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Thermodynamic Consistency of the Modified Poisson-Boltzmann Equation in the Electric Double Layer

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The thermodynamic consistency of the modified Poisson-Boltzmann equation in the electric double layer is considered. The osmotic and the activity coefficients predicted by the theory (from the contact values of the density profiles) are compared with the available Monte Carlo data for a 1:1/2:2 valency restricted primitive model electrolyte, and with the experimental results for the monovalent salts LiCl, KCl, and NaCl. Comparisons are also made with the hypernetted chain osmotic coefficients for the 1:1, 1:2, and 2:2 salts. It is seen that overall for monovalent electrolyte/salts the modified Poisson-Boltzmann theory applied to the interface is satisfactory, being of comparable accuracy to the hypernetted chain theory.

Introduction

Studies of the electrical double layer phenomena are of considerable importance for all branches of electrochemistry and colloid chemistry as well as for various aspects of biophysical sciences. Due to the continual and widespread interest, the theoretical treatments of the double layer structure, pioneered by the Poisson-Boltzmann (PB) approach of Gouy,¹ Chapman,² and Stern,³ have undergone numerous improvements concerning both the underlying physical models and the statistical mechanics methods applied. Among important effects neglected in traditional approaches the fluctuation potential, the wall-ion exclusion volume, the long-range ion-ion correlations, image forces, and quite recently, some of the effects related to the molecular structure of the solvent have been examined. A widely used reference model for the double layer in recent years has been that of a restricted primitive model (RPM) electrolyte (equisized charged hard spheres embedded in a dielectric continuum) next to a planar uniformly charged interface. For this model, the classical PB treatment has been complemented by extensive Monte Carlo (MC) simulations, and theoretical approaches based on the liquid structure integral equations and a potential analysis using a modified Poisson-Boltzmann (MPB) equation.⁴ The latter theory has origins in the classical statistical mechanical work of Kirkwood⁵ and Loeb,⁶ and to date has been one of the most successful theories in reproducing the MC results for the structural features of the model interface.⁷ Further, it has been shown that even a rather approximate consideration of the fluctuation potential and the exclusion volume corrections compared to those utilized in the MPB and related theories may in some cases essentially improve the interpretations of both the thermodynamic⁸⁻¹¹ and transport properties of colloidal solutions.^{12,13} Along with favorable comparisons with the experiment and the computer simulations, additional tests of the internal consistency of the method reflecting the effects of the approximations involved would be desirable. Exact theoretical treatments of the electrical double layer must satisfy the contact theorem¹⁴⁻¹⁶ relating the contact values of the singlet density profiles to the surface charge and the bulk pressure of the solution, eventual deviations from the expected value being a measure of the approximations of the method considered. As has been already shown¹⁷ the contact theorem is fairly well satisfied

by the recent version of the MPB equation, namely the MPB5 theory, at various conditions. Applying the contact theorem to a neutral interface dividing the solution and the solvent in an osmotic equilibrium the relation between the osmotic pressure and the contact number density of ions can be obtained as confirmed by a more general approach based on the differentiation of the configuration integral with respect to the volume of the solution.^{18,19} From the osmotic pressure other thermodynamic properties of the bulk electrolyte can be derived directly from the interfacial concentration profiles. In the present note the osmotic and activity coefficients of electrolyte solutions at various concentrations will be calculated from the contact values of the wall-ion distribution functions predicted by the MPB equation and its thermodynamic consistency will be estimated via a comparison with the results of other electrolyte theories as well as with selected experimental data or the MC results.

Theory

The MPB Equation. The approximations involved in the derivation of the MPB equation for the RPM double layer and the

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details of the analytical techniques used have been extensively discussed elsewhere.^{17,20,21} We therefore restrict ourselves here to outlining the final equations of the theory.

For no imaging, the MPB equation for the mean electrostatic potential $\psi(x)$ at a perpendicular distance x from the planar uniformly charged interface reads

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi}{\epsilon} \sum_s e_s n_s^0 g_s(x) \quad x > a/2 \quad (1)$$

$$\psi(x) = \psi(0) - \frac{4\pi\sigma}{\epsilon} x \quad 0 \leq x \leq a/2 \quad (2)$$

$$g_s(x) = \xi_s(x) \exp \left[-\frac{\beta e_s}{2} \left\{ \frac{(F - F_0)e_s}{\epsilon a} + F\psi(x+a) + F\psi(x-a) - \frac{F-1}{a} \int_{x-a}^{x+a} dy \psi(y) \right\} \right], \quad x > a/2 \quad (3)$$

In the above equations, $g_s(x)$ ($s = i, j$) is the singlet wall-ion distribution function for an ion type s , e_s , n_s^0 are the charge and mean bulk number density of ions of species s with a being the common ionic diameter, σ the surface charge density, ϵ the constant dielectric permittivity, and $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T the absolute temperature).

In eq 3, $\xi_s(x) = g_s(x; e_s=0)$ is the exclusion volume term which is treated by using an approach based on the Bogoliubov-Born-Green-Yvon hierarchy²²

$$\xi_s(x) = H\left(x - \frac{a}{2}\right) \exp \left[B_s(x) + \frac{4\pi}{3} \sum_i n_i^0 a^3 \right] \quad (4)$$

$$B_s(x) = \pi \sum_i n_i^0 \int_{\max(a/2, x-a)}^{x+a} dy g_i(y) [(y-x)^2 - a^2] \quad (5)$$

Here $H(x)$ is the Heaviside unit step function, and

$$F = \frac{4}{4 + \kappa(a + 2x)} \quad a/2 \leq x \leq 3a/2 \quad (6)$$

$$F = \frac{1}{1 + \kappa a} \quad x \geq 3a/2 \quad (7)$$

$$F_0 = \lim_{x \rightarrow \infty} F = \frac{1}{1 + \kappa_0 a} \quad (8)$$

$$\kappa^2 = \frac{4\pi\beta}{\epsilon} \sum_s e_s^2 n_s^0 g_s(x) \quad (9)$$

$$\kappa_0^2 = \lim_{x \rightarrow \infty} \kappa^2 = \frac{4\pi\beta}{\epsilon} \sum_s e_s^2 n_s^0 \quad (10)$$

In the above equations, κ is the local Debye-Hückel parameter and κ_0 the bulk Debye-Hückel constant. Equations 1, 3, and 4 are collectively called the MPB equation for the RPM double layer.

Thermodynamic Properties of an Electrolyte Solution Expressed in Terms of the Interfacial Ionic Concentration. The electrolyte solution in an osmotic equilibrium with the solvent can be viewed as a special example of the electrical double layer at a neutral interface and at uniform permittivity. According to previous works the MacMillan-Mayer osmotic pressure of the solution is then related to the contact number density of the ions by

$$\Pi = \frac{1}{\beta} \sum_i n_i^c \quad (11)$$

where $n_i^c = n_i^0 g_i^c$ is the number density of ions of species i at the

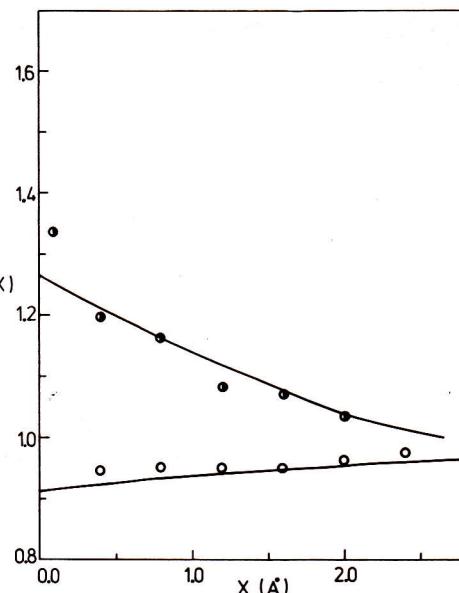


Figure 1. 1:1 Ionic (singlet) density profiles next to a planar hard uncharged interface at $c = 0.1045 \text{ mol dm}^{-3}$: lower curve, — MPB, \circ MC, and $c = 1.98 \text{ mol dm}^{-3}$; upper curve — MPB, \bullet MC.

wall-ion contact plane, with g_i^c being the contact value of the wall-ion distribution function. In the case of symmetrical electrolytes $n_+^c = n_-^c$, the subscripts + and - referring to co-ions and counterions, respectively, eq 11 can be rewritten in a remarkably simple form

$$\phi = g_{\pm}^c \quad (12)$$

where ϕ is the MacMillan-Mayer osmotic coefficient $\phi = \Pi/\beta / \sum_i n_i^0$. Knowing the osmotic pressure as a function of the concentration, the excess free energy and the remaining thermodynamic quantities can be calculated. In the present work, however, the direct relation for the activity coefficient of the solute

$$\ln f_{\pm} = \int_0^c (\phi - 1) d \ln c + (\phi - 1) \quad (13)$$

will be applied. Above, c is the solute concentration and f_{\pm} is the mean ionic activity coefficient.

Results and Discussion

The MPB equation was solved numerically for a neutral wall by using a quasi-linearization iterative method. Details of the numerical techniques and the quasi-linearization procedure have been discussed in ref 21 and 22. We have performed the calculations at the MC parameters^{18,23,24} of $a = 4.25 \times 10^{-10} \text{ m}$, $\epsilon = 78.5$, and $T = 298 \text{ K}$ for the 1:1 and 2:2 electrolytes and for the 1:2 and 2:2 electrolytes at the HNC parameters of Rasaiah,²⁵ while for the salts NaCl and KCl ionic diameters were taken from the literature,²⁶ $a = 3.97 \times 10^{-10} \text{ m}$ and $a = 3.63 \times 10^{-10} \text{ m}$, respectively. The integral in the Gibbs-Duhem equation (eq 13) was evaluated by using the Simpson rule. For this purpose, we determined c at a series of concentrations, the lowest being $c = 10^{-4} \text{ mol dm}^{-3}$, such that the difference between the logarithms of successive concentrations, $\Delta \ln c = (\ln c_{j+1} - \ln c_j)$ was constant. The contact g_{\pm}^c 's were seen to vary fairly slowly and smoothly with concentration. In applying the Simpson rule we took 80 intervals between $c = 10^{-4} \text{ mol dm}^{-3}$ and $c = 2 \text{ mol dm}^{-3}$ with $\Delta \ln c = 0.12379$. A test was also performed with 40 intervals. There were hardly noticeable differences.

We first give an example, in Figure 1, of the MPB concentration profiles of ions for 1:1 electrolytes very close to a neutral im-

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TABLE I: Comparison of the Osmotic Coefficient ϕ for the RPM 1:1 Electrolyte Determined by Eq 12 and the Double Layer MPB and HNC/HNC Theories; by the Virial Equation and the Bulk MPB Theory (MPB_B); by the Virial Equation and the Bulk HNC Theory (HNC_B); by Eq 12 in HNC_N Approximation; and by the Monte Carlo Simulations (MC)^a

c /(mol dm ⁻³)	ϕ (MPB)	ϕ (HNC/HNC)	ϕ (MPB _B)	ϕ (HNC _B)	ϕ (HNC _N)	ϕ (MC)
0.00911	0.955	0.987	0.970	0.970	0.985	0.970
0.10376	0.913	0.974	0.945	0.945	0.977	0.945
0.42502	0.944	1.023	0.980	0.980	1.015	0.977
1.0001	1.05	1.153	1.09	1.093	1.110	1.094
1.9676	1.26	1.456	1.34	1.351	1.340	1.346

^aThe Monte Carlo values are from ref 23.

permeable interface at two concentrations, 0.1045 mol dm⁻³ and 1.98 mol dm⁻³, in comparison with the available Monte Carlo data for the same RPM system.¹⁸ To analyze the curves we note that for symmetrical valences the mean electrostatic potential $\psi(x)$ is zero, giving from eq 3

$$g_s(x) = \xi_s(x) \exp \left[-\beta e_s^2 \frac{(F - F_0)}{2\epsilon a} \right] \quad (14)$$

So for small $\beta e_s^2(F - F_0)/2\epsilon a$ the distribution function $g_s(x)$ essentially splits into the product of an electrical and nonelectrical term since the effect of the charges e_s on $\xi_s(x)$ is secondary. From eq 4 and 5 the value of the exclusion volume term $\xi_s(x)$ will be similar to that of the BBGY $g_s(x)$ for uncharged hard spheres against a planar hard wall. For the parameters in the Figure 1 $F - F_0$ is small and positive near the wall due to the distortion of the atmosphere of the ion s . We thus have that at the lower concentration the exclusion volume term effect leading to a positive adsorption of the ions at the interface is not as important as the long-range ion-ion correlation which is reflected in a decrease of the concentration profiles. As c increases, however, the geometric packing effects due to increased hard-core interaction begin to dominate over the electrostatic part and a considerable increase in the ion concentration next to the surface is observed in conformity with the known osmotic behavior. In both cases, the contact number density is underestimated by the MPB equation, which may be attributed to inaccuracies in the calculation of the fluctuation potential near the interface.

A similar behavior pattern occurs for the 2:2 distribution function as the concentration increases from zero. Due to the increased ion-ion interaction the drop in $g_s(x)$ below unity near the wall is greater than in the 1:1 case. Although not displayed in Figure 1 the MPB plot at 1.98 M has a small damped oscillatory behavior for large x which stems from the hard-core effects calculated through $\xi_s(x)$.

In Table I and Figure 2 the 1:1 osmotic coefficients given by the RPM electrolyte are compared to the results of the Monte Carlo simulations²³ and to the osmotic coefficients obtained by the virial equation by using the bulk MPB results²⁷⁻²⁹ and the bulk hypernetted chain (HNC) results for the ion-ion correlations.^{30,31} A comparison with the HNC osmotic coefficients obtained by eq 12 would also be interesting. In Table I we have also included the ϕ as given by eq 12 with g_{\pm}^c calculated³² by using the HNC/HNC approximation for the planar double layer.^{4,7} In addition, we include the results of an alternative treatment of the planar interfacial system by applying the standard HNC routine designed for spherically symmetrical systems. This can be done by replacing the planar interface by an additional, extremely dilute neutral spherical solute of diameter sufficiently exceeding the range of the ion-ion correlations. A set of calculations of this type has been carried out in this work by using the Rossky-Dale algorithm described elsewhere.³³ For technical reasons only diameters of

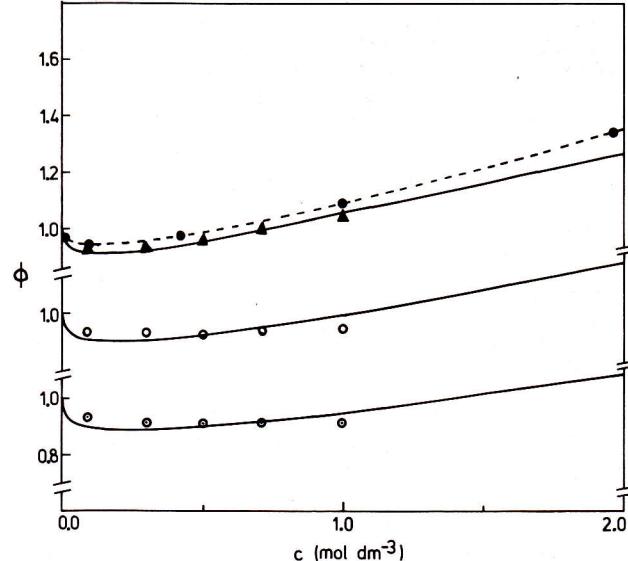


Figure 2. Concentration dependence of theoretical, experimental and Monte Carlo osmotic coefficients of monovalent electrolytes: — MPB; --- HNC, ● MC, ▲ LiCl (expt); ○ NaCl (expt), ○ KCl (expt). The NaCl and KCl MPB plots are for experimental radii.

the neutral component a_N equal to or below 40×10^{-10} m could be considered. The range of the ion-ion correlations is comparable to the Debye screening length $1/\kappa_0$ which becomes small compared to a_N at high concentrations. It is therefore expected that the HNC osmotic coefficient approximated by the contact value of the ion-neutral solute correlation function will approach the correct osmotic coefficient with increasing concentration. The osmotic coefficient obtained by this approach and tabulated in the sixth column of Table I, $\phi(HNC_N)$, seem to support the above considerations and are, at higher concentrations, very close to the bulk HNC results.

Considering the deviations of the MPB osmotic coefficients given by eq 12 from the Monte Carlo and the bulk MPB and the bulk HNC values, see Figure 2 and Table I, it appears that slightly low contact number densities are predicted by the MPB equation over the whole range of concentrations including those where the hard-core effects are unimportant. It is therefore most likely that a more detailed account of the fluctuation potential problem next to the interface is needed in order to remove the above deficiency. In general, a rather satisfactory osmotic behavior is predicted by the MPB theory. Note, however, that the HNC/HNC theory of the double layer overestimates the osmotic coefficient as compared to the MC results and to the theories of the bulk electrolyte. Comparing the HNC and the MPB theories for both the bulk and the double layer, respectively, vis-a-vis the MC results for ϕ , we notice that in either case, the predictions of the MPB theory are as good as those from the HNC approximation. When applied to the bulk phase, both the theories reproduce the simulation results almost quantitatively whereas the osmotic coefficient deduced from the double layer contact densities display entirely comparable deviations from the MC data. It ought to be emphasized here that the present procedure is a limited thermodynamic test of the

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TABLE II: Comparison between the MPB and Monte Carlo Activity Coefficients for the 1:1 RPM Electrolyte at Different Concentrations^a

$c/(mol\ dm^{-3})$	$\ln f_{\pm}\ MC$	$\ln f_{\pm}\ MPB$
0.01158	-0.087	-0.148
0.1002	-0.232	-0.336
0.495	-0.249	-0.416
1.003	-0.127	-0.306
1.994	0.271	-0.011

^aThe Monte Carlo values are from ref 24.

TABLE III: Comparison of the Osmotic Coefficients ϕ for the RPM 2:2 Electrolyte Determined by Eq 12 and the Double Layer MPB, by the Virial Equation and the Bulk MPB Theory (MPB_B), and by the Virial Equation and the Bulk HNC Theory (HNC_v)

$c/(mol\ dm^{-3})$	$\phi(MPB)$	$\phi(MPB_B)$	$\phi(HNC_v)$
0.005 ^a	0.750	0.792	
0.05 ^a	0.515	0.634	
0.0625	0.490	0.616	0.645
0.25	0.423	0.561	0.588
0.5 ^a	0.476	0.586	
0.5625	0.478	0.583	0.603
1.0	0.598	0.656	0.667
2.0	0.900	0.892	0.887

^aAt these concentrations, the physical parameters used are $a = 4.25 \times 10^{-10} m$, $\epsilon = 78.5$, and $T = 298 K$.

double layer MPB theory, at $\sigma = 0$, and that our idea is not to predict accurately the thermodynamic properties since the bulk MPB theory gives very good results, but to show that these properties as predicted by the contact g 's are (i) at par overall with the corresponding results from the HNC/HNC theory, and (ii) reasonable estimates of their bulk theory values.

Since a comparison with some experimentally known systems is also interesting the measured osmotic coefficients of LiCl, NaCl, and KCl solutions reduced to the McMillan-Mayer level³⁴ are compared with the predictions of the eq 12 in the MPB approach for the RPM electrolytes with ionic diameters for the given salts from the literature.²⁶ The LiCl data, however, are compared to those for the (1:1) RPM with $a = 4.25 \times 10^{-10} m$ which is close to the literature value $a_{LiCl} = 4.32 \times 10^{-10} m$. In all cases a reasonable agreement between the experiment and the prediction of the MPB equation is observed.

In Table II the logarithms of the mean activity coefficients of the RPM electrolyte calculated via the Gibbs-Duhem eq 13 are compared to the results of the grand canonical ensemble Monte Carlo simulations.²⁴ Except at the two highest concentrations, an agreement between the Monte Carlo and the MPB results comparable to that observed with the osmotic coefficient is found.

According to the previous experience, the effects of the approximation scheme may be more pronounced with higher valency electrolytes.¹⁷ In Table III we have listed the MPB ϕ for a 2:2 valency RPM electrolyte, calculated both from the double layer and the bulk theories,²⁸ along with the corresponding bulk HNC results.³⁵ We carried out calculations for this system at the MC

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TABLE IV: Comparison of the Osmotic Coefficients for the RPM 1:2 Electrolyte Determined by Eq 11 and the Bulk HNC Theory (HNC_v)

$c/(mol\ dm^{-3})$	$\phi(MPB)$	$\phi(HNC_v)$
0.00067	0.952	0.9676
0.005	0.888	0.9239
0.05	0.775	0.8502
0.1	0.753	0.8353
0.2	0.754	0.8358
0.4	0.800	0.8696
0.6	0.862	0.9199
0.8	0.930	0.9796
1.0	0.999	1.0475
1.333	1.12	1.1778

parameters³⁶ of $a = 4.2 \times 10^{-10} m$, $\epsilon = 78.356$, and $T = 298.16 K$. These were also the parameters used in the bulk MPB and HNC calculations. Three sets of results for the MPB (double layer and the bulk), at $c = 0.005$, 0.05 , and $0.5 M$, respectively, are also shown at the usual double layer parameters of $a = 4.25 \times 10^{-10} m$, $\epsilon = 78.5$, and $T = 298 K$. MC results show that the bulk MPB theory is as good as the bulk HNC theory in predicting ϕ for this 2:2 valency system particularly at the lower concentrations,^{28,29,37,38} both the theories decreasing in accuracy as the concentration increases.²⁹

We also present in Table IV some 1:2 osmotic coefficients at the HNC parameters of Rasaiah²⁵ (the above 2:2 MC parameters). Unsymmetrical valency electrolytes are of interest as the ion density profiles differ for the two ionic species so that the mean electrostatic potential $\psi(x)$ is nonzero. Although small, this mean electrostatic potential can be of the same order of magnitude as $\beta e_s^2(F - F_0)/2\epsilon a$ and hence is important in influencing the behavior of $g_s(x)$. This is especially true for $\kappa_0 a > 1.15$ ($c \gtrsim 0.23 M$)³⁹ when $\psi(x)$ takes on a damped oscillatory behavior.

The osmotic coefficients for these higher valency salts again show the same qualitative trend as those calculated from the bulk theories, the 1:2 salts being in slightly better agreement. As expected eq 11 yields the best approximation to ϕ for the 1:1 case. Still the relative deviations in the excess part of the osmotic coefficient, $\phi - 1$, in the 1:1, 1:2, and 2:2 systems are of the same order of magnitude. On the whole, it therefore appears that the approximations involved in the MPB treatment of the interfacial double layer do not lead to serious violations of the thermodynamic consistency of the system.

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