag{4}$$

The velocity v_{ji} of an ion of species i in the vicinity of an ion of species j is given by

$$v_{ji} = v_i^s + \omega_i(\mathbf{K}_{ji} - k_B T\,\nabla \ln f_{ji}) \tag{5}$$

where the diffusion coefficient D_i of the ion i is related to its generalized mobility ω_i by the relation $\omega_i = D_i/k_BT$ (k_B is the Boltzmann constant and T is the absolute temperature), v_i^s is the average relative velocity of the solvent with respect to the ion of species i and $\mathbf{K}_{ji}$ is the force acting on an ion of species i in the neighbourhood of species j

$$\mathbf{K}_{ji} = \mathbf{k}_i\,(1 + \delta k_i/k_i) - e_i\,\nabla\,\psi_j \tag{6}$$

In equation (6) $\mathbf{k}_i$ is the acting (diffusive or electric) force on an ion i: for conductance the external force is an electric field and for self–diffusion the external force is a gradient of the chemical potential corresponding to a gradient of isotopic concentration for the diffusing tracer.

$\delta\mathbf{k}_i$ is the relaxation force

$$\delta\mathbf{k}_i = -\sum_j \rho_j \int_0^\infty \nabla(V_{ij}^{Cb} + V_{ij}^*)h'_{ij}d\mathbf{r} \tag{7}$$

where V_{ij}^{Cb} is the Coulomb potential and V_{ij}^* is the hard sphere potential where we introduce the sum of the crystallographic radii of the two ions σ_{ij}.

ψ_j is the electric potential around an ion j and can be expressed as the sum of an equilibrium part (superscript ^{0}) and a part that is proportional to the external perturbation (superscript $'$), in the linear response theory.

$$\psi_j(r,t) = \psi_j^0(r) + \psi'_j(r,t) \tag{8}$$

Without external force the potentials of mean force are related to the pair distribution functions by the equilibrium relation

$$g_{ij}^0 = \exp\left(-e_j\psi_i^0/(k_BT)\right) = \exp\left(-e_i\psi_j^0/(k_BT)\right) = g_{ji}^0 \tag{9}$$

which also displays the symmetry of the correlation function.

In the nonequilibrium case, the nonequilibrium potentials ψ'_j are related to the nonequilibrium total distribution functions h'_{ij} by means of the Poisson equation (in cgs units),

$$\Delta\psi'_j = -(1/\epsilon_0\epsilon)\sum_i \rho_i e_i h'_{ji} \tag{10}$$

since the unperturbed parts can be provided by any modern equilibrium statistical theory such as HNC (14) or MSA (15).
$\epsilon_0\epsilon_r$ is the permittivity of the solvent, ρ_j is the particle density [ions/volume] and e_j the charge of the ion j.
The continuity equations may be expressed in terms of perturbed and equilibrium terms. The number of relevant continuity equations, as well as the form of the term under consideration depend on the transport phenomena, self–diffusion or conductivity.
In any case the continuity equations can be written in the form of an inhomogeneous differential equation of the type

$$\left(\Delta - \kappa_r^2\right) h(r) = F(\mathbf{r}, \mathbf{k}) \tag{11}$$

where κ_r is a function of the generalized individual mobilities and $F(\mathbf{r}, \mathbf{k})$ is the driving force. It corresponds to the right–hand side of the continuity equation.
The solutions of equation (11) may be classified as first–order, or second–order solutions, according to the expansion of the continuity equation showing two kinds of terms: terms yielding the limiting laws in $\sqrt{c}$ by the use of the Debye Hückel equilibrium pair distribution functions (6) (first–order terms) as the input and terms leading to terms of higher order in concentration with the same distribution functions (second–order terms).
The contribution of the second-order terms is always small for concentrations lower than 0.5 M for most 1-1 electrolytes in aqueous solution. It can then be neglected as first approximation.
The adaptation of the solution to the particular transport coeffficient and to the required order in concentration will be presented in the next sections.

3 Self-Diffusion

For self-diffusion the relaxation forces are the only relevant contributions and the hydrodynamic interactions do not play any significant role in this range of concentration except for low viscosity solvents. The resolution of equation (11) yields following expression:

$$\delta k_1^1/k_1 = -Z_1^2 e^2 \left(\kappa^2 - \kappa_{d_1}^2\right) \left(1 - e^{-2\kappa_{d_1}\sigma}\right) / \left(6\epsilon k_B T\sigma\left(1+\Gamma\sigma\right)^2 \left[\kappa_{d_1}^2 + 2\Gamma\kappa_{d_1} + 2\Gamma^2\left(1 - e^{-\kappa_{d_1}\sigma}\right)\right]\right) \tag{12}$$

The superscript 1 denotes first-order equation and the subscript 1 indicates the tracer ion. Here $1/\Gamma$ is the MSA length parameter corresponding to Debye's $1/\kappa$ and with, using an average diameter :

$$\kappa^2 = \left(4\pi e^2/\left(\epsilon k_B T\right)\right) \sum_n \rho_n Z_n^2 = 4\Gamma^2\left(1+\Gamma\sigma\right)^2 \tag{13}$$

$$\kappa_{d_1}^2 = \left(4\pi e^2/\left(\epsilon k_B T\right)\right) \sum_n \rho_n Z_n^2 D_n^o/\left(D_1^o + D_n^o\right) \tag{14}$$

The formal expression of the diffusion coefficient becomes then

$$D_1 = D_1^o\left(1 + \delta k_1^1/k_1^1\right) \tag{15}$$

where D_i^o is the diffusion coefficient at infinit dilution of an ion i.

4 Conductance of two simple ionic species

In conductance, anions and cations move in opposite direction, and not only the relaxation effect, but also the effect of hydrodynamic interactions must be taken into account.

4.1 Relaxation

The resolution of equation (11) yields following expression, with $\mathbf{k}_i = Z_i e\mathbf{E}$:

$$\frac{\delta k_1^1}{k_1} = \frac{\delta k_2^1}{k_2} = \frac{\delta E}{E} = \frac{-\kappa_q^2 e^2 \mid Z_1 Z_2 \mid}{3\epsilon k_B T\sigma\left(1+\Gamma\sigma\right)^2} \frac{e^{-\kappa_q\sigma}}{\left[\kappa_q^2 + 2\Gamma\kappa_q + 2\Gamma^2\left(1 - e^{-\kappa_q\sigma}\right)\right]}$$

$$\times \left(sinh(\kappa_q\sigma) - \left(\epsilon k_B T \left(cosh(\kappa_q\sigma) - \left(sinh(\kappa_q\sigma)/(\kappa_q\sigma)\right)\right) / (e_i e_j)\right)\right) \tag{16}$$

with

$$\kappa_q^2 = \left(4\pi e^2 / (\varepsilon k_B T)\right) \left(\left(\rho_i Z_i^2 D_i^o + \rho_j Z_j^2 D_j^o\right) / \left(D_i^o + D_j^o\right)\right) \tag{17}$$

4.2 Electrophoretic effect

The electrophoretic contribution is due to hydrodynamic interaction between the ions and the solvent molecules. The first order term is given by

$$\delta \mathbf{v}_i^{el} = \sum_j \rho_j e_j \int_0^\infty h_{ij}^0(r) \mathcal{T} \mathbf{E}\, d\mathbf{r} \tag{18}$$

where $\mathcal{T}$ is the Oseen tensor

It can be shown that the MSA pair distribution functions give an easy extension of Henry's law for electrophoretic mobility (13)

$$\delta u_i^{el} / u_i^o = \left(-k_B T / (3\pi\eta D_i^o)\right) \left(\Gamma / [1 + \Gamma\sigma]\right) \tag{19}$$

The total equivalent conductance is given by $\Lambda = \sum_i \lambda_i$ and

$$\lambda_i = \lambda_i^o \left(1 + \delta u_i^{el} / u_i^o\right) (1 + \delta E / E) \tag{20}$$

where λ_i^o is the individual equivalent conductance of the ith ion at infinite dilution.

5 Conductance in electrolyte mixtures and micellar systems

Conductance of solutions containing more than two ions was first theoretically studied in a systematic way by Onsager and Kim in 1957. (4). Their theoretical expressions (limiting laws), are in agreement with experiment until bulk salt concentrations of 0.01M. Later Quint & Viallard (16) were able to extend this limit to 0.1M, by introducing finite ionic size corrections (extended limiting law) in Debye-Hückel equilibrium pair distribution functions.

In this part we present new results concerning the theoretical description of conductance for solutions containing three ionic species. The model has been tested on NaCl/KCl mixtures and reproduces the experimental values in a very satisfying manner, within a large concentration range.

With our ionic strength correction we get for the conductance

$$\chi_{sp} \left(\Omega^{-1} cm^{-1}\right) = \left(10 e^2 N_A / (k_B T)\right) \sum_{i=1}^{3} c_i D_i^o z_i^2 \left(1 + \left(\delta v_i^{hyd} / v_i^o\right)\right) \left(1 + \left(\delta k_i^{rel} / k_i\right)\right) \tag{21}$$

where c_i is the molar concentration for the component and v_i^o is the velocity at infinite dilution (without ionic strength correction). For an ion i, δk_i^{rel} is the correction on electrical force due to relaxation effect and δv_i^{hyd} is the velocity increment due to hydrodynamic interaction.

We express now the conductance as the specific conductivity χ_{sp} divided by the common ion concentration c_2 (molar conductivity): $\Lambda \left(cm^2 \Omega^{-1} mol^{-1}\right) = 1000 \chi_{sp} / c_2$.

In this description we worked with individual closest approach distances. Our idea was to apply the same approach to 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 is constituted by monomeric surfactant ions and their counterions. At and 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 monomer surfactant, a fraction of counterions (not condensed) and the micelles. The consequence of the formation of micelles is a sudden change of slope of the conductivity versus surfactant concentration curve.

An important problem in the case of micellar solutions is that the various species have widely dissymetric size and electrical charges. The MSA may not be valid under such conditions as the concentration increases. However, at high volume fraction, those are the more important sources of interactions. Being aware of these limitations, we have compared our model to experimental data for two ionic surfactants: one anionic surfactants: sodium dodecylsulfate (SDS) up to a concentration of 0.1 M and one cationic surfactant dodecyltrimethylammonium bromide (DTAB) up to 0.1 M. At the highest concentration, the solute volume fraction is 0.1, a value for which our approximations should still be valid.

6 Comparison with experimental results and discussion.

Figure 1 shows the experimental and theoretical self-diffusion coefficient of Cs^+ up to 1 M. The theoretical curve, based on the MSA treatment with the same average diameter as for conductance, is in good agreement with the experimental results.

Figure 2 shows an exemple of conductance of aqueous alkaline metal halide solutions known to be dissociated electrolytes within reasonable concentration ranges. We present the experimental and theoretical conductance of CsCl up to 1 M. The theoretical curve, based on the MSA treatment, were done using mean size parameters σ adjusted in order to have a good agreement with the experimental results. These parameters are found to be slightly higher or approximatively equal to the sum of the cristallographic. The other input parameters are the D_i^0 values, the dielectric constant and the viscosity of the solvent and the temperature.

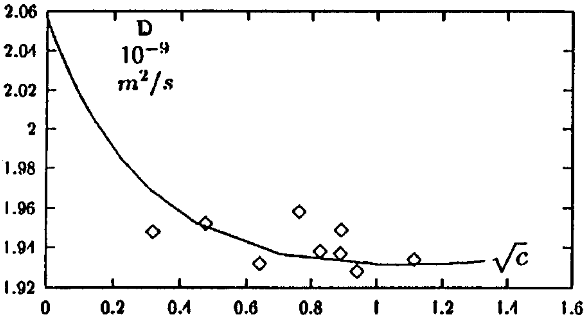

Fig. 1. Self-diffusion coefficient of Cs^+ in aqueous CsCl solutions at 25°C as a function of the square root of molarity. (◇) : experimental values taken from ref (17). (—): theoretical values predicted by the MSA expression with average diameter σ = 3.48 Å.

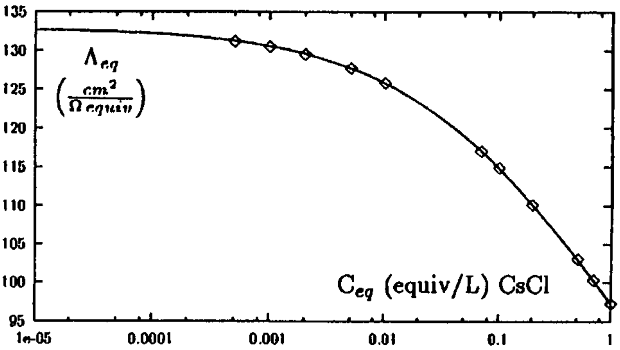

Fig. 2. Equivalent conductance of aqueous CsCl solutions at 18°C as a function of the molarity. (◇) : experimental values taken from ref (18). (—): theoretical values predicted by the MSA expression with average diameter σ = 3.48 Å.

Our approach has proved its efficiency for several unassociated and weakly associated systems. The combination of the chemical model and the MSA yields an extension of this theory for partly associated electrolytes. This approach (12) gives also a good agreement between theory and experimental results for concentration range up to 1 M. Extensions to other transport coefficients are currently under way.

Concerning the conductance of mixed electrolytes, there are very few experimental data available in the literature for electrolyte mixtures at moderate and high concentration. This could be due to the lack of any satisfying theoretical model for concentrations in both diluted and concentrated domains. We present here the results for the mixture NaCl/KCl. The two figures presented in the following give the conductance as a function of the proportion of one of the salts (KCl), for different total salt concentration. One test of the theory presented here is the asymptotic convergence of our results for low concentration toward those of Onsager-Kim, which tend themselves to the ideal behavior. We present then for the lowest concentrations (figure 3), Onsager-Kim limiting law, as well as the ideal law (no interaction). For vanishing concentrations, all curves merge.

Our expressions involve individual ionic closest approach distances, in order to describe properly dissymmetrical systems. We have the three distances to consider. We take two sets of values: the crystallographic radii, which constitute the minimum values and the crystallographic radii augmented by a factor of 10%, which is a common choice in this type of description.

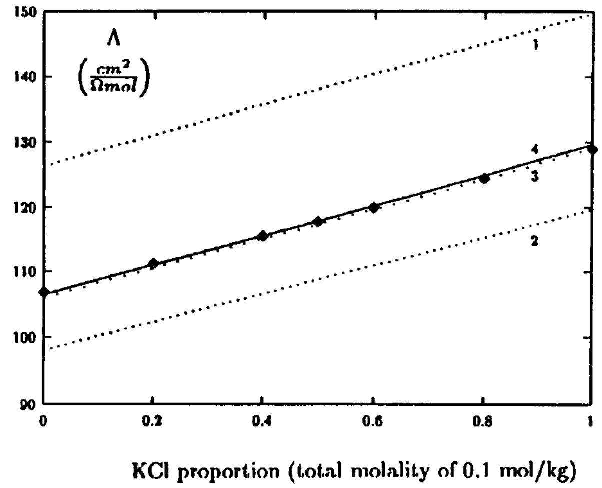

Fig. 3. Conductance of the NaCl/KCl mixture for an total molality of 0.1 mol/kg. (◆) : experimental data (16), 1 : Ideal case, 2 : Limiting law (Onsager), 3 : Our results (MSA) with cristallographic radii, 4 : Our results (MSA) with cristallographic radii augmented by a factor of 10%.

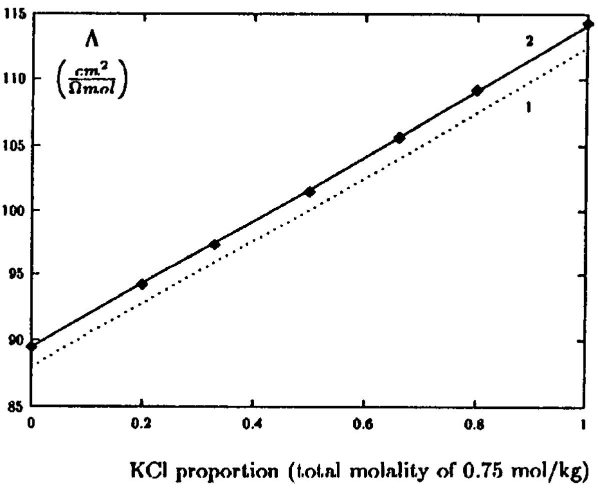

Fig. 4. Conductance of the NaCl/KCl mixture for an total molality of 0.75 mol/kg. (◆) : experimental data (19), 1 : Our results (MSA) with cristallographic radii, 2 : Our results (MSA) with cristallographic radii augmented by a factor of 10%.

On the figure 3, we remark that both choices of distance are in good agreement with experiment, due to the small contribution of hard sphere interactions for low concentrations.

On the opposite, on figure 4, we see a noticeble difference between the two sets of ionic radii, whereas the ideal and limiting law models are out the frame of the figures. We have an excellent agreement with the experimental values by taking the crystallographic radii augmented by a factor of 10%, until above 1M. After that limit, not only the validity of our MSA model is questionable, but the data are not available, even for NaCl-KCl. A further extension of the theory would imply also a change in the equilibrium model. One possibility would be the use of HNC or of other improvements for MSA (soft MSA, exp MSA, ...). The problem is the the connection to low concentration (limiting laws) and the increase in adjustable parameters. For the moment we remain at the MSA level.

An other interesting application is the description of micellar systems. The conductance is the ratio of the conductivity over the total monomer concentration. Our results are compared with the ideal conductance Λ_{id} and Onsager's result. Λ_{id} is the sum of the conductance of the ions at infinite dilutions multiplied by the concentration of each ionic species and divided by the total monomer concentration c^t_{mon}) and Onsager's conductance is the calculated value using Onsager's theory (4) divided by the total monomer concentration.

The parameters which enter our conductance equation are, for each ionic species, its diffusion coefficient at infinite dilution D^o_i, or its conductance at infinite dilution λ^o_i, and the electrolyte minimum distance of approach σ_i. For the simple counterions, Na^+ and Br^-, these two parameters are known. For the monomer surfactant and micelles, we suppose that these radii are close to the hydrodynamic radii extracted from the monomeric diffusion coefficient using the approximation of a perfect sticking:

$$r^{hyd} = k_B T/(6\pi\eta_o D^o) \tag{22}$$

As the diffusion coefficients at infinite dilution can either be taken from the literature or considered as adustable parameters the hydrodynamic radii is also directly deduce from the diffusion coefficient through Eq.22. In effect, below the cmc, besides the minimum distance of approach, the diffusion coefficient at infinite dilution is the only unknown in our expressions. As for the micelles (above the cmc), in addition to the diffusion coefficient and its minimum distance of approach, the aggregation number n_{agg} (the number of monomer per micelle) a quantity which may vary with concentration, and the apparent charge, Z^{app} which is directly related to the degree of ion condensation, must be known. In order to simplify this first contribution, we have admitted that all these parameters remained constant as the surfactant concentration varies. This restriction enabled us to define the concentration of the various ionic constituents: monomers, micelles, counterions.

The surfactants used in this investigation being 1-1 electrolytes, below the cmc, the monomer concentration was equal to the counterion concentration. Above the cmc, any addition of surfactant will be considered as being part of a micelle. This is strictly speaking the pseudo-phase model of micelle formation. The concentrations of the various constituents are: $c_{mon} = cmc$, $c_{mic} = (c^{t}_{mon} - cmc)/n_{agg}$ and $c_{counterion} = cmc + \mid Z^{app} \mid c_{mic}$, where $c_{counterion}$ is the counterion concentration and c_{mic} is the micellar concentration.

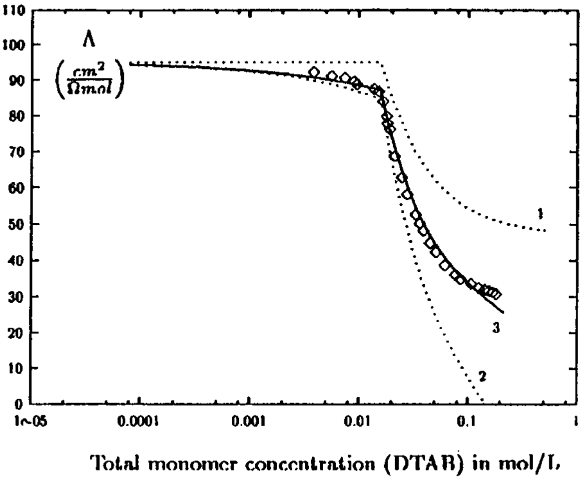

Fig. 5. Conductance of dodecyltrimethylammonium bromide (DTAB) as a function of total monomer concentration. (◇) : experimental data. 1 : Ideal case, 2 : Limiting law (Onsager), 3 : Our results (MSA). Parameters : $r^{hyd}_{mon} = 5.4$ Å, $r_{Br-} = 1.1 \times 1.97$ Å, $r^{hyd}_{mic} = 21.3$ Å, $D^{o}_{mon} = 4.5\ 10^{-10} m^2 s^{-1}$, $D^{o}_{Br-} = 2.079\ 10^{-9} m^2 s^{-1}$, $D^{o}_{mic} = 1.15\ 10^{-10} m^2 s^{-1}$ (20). Aggregation number of the micelles $n_{agg} = 60$ (20). Apparent charge $Z^{app} = +18$ (20).

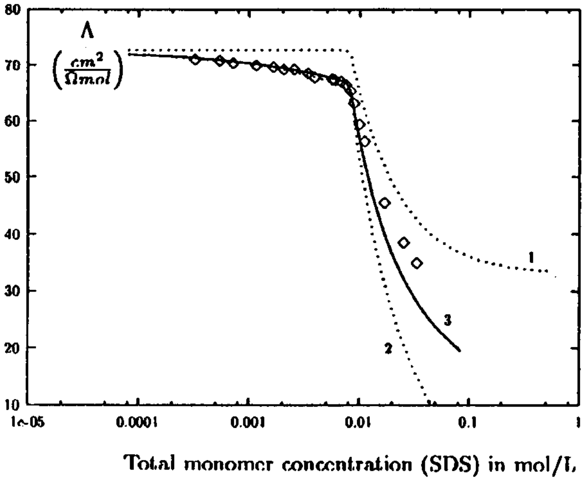

Fig. 6. Conductance of sodium dodecylsulfate (SDS) as a function of total monomer concentration. (◇) : experimental data (21). 1 : Ideal case, 2 : Limiting law (Onsager), 3 : Our results (MSA). Parameters : $r^{hyd}_{mon} = 4.1$ Å, $r_{Na+} = 1.1 \times 0.97$ Å, $r^{hyd}_{mic} = 21.3$ Å, $D^{o}_{mon} = 6.0\ 10^{-10} m^2 s^{-1}$ (22), $D^{o}_{Na+} = 1.333\ 10^{-9} m^2 s^{-1}$, $D^{o}_{mic} = 1.15\ 10^{-10} m^2 s^{-1}$ (22). Aggregation number of the micelles $n_{agg} = 70$ (23). Apparent charge $Z^{app} = -18$ (23).

Figure 5 presents a comparison between theory and experiment for the cationic surfactant. The experimental results are very reasonably reproduced. We had no value for D^{o}_{mon} for that system. All the other parameters were taken from Walrand et. al. (20). They were deduced from quasi-elastic light-diffusion experiments.

Figure 6 presents the same comparison for the anionic surfactant, SDS. The experiment values were taken from the literature (21). We observe again a very good agreement between theory and experiment. No adjustable parameter was here necessary as the D^{o} values for monomers and micelles were available from Lindman et.al. (22). These data had been obtained from Fourier Transform Proton NMR experiments (^{1}H FT NMR) and tracer-diffusion.

The effect of changing the values of the different parameters which have to be introduced in the theory is interesting. Small variations have little consequences on the shape of the curves. The largest effect arises from changes in the aggregation number. Experimentally it has been shown (24) that for SDS, the aggregation number varies from approximately 70 at the cmc to 120 at 0.1M. i As all other parameters have remained unchanged, the increase of n_{agg} reflects simply the decrease of the micelle concentration. Experimentally it is observed that n_{agg} varies less with concentration for anionic micelles than for cationic ones. This may be the consequence of the somewhat better description of the DTAB than of SDS system. This result was predictable. The cmc of DTAB is equal to 0.016 M, whereas that of SDS is 0.0081 M. Our description of the surfactant behavior below the cmc raises no problem, contrary to the micelle/counterion interaction. Thus the theoretical treatment is certainly better the higher the cmc.

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References

1. L. Onsager, *Phys. Z.* **27**, 388 (1926) and **28**, 277 (1927).
2. L. Onsager and R.M. Fuoss. *J. Phys. Chem.* **36**, 2689 (1932).
3. L. Onsager, *Ann. N. Y. Acad. Sci.* **46**, 263 (1945).
4. L. Onsager and S.K. Kim. *J. Phys. Chem.* **61**, 215 (1957).
5. P. Debye, *J. Chem. Phys.* **1**, 13 (1933).
6. P. Debye and E. Hükel. *Phys. Z.* **24**, 185 (1923).
7. C. Micheletti and P. Turq. *J. Chem. Soc. Faraday. Trans II* **73**, 743 (1976).
8. W. Ebeling and M. Grigo. *J. Solution Chem.* **11**, 151 (1982).
9. O. Bernard, W. Kunz, P. Turq, and L. Blum. *J. Phys. Chem.* **96**, 398 (1992).
10. S. Durand-Vidal, J.-P. Simonin, P. Turq, and O. Bernard. *J. Phys. Chem.* **99**, 6733 (1995).
11. O. Bernard, W. Kunz, P. Turq, and L. Blum. *J. Phys. Chem.* **96**, 3833 (1992).
12. A. Chhih, P. Turq, O. Bernard, J.M.G. Barthel and L. Blum. *Ber. Bunsenges. Phys. Chem.* **98(12)**, 1516 (1994).
13. O. Bernard, P. Turq and L. Blum. *J. Phys. Chem.* **95(23)**, 9508 (1991).
14. J. C. Rasaiah and H. L. Friedman. *J. Phys. Chem.* **72**, 3352 (1968).
15. E. Waisman and J. L. Lebowitz. *J. Chem. Phys.* **56(6)** 3086 (1971).
16. J. Quint, *Thèse de Doctorat d'Etat.* Université de Clermont-Ferrand, Fr. (1976).
17. J. Anderson and R. Paterson. *J. Chem. Soc. Faraday I* **71**, 1335 (1975).
18. *International Critical Tables of Numerical data, Physics, Chemistry and Technology.* published for the National Research Concil by the McGRAW-HILL Book Compagny, Inc. (1927).
19. D. Urban, A. Geret, H.-J. Kiggen and H. Schönert. *Z. für Phys. Chem.* **137**, 66 (1983).
20. S. Walrand, L. Belloni and M. Drifford. *J. Physique* **47**, 1565 (1986).
21. B.D. Folckhart and H. Graham. *J. Coll. Sci.* **8**, 428 (1953).
22. B. Lindman, M.-C. Puyal, N. Kamenka, R. Rymden and P. Stilbs. *J. Phys. Chem.* **88**, 5048 (1984).
23. D.F. Evans and B.W. Ninham. *J. Phys. Chem.* **87**, 5025 (1983).
24. J.B. Hayter and J. Penfold. *J. Chem. Soc., Faraday Trans I* **77**, 1851 (1981).