In conclusion, while attempting to expose the location of the probe, $Ru(bpy)_3^{2+}$, in micellar and hemimicellar environments, our study has provided useful insights into the problem of localization of excitation energy itself. In general, the bound probe molecule resides within the surfactant aggregates rather than as counterions, in both micellar and hemimicellar cases.

Adsorption of Monovalent Ions in Thin Spherical and Cylindrical Diffuse Electrical Double Layers

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Analytic expressions for the adsorption of ions in spherical and cylindrical diffuse electrical double layers are derived on the basis of the Poisson–Boltzmann equation. The expressions are expansions in inverse powers of the reduced radius of curvature κa and are valid for thin double layers. The results are in very good agreement with numerical calculations.

Introduction

A great deal of attention has been lavished upon the diffuse electrical double layer at curved interfaces. This interest is due to numerous interesting phenomena in colloid science that are directly connected to the existence of these curved electrical double layers. To mention a few: the electrophoretic mobility of charged colloidal particles,[1,2] the influence of the electrolyte concentration on the stability and shape of micelles and microemulsions of ionic surfactants,[3-6] the behavior of rodlike polyelectrolytes,[7-9] and the curvature elasticity of charged membranes.[10-12] Another example is the negative adsorption of the co-ions in the curved electrical double layer, for which we will derive approximate analytical expressions in this paper. Our interest in this matter originates from the observation that the negative adsorption of co-ions in Winsor II microemulsion systems leads to an increased salt concentration in the excess water phase.[13-16] This in turn strongly affects the phase equilibria in these microemulsion systems.[17]

In the literature concerning these kind of phenomena, the diffuse part of the electrical double layer is usually described by the Poisson–Boltzmann (PB) equation. Although more sophisticated approaches such as computer simulations and numerical solutions of integral equations such as the hypernetted chain approximation are currently applied to double-layer problems, the relatively simple PB equation often yields a good description of the diffuse double layer. Because of its importance, the subject has attracted considerable theoretical attention, resulting in numerical[18] and approximate analytical solutions.[19]   For thin double layers the electrical potential can be expanded in the small parameter $1/\kappa a$ (a is the radius of curvature, κ is the reciprocal Debye length), yielding accurate analytical approximations. This promising approach was initiated by Dukhin and co-workers[20,21] and further elaborated by Stokes,[22] Sherwood,[23] Chew and Sen,[24] and Natarajan and Schechter.[19] Using the resulting expressions for the potential at the surface, the electrical part of the surface free energy for spherical[11,12,22,25] and cylindrical[11,12] double layers can be obtained. Recently Ramanathan[26] derived a bound for the difference between the solution to the spherical case and the flat plate. This result implies that for $\kappa a > 1$ the solution to the spherical case is a perturbation off the flat plate solution. While the perturbation technique can be validated rigorously when κa is large, the results in the present paper show how large it should be.

In the present paper we will show how analytical expressions for the co-ion adsorption in curved electrical double layers can be obtained from the electrical part of the surface free energy. Numerical calculations were performed to verify the accuracy of the expressions for the surface potential and the co-ion adsorption. It turns out that the accuracy of these expressions is remarkable for κa values larger than 3, irrespective of the surface potential. The equations are therefore applicable in colloid research.

Calculation of the Co-ion Adsorption in the Flat Electrical Double Layer

Surface excesses of ions in the electrical double layer are usually calculated by performing an integration over the volume V, of the system, following the definition of the surface excess:

$$\Gamma_i \equiv \int_V (c_i(\vec{r}) - c_i^\circ) \, d\vec{r}/A \tag{1}$$

where $c_i(\vec{r})$ is the concentration of ion i on the position $\vec{r}$, and c_i°

(1) Wiersema, P. H.; Loeb, A. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* **1966**, *22*, 78.
(2) O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1607.
(3) Overbeek, J. Th. G.; Stigter, D. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 1265.
(4) Overbeek, J. Th. G. *Faraday Discuss. Chem. Soc.* **1978**, *65*, 7.
(5) Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1983**, *87*, 2996.
(6) Evans, D. F.; Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344.
(7) Fuoss, R. M.; Katchalsky, A.; Lifson, S. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 579.
(8) Philip, J. R.; Wooding, R. A. *J. Chem. Phys.* **1970**, *52*, 953.
(9) Ramanathan, G. V. *J. Chem. Phys.* **1983**, *78*, 3223.
(10) Winterhalter, N.; Helfrich, W. *J. Phys. Chem.* **1988**, *92*, 6865.
(11) Mitchell, D. J.; Ninham, B. W. *Langmuir* **1989**, *5*, 1121.
(12) Lekkerkerker, H. N. W. *Physica A* **1989**, *159*, 319.
(13) Tosh, W. C.; Jones, S. C.; Adamson, A. W. *J. Colloid Interface Sci.* **1969**, *31*, 297.
(14) Biais, J.; Barthe, M.; Bourrel, M.; Clin, B.; Lalanne, P. *J. Colloid Interface Sci.* **1986**, *109*, 576.
(15) van Nieuwkoop, J.; Snoei, G. *J. Colloid Interface Sci.* **1985**, *103*, 400.
(16) de Bruyn, P. L.; Overbeek, J. Th. G.; Verhoeckx, G. J. *J. Colloid Interface Sci.* **1989**, *127*, 244.
(17) van Aken, G. A.; de Bruyn, P. L.; Lekkerkerker, H. N. W.; Overbeek, J. Th. G., manuscript in preparation.

(18) Loeb, A. L.; Wiersema, P. H.; Overbeek, J. Th. G. *The Electrical Double Layer around a Spherical Colloidal Particle*; MIT Press: Cambridge, MA, 1961.
(19) For a concise review see: Natarajan, R.; Schechter, R. S. *J. Colloid Interface Sci.* **1984**, *99*, 50.
(20) Dukhin, S. S.; Semenichin, N. M.; Shapinskaya, L. M. *Dokl. Phys. Chem.* **1970**, *193*, 540.
(21) Dukhin, S. S.; Derjaguin, B. V. In *Surface and Colloid Science*; Matijevic, E., Ed.; Wiley: New York, 1974; Vol. 7, p 130.
(22) Stokes, A. N. *J. Chem. Phys.* **1976**, *65*, 261.
(23) Sherwood, J. D. *J. Fluid Mech.* **1980**, *101*, 609.
(24) Chew, W. C.; Sen, P. N. *J. Chem. Phys.* **1982**, *77*, 2042.
(25) Overbeek, J. Th. G.; Verhoeckx, G. J.; de Bruyn, P. L.; Lekkerkerker, H. N. W. *J. Colloid Interface Sci.* **1987**, *119*, 422.
(26) Ramanathan, G. V. *J. Chem. Phys.* **1988**, *88*, 3887.

is the concentration of ion i at a distance far from the surface, where the solution is neutral. A is the surface area of the charged surface.

Describing the electrostatic interactions between the ions through the mean field electrical potential $\psi(\vec{r})$, we may calculate the concentration $c_i(\vec{r})$ by use of the Boltzmann expression

$$c_i(\vec{r}) = c_i{}^\circ \exp(-z_i F\psi(\vec{r})/RT) \qquad (2)$$

The electrical potential is related to the charge density by the Poisson equation

$$\nabla^2\psi(\vec{r}) = -\frac{\rho(\vec{r})}{\epsilon_r\epsilon_0} = -\frac{F\sum_i z_i c_i(\vec{r})}{\epsilon_r\epsilon_0} \qquad (3)$$

where $\epsilon_r\epsilon_0$ is the dielectric constant of the medium, and z_i is the charge number of the ion, including the sign. Combination of eq 2 and 3 yields the well-known PB equation, which for a 1:1 electrolyte takes the form

$$\nabla^2\Psi(\vec{r}) = \kappa^2 \sinh(\Psi(\vec{r})) \qquad (4)$$

In eq 4 Ψ is the reduced potential, $\Psi = F\psi/RT$, and κ is the inverse Debye length, defined by

$$\kappa = \left(\frac{2F^2 c_{el}}{\epsilon_r\epsilon_0 RT}\right)^{1/2} \qquad (5)$$

where c_{el} is the electrolyte concentration in the bulk. Without loss of generality we will from now on assume that the surface is positively charged. For a flat double layer and a 1:1 electrolyte the exact solution of the PB equation is well-known:

$$\tanh(\Psi(x)/4) = \tanh(\Psi_0/4)\exp(-x) \qquad (6)$$

where $x = \kappa r$ is the reduced distance from the surface, and Ψ_0 is the reduced potential at the surface. From eq 6 it follows that the surface potential can be expressed in terms of the surface charge density as

$$\Psi_0 = 2\ln(p + q) \qquad (7)$$

where

$$p = \frac{1}{2}|d\Psi/dx|_{surface} \qquad (8)$$

$$q = (p^2 + 1)^{1/2} \qquad (9)$$

Through the equation of Gauss the quantity p is related to the surface charge density σ:

$$p = \frac{F\sigma}{2\epsilon_r\epsilon_0 RT\kappa} = \frac{\sigma}{(8\epsilon_r\epsilon_0 RTc_{el})^{1/2}} \qquad (10)$$

Combining eqs 6 and 7, one can write

$$\Psi(x) = 2\ln\left(\frac{1 + \left(\dfrac{p+q-1}{p+q+1}\right)\exp(-x)}{1 - \left(\dfrac{p+q-1}{p+q+1}\right)\exp(-x)}\right) \qquad (11)$$

To evaluate the co-ion adsorption for 1:1 electrolytes, there are two different analytical approaches. The usual procedure is to perform the integration over the concentration profile:

$$\Gamma_{co\text{-}ion} = c_{el}\kappa^{-1}\int_0^\infty [\exp(-\Psi(x)) - 1]\,dx \qquad (12)$$

resulting in[27,28]

$$\Gamma_{co\text{-}ion} = 2\kappa^{-1}c_{el}[\exp(-\Psi_0/2) - 1] \qquad (13)$$

For a given surface charge density, one obtains by substitution of eq 7

$$\Gamma_{co\text{-}ion} = -2\kappa^{-1}c_{el}(p + 1 - q) \qquad (14)$$

(27) Klaarenbeek, F. W. Thesis, Utrecht, 1946, p 96.
(28) Overbeek, J. Th. G. *Prog. Biophys. Biophys. Chem.* **1956**, *6*, 57.

The second way to calculate the co-ion adsorption for 1:1 electrolytes makes use of the free energy of the electrical double layer f_{el} through an equation very similar to the Gibbs adsorption equation:

$$df_{el} = -\Gamma_{counterion}\,d\mu_{counterion} - \Gamma_{co\text{-}ion}\,d\mu_{co\text{-}ion} \qquad (15)$$

with

$$f_{el} \equiv \int_0^\sigma \psi_0(\sigma')\,d\sigma' \qquad (16)$$

The derivation of eq 15 is presented in the Appendix. In this derivation we consider only the electrostatic forces between the ions and describe the solvent as a homogeneous medium with a dielectric permittivity $\epsilon_r\epsilon_0$. Because the same approximations are also made in the derivation of the PB equation, they introduce no further restriction to the validity of the resulting equations for the co-ion adsorption. Since the interfacial region remains overall uncharged, the co-ion and counterion adsorption are related through

$$\Gamma_{counterion} - \Gamma_{co\text{-}ion} = \sigma/F \qquad (17)$$

For the chemical potentials of the co-ions and the counterions we take the concentration dependence for the ideal solution:

$$d\mu_{co\text{-}ion} = d\mu_{counterion} = RT\,d\ln c_{el} = 2RT\,d\ln\kappa \qquad (18)$$

This is legitimate because ideal behavior is also assumed in the Poisson–Boltzmann equation. Combining eqs 15, 17, and 18, we obtain the following expression of the co-ion adsorption:

$$\Gamma_{co\text{-}ion} = -\frac{1}{2}\left[\frac{\sigma}{F} + \frac{\kappa}{2RT}\left(\frac{\partial f_{el}}{\partial\kappa}\right)\right] \qquad (19)$$

For the flat double layer we obtain f_{el} by performing the integration indicated by eq 16, using eq 11 for the surface potential:

$$f_{el} = (RT/F)^2\epsilon_r\epsilon_0\kappa(4(p\ln(p+q) - q + 1)) \qquad (20)$$

By substitution of the expression for f_{el} in eq 19 and taking the derivative, we retrieve eq 14 for the co-ion adsorption in the flat electrical double layer.

Although the second method may seem to be a more cumbersome way to derive an analytical expression for $\Gamma_{co\text{-}ion}$, it has the advantage that basically only the surface potential of the double layer is required. Particularly for curved surfaces this will prove to be a great advantage.

Surface Potential and Co-ion Adsorption for Curved Electrical Double Layers

For the sphere and cylinder the PB equation, eq 4, can be written in the form

$$\frac{d^2\Psi}{dx^2} + \frac{m}{x}\frac{d\Psi}{dx} = \sinh\Psi \qquad (21)$$

where x is the reduced radial coordinate $x = \kappa r$, with r the distance from the center of the sphere or the axis of the cylinder. For a sphere $m = 2$, and for a cylinder $m = 1$. Note that for $m = 0$ we obtain the PB equation for a plate plate. In the case of thin double layers the term $(m/x)(d\Psi/dx)$ is small near the surface and can therefore, in a zeroth-order approximation, be neglected. This reduces the problem to that of a flat plate. Regarding the neglected terms as a perturbation of the problem of the flat plate, the solution can be expanded in terms of a power series in the small parameter $1/\kappa a$. In this way an accurate expression for Ψ_0 can be obtained:[11,12,22,25]

$$\Psi_0 = 2\ln(p+q) \mp \frac{1}{\kappa a}\frac{2m(q-1)}{pq} +$$

$$\left(\frac{1}{\kappa a}\right)^2\left\{\frac{m^2(q-1)^2(2q+1)}{p^3 q^3} - \frac{2m(m-1)\ln\left(\dfrac{q+1}{2}\right)}{pq}\right\} \qquad (22)$$

TABLE I: Comparison between Surface Potentials Ψ_0 Calculated with Eq 22 and the Values Calculated Numerically, for Spheres with $\kappa a = 3$, and Several Values of p: Double Layer inside a Sphere

	values calcd with eq 22 Ψ_0 with $1/\kappa a$ up to order			numerical values	
p	0	1	2	Ψ_0	10Ψ in center
0.25	0.4949	0.6542	0.7032	0.7167	2.10
0.5	0.9624	1.2440	1.3131	1.3163	3.69
1	1.7628	2.1533	2.1973	2.1811	5.53
2	2.8873	3.2558	3.2495	3.2397	7.06
4	4.1894	4.4419	4.4255	4.4237	8.09
8	5.5529	5.6989	5.6899	5.6898	8.69
16	6.9334	7.0116	7.0080	7.0080	9.02

In this equation the upper sign refers to the electrical double layer outside the sphere or cylinder, and the lower sign refers to the electrical double layer inside the sphere or cylinder. In the derivation of eq 22 for the double layer inside the sphere or cylinder, we made the approximation of zero potential at the center. Note that for high values of p the terms in $1/\kappa a$ and $(1/\kappa a)^2$ become very small, and in the limit $p \to \infty$ the surface potential approaches the flat plate value $2 \ln (p + q)$, regardless of the curvature of the surface. We further note the interesting feature that in the limit of $p \to 0$, the $1/\kappa a$ expansion (22) yields the same terms as can be found from the exact analytical solution of the linearized PB equation for a sphere and cylinder.

The above expression for Ψ_0 is used to obtain the electrical part of the surface free energy, by performing the integration indicated by eq 16. This leads to the following expression:[11,12,22,25]

$$f_{el} = \left(\frac{RT}{F}\right)^2 \epsilon_r \epsilon_0 \kappa \left[4\{p \ln (p + q) - q + 1\} \mp \frac{4m}{\kappa a} \ln \left(\frac{q + 1}{2}\right) + \frac{1}{(\kappa a)^2} \left\{ \frac{m^2(q - 1)(q + 2)}{(q + 1)q} - 2m(m - 1) \int_{z=2/(q+1)}^{z=1} \frac{\ln z}{z - 1} dz \right\} \right] \quad (23)$$

In eq 23 the upper sign again refers to the electrical double layer outside the sphere or cylinder, and the lower sign refers to the electrical double layer inside the sphere of cylinder.

We will now make use of the expressions for the surface free energy for the spherical and cylindrical charged surface to calculate the co-ion adsorption. Substitution of eq 23 into eq 19 leads to the following expressions for the co-ion adsorption. Defining the scaled adsorption $\mathcal{A}$ as follows:

$$\Gamma_{co\text{-}ion} = -2\kappa^{-1} c_{el} \mathcal{A} \quad (24)$$

we find

$$\mathcal{A} = p + 1 - q \mp \frac{1}{\kappa a}\left(m\frac{1 - q}{q}\right) + \left(\frac{1}{\kappa a}\right)^2 \left[\frac{m^2}{4}\left(-1 - \frac{2}{q(q + 1)} + \frac{2}{q^3}\right) + \frac{m(m - 1)}{2}\left\{\frac{2}{q} \ln\left(\frac{1 + q}{2}\right) + \int_{z=2/(q+1)}^{z=1} \frac{\ln z}{z - 1} dz\right\} \right] \quad (25)$$

Also here the upper sign refers to the electrical double layer outside the sphere or cylinder, and the lower sign refers to the electrical double layer inside the sphere or cylinder.

Note that in the limiting case $\kappa a \to \infty$ one retrieves for $\mathcal{A}$ the expression for the flat electrical double layer. In the limit $p \to \infty$ one obtains

$$\mathcal{A}(p \to \infty) = 1 \pm \frac{2}{\kappa a} + \frac{(\pi^2/6) - 1}{(\kappa a)^2}, \quad \text{sphere} \quad (26)$$

$$\mathcal{A}(p \to \infty) = 1 \pm \frac{1}{\kappa a} + \frac{-1/4}{(\kappa a)^2}, \quad \text{cylinder} \quad (27)$$

In contrast to the expression for Ψ_0, eq 22, the equation for $\mathcal{A}$ remains dependent of κa in the limit $p \to \infty$. This is due to the fact that the co-ion adsorption results from the decreased co-ion concentration over the whole extent of the diffuse double layer. Therefore the co-ion adsorption dependent of curvature as long as the thickness of the diffuse double layer ($\sim\kappa^{-1}$) is of the same order as the radius of curvature a of the charged surface.

Although it is possible to derive accurate numerical solutions starting with the Poisson–Boltzmann equation in its untruncated form, the analytical approximations discussed here have the advantage that they give more insight into the physics of the problem. The evaluation of the integral in eq 25 is very easily performed on a simple computer or alternatively can be expressed in two rapidly converging power series:[25]

$$\int_x^1 \frac{\ln z \, dz}{1 - z} = -\sum_{i=1}^\infty \frac{(1 - x)^i}{i^2} = -\frac{\pi^2}{6} + \ln x \ln (1 - x) + \sum_{i=1}^\infty \frac{x^i}{i^2} \quad (28)$$

Comparison with Numerical Calculations and Discussion

We checked the validity of the approximate analytical expressions for the surface potential Ψ_0 and the scaled adsorption $\mathcal{A}$, derived in the previous section, by comparison with numerical calculations. The numerical solutions were obtained by converting the second-order PB equation into the equivalent system of two first-order differential equations and solving these equations simultaneously with a one-step fifth-order Taylor series method. The procedure is started with a guess for an initial value for Ψ at a distance far from the surface. For the double layer inside the sphere or cylinder we start with the potential at the center. This initial value of Ψ is adjusted until $(d\Psi/dx)_{surface}$ corresponds to the desired value. The accuracy of the numerical procedure was estimated by comparing the results obtained for a flat double layer with the exact values. The numerical results for the surface potential and the adsorption are exact to five significant digits.

In Tables I–IV we compare numerical results for the surface potential Ψ_0 with the values calculated with eq 22 for double layers inside and outside spheres and cylinders and with a reduced radius $\kappa a = 3$. We varied p between 0.25 and 16, which approximately spans the range of surface charge densities encountered in colloidal systems. We find that the approximate analytical expressions up to order $(1/\kappa a)^2$ yields results that lie within 3% of the exact numerical results.

In Tables V–VIII we compare the numerical values for the reduced co-ion adsorption with the values of eq 25 for double layers inside and outside spheres and cylinders, and with a reduced radius $\kappa a = 3$. We find that the approximate analytical expression up to order $(1/\kappa a)^2$ is accurate for double layers outside the sphere and cylinder, and the results lie within 2% of the exact numerical values. For double layers inside the sphere and cylinder the approximate analytical expression is less accurate, due to the approximation of zero potential at the center. This deviation becomes larger for larger values of p, but stays within 10% for $p = 16$.

In Tables IX and X we investigate the dependence of the accuracy of the approximate analytical expressions for Ψ_0 and $\mathcal{A}$ on the radius of curvature of the charged surface, for the chosen value of $p = 2$. For double layers outside spheres and cylinders we observe that values for Ψ_0 and $\mathcal{A}$ obtained with the approximate analytical expression lie within 2% of the exact numerical values, when $\kappa a > 2$.

For double layers inside spheres and cylinders, regardless of the value of κa, the potential at the center will, of course, not be zero. We note, however, that the assumption of a thin double layer (introduced by the approximation $\psi(\text{center}) = 0$)) does not introduce serious errors in ψ_0 when $\kappa a > 2$ and in $\mathcal{A}$ with $\kappa a > 4$. This is largely due to the fact that especially for high surface potentials, the double layer is strongly concentrated near the

TABLE II: As in Table I, but for the Double Layer outside a Sphere

	values calcd with eq 22 Ψ_0 with $1/\kappa a$ up to order			numerical values
p	0	1	2	Ψ_0
0.25	0.4949	0.3357	0.3847	0.3736
0.5	0.9624	0.6809	0.7500	0.7390
1	1.7628	1.3722	1.4163	1.4200
2	2.8873	2.5188	2.5125	2.5201
4	4.1894	3.9369	3.9205	3.9219
8	5.5529	5.4070	5.3980	5.3979
16	6.9334	6.8553	6.8518	6.8518

TABLE III: As in Table I, but for the Double Layer inside a Cylinder

	values calcd with eq 22 Ψ_0 with $1/\kappa a$ up to order			numerical values	
p	0	1	2	Ψ_0	10Ψ in center
0.25	0.4949	0.5746	0.5934	0.6043	1.223
0.5	0.9624	1.1032	1.1319	1.1456	2.250
1	1.7628	1.9580	1.9838	1.9925	3.626
2	2.8873	3.0715	3.0819	3.0851	4.922
4	4.1894	4.3157	4.3179	4.3191	5.836
8	5.5529	5.6259	5.6263	5.6267	6.380
16	6.9334	6.9725	6.9725	6.9727	6.678

TABLE IV: As in Table I, but for the Double Layer outside a Cylinder

	values calcd with eq 22 Ψ_0 with $1/\kappa a$ up to order			numerical values
p	0	1	2	Ψ_0
0.25	0.4949	0.4153	0.4341	0.4299
0.5	0.9624	0.8217	0.8503	0.8446
1	1.7628	1.5675	1.5933	1.5896
2	2.8873	2.7030	2.7134	2.7124
4	4.1894	4.0632	4.0654	4.0651
8	5.5529	5.4800	5.4803	5.4802
16	6.9334	6.8944	6.8944	6.8944

TABLE V: Comparison between Reduced Adsorption $\mathcal{A}$ Calculated with Eq 25 and the Values Calculated Numerically, for Spheres with $\kappa a = 3$, and Several Values of p: Double Layer inside a Sphere

	values calcd with eq 25 $\mathcal{A}$ with $1/\kappa a$ up to order			numerical values
p	0	1	2	$\mathcal{A}$
0.25	0.2192	0.1993	0.1899	0.1867
0.5	0.3820	0.3116	0.2833	0.2809
1	0.5858	0.3905	0.3424	0.3584
2	0.7639	0.3954	0.3687	0.4044
4	0.8769	0.3719	0.3866	0.4276
8	0.9377	0.3538	0.3966	0.4388
16	0.9688	0.3437	0.4011	0.4442
∞	1.0000	0.3333	0.4050	

TABLE VI: As in Table V, but for the Double Layer outside a Sphere

	values calcd with eq 25 $\mathcal{A}$ with $1/\kappa a$ up to order			numerical values
p	0	1	2	$\mathcal{A}$
0.25	0.2192	0.2391	0.2298	0.2325
0.5	0.3820	0.4524	0.4241	0.4310
1	0.5858	0.7811	0.7329	0.7374
2	0.7639	1.1325	1.1057	1.0974
4	0.8769	1.3819	1.3966	1.3855
8	0.9377	1.5217	1.5645	1.5550
16	0.9688	1.5939	1.6513	1.6427
∞	1.0000	1.6667	1.7383	

surface. Details of what happens more than a few times $1/\kappa$ away from the surface contribute little to the final value of the free energy and salt exclusion.

TABLE VII: As in Table V, but for the Double Layer inside a Cylinder

	values calcd with eq 25 $\mathcal{A}$ with $1/\kappa a$ up to order			numerical values
p	0	1	2	$\mathcal{A}$
0.25	0.2192	0.2093	0.2057	0.2026
0.5	0.3820	0.3468	0.3353	0.3266
1	0.5858	0.4882	0.4638	0.4488
2	0.7639	0.5797	0.5492	0.5315
4	0.8769	0.6244	0.5948	0.5757
8	0.9377	0.6458	0.6173	0.5976
16	0.9688	0.6562	0.6283	0.6083
∞	1.0000	0.6667	0.6389	

TABLE VIII: As in Table V, but for the Double Layer outside a Cylinder

	values calcd with eq 25 $\mathcal{A}$ with $1/\kappa a$ up to order			numerical values
p	0	1	2	$\mathcal{A}$
0.25	0.2192	0.2292	0.2256	0.2266
0.5	0.3820	0.4172	0.4057	0.4088
1	0.5858	0.6834	0.6590	0.6647
2	0.7639	0.9482	0.9177	0.9243
4	0.8769	1.1294	1.0998	1.1070
8	0.9377	1.2297	1.2013	1.2091
16	0.9688	1.2813	1.2534	1.2614
∞	1.0000	1.3333	1.3056	

TABLE IX: Comparison between Approximate Analytical and Numerical Values for Ψ_0 and $\mathcal{A}$ for Several Reduced Radii of Charged Spherical Surfaces (the Value of p Kept Constant at 2)

	double layer inside sphere				double layer outside sphere			
	Ψ_0		$\mathcal{A}$		Ψ_0		$\mathcal{A}$	
κa	eq 22	num	eq 25	num	eq 22	num	eq 25	num
1	3.9363	3.7391	−0.5823	0.1588	1.7252	1.8938	1.6288	1.5206
2	3.4259	3.3903	0.1510	0.2961	2.3204	2.3453	1.2566	1.2329
3	3.2495	3.2398	0.3687	0.4044	2.5125	2.5201	1.1057	1.0974
4	3.1601	3.1565	0.4725	0.4827	2.6074	2.6106	1.0253	1.0215
5	3.1061	3.1044	0.5332	0.5370	2.6639	2.6656	0.9754	0.9734
6	3.0700	3.0690	0.5730	0.5748	2.7014	2.7024	0.9415	0.9403
8	3.0246	3.0242	0.6220	0.6227	2.7482	2.7486	0.8984	0.8978
10	2.9973	2.9971	0.6510	0.6513	2.7762	2.7764	0.8721	0.8718
20	2.9424	2.9424	0.7081	0.7081	2.8319	2.8319	0.8186	0.8186

TABLE X: As in Table IX, but for a Cylinder

	double layer inside cylinder				double layer outside cylinder			
	Ψ_0		$\mathcal{A}$		Ψ_0		$\mathcal{A}$	
κa	eq 22	num	eq 25	num	eq 22	num	eq 25	num
1	3.5335	3.4693	−0.0632	0.2319	2.4280	2.4107	1.0423	1.1539
2	3.1870	3.1908	0.4189	0.4130	2.6343	2.6313	0.9717	0.9909
3	3.0819	3.0851	0.5492	0.5315	2.7134	2.7124	0.9177	0.9243
4	3.0313	3.0327	0.6086	0.5994	2.7549	2.7545	0.8850	0.8880
5	3.0016	3.0022	0.6424	0.6382	2.7805	2.7802	0.8635	0.8652
6	2.9820	2.9823	0.6642	0.6621	2.7977	2.7976	0.8484	0.8494
8	2.9578	2.9579	0.6906	0.6898	2.8196	2.8196	0.8287	0.8292
10	2.9435	2.9435	0.7059	0.7056	2.8329	2.8329	0.8165	0.8167
20	2.9151	2.9152	0.7356	0.7356	2.8599	2.8599	0.7909	0.7909

Conclusions

In this article we presented approximate analytical expressions for the surface potential, the electrical part of the surface free energy, and the co-ion adsorption, for thin, curved, diffuse double layers. The expressions are based on a series expansion up to power 2 of the small parameter $1/\kappa a$.

The expressions for the surface potential and co-ion adsorption are found to be accurate (better than 2%) when the reduced curvature κa of the charged surface exceeds 2 and 4, respectively. This accuracy will be sufficient for most applications in colloid research.

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Appendix. Derivation of the Adsorption Equation for Ions in an Electrical Double Layer (Eq 15)

Consider a system with a constant volume V, consisting of n_i moles of species i, with valence number z_i. Inside the system is a charged surface, with an area A, in contact with the solution via an electrical double layer. The charged surface has a constant curvature, which need not be zero. Similar to the approximations that are made in the PB equation, we will assume that only electrical forces are present in the double layer. Of course, when we only consider the electrical forces, the electrical double layer is unstable and would not form spontaneously. In real physical systems a driving force, such as the chemical adsorption of a potential-determining ion, is present. However, we omit the specification of a driving force because it is not essential for this derivation and would cause unnecessary complications.

The situation inside the system is conveniently described by defining excess quantities that are due to the presence of the electrical double layer. Following the Gibbs treatment of the surface tension, we define

$$F = F^s + F^r \tag{A1}$$

$$n_i = n_i^s + n_i^r \tag{A2}$$

$$S = S^s + S^r \tag{A3}$$

where the superscript r refers to the reference system, for which the concentrations of the ions are constant throughout the system and equal to the concentrations far from the charged surface in the actual system. The superscript s refers to the excess quantities due to the presence of the electrical double layer.

The differential of the excess free energy the double layer dF^s, at constant surface charge density σ, is given by

$$dF^s = -S^s \, dT + \sum_i \mu_i \, dn_i^s + f_{el} \, dA \tag{A4}$$

On the right-hand side of eq A4 the first term gives the temperature dependence of F^s, the contribution $\sum_i \mu_i \, dn_i^s$ originates from the excess of the ions in the interfacial region, and the contribution $f_{el} \, dA$ is due to the excess electrical energy in the double layer. The excess Helmholtz free energy is a homogenous function of first order in A and n_i^s. Therefore we can integrate over these extensive variables at constant T, yielding

$$F^s = f_{el}A + \sum_i \mu_i n_i^s \tag{A5}$$

By subtracting from eq A4 the equation obtained from general differentiation of eq A5, we obtain the Gibbs–Duhem equation

$$S^s \, dT + \sum_i n_i \, d\mu_i^s + A \, df_{el} = 0 \tag{A6}$$

A rearrangement of eq A6 finally yields, for constant T and σ

$$df_{el} = -\sum_i \Gamma_i \, d\mu_i \tag{A7}$$

Comparison of a Primitive Model Perturbation Theory with Experimental Data of Simple Electrolytes

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Perturbation theory of the restricted primitive model is applied to some simple electrolytes and compared with experimental data of activity coefficients. The theory fits the data well with only one parameter, the diameter of the ion. However, the fitted diameter is inconsistent with Pauling's diameter.

Introduction

Debye and Hückel's theory of simple electrolytes[1] has been well tested against many experimental data. Their theory has been accepted to be exact in the infinite dilute solution limit. For higher concentrations, typically >0.002 M, the Debye–Hückel limiting law is found to be incorrect. Over the years, numerous theories have been introduced to improve the Debye–Hückel theory. These include modifications of the Debye–Hückel equation, empirical approaches, and statistical mechanics based theories. So far, none of the theories has been completely satisfactory. The representative empirical theories are Pitzer's virial development[2] and NRTL theory of Chen et al.[3] These are being used in industry. However, the parameters in empirical correlations are not available for many electrolytes, and the extrapolation to other conditions is difficult. Statistical mechanics theories centered around two Hamiltonian models: the primitive model in which the solvent is a continuum,

and the ion–dipole model in which the solvent is modeled as dipolar hard spheres. Variations exist in the techniques of solving the corresponding partition function and distribution functions in the modeled system. Several reviews have appeared on this subject.[4] Perturbation theories were developed by Stell and Lebowitz[5] for the primitive model and by Henderson et al.[6] for the ion–dipole model. Waisman and Lebowitz[7] and Blum[8] have solved the mean spherical approximation (MSA) for the primitive model and Blum[9] and Adelman and Duetsch[10] have solved the MSA for the ion–dipole model. The hypernatted chain (HNC) integral equation of the primitive model was solved by Rasaiah and Friedman,[11]

(1) Debye, P.; Hückel, E. *Phys. Z* **1923,** *24,* 185.
(2) Pitzer, K. S. *J. Phys. Chem.* **1973,** *77,* 268.
(3) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. A. *AIChE J.* **1979,** *25,* 820.

(4) Hafskjoid, B.; Stell, G. In *The Liquid State of Matter: Fluids, Simple and Complex;* Montroll, E. W., Lebowitz, J. L., North-Holland,: 1982; p 175. Friedmann, H. *Ann. Rev. Phys. Chem.* **1981,** *32,* 179.
(5) Stell, G.; Lebowitz, J. L. *J. Chem. Phys.* **1968,** *48,* 3706.
(6) Henderson, D.; Blum, L.; Tani, A. In *ACS Symposium Series No. 300;* Chao, K. C.; Robinson, R. L., American Chemical Society: Washington, DC., 1986.
(7) Waisman, E.; Lebowitz, J. L. *J. Chem. Phys.* **1972,** *56,* 3086, 3093.
(8) Blum, L. *Theor. Chem.* **1980,** *5,* 1.
(9) Blum, L. *Chem. Phys. Lett.* **1974,** *26,* 200. Blum, L. *J. Chem. Phys.* **1974,** *61,* 2129.
(10) Adelman, S. A.; Deutch, M. J. *J. Chem. Phys.* **1974,** *60,* 3935.