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Application of a recently proposed test to the hypernetted chain approximation for the electric double layer

D.Henderson[1]*, M.Alawneh[1], R.Saavedra-Barrera[2], M.Lozada-Cassou[3]

[1] Department of Chemistry and Biochemistry, Brigham Young University, Provo UT 84602–5700

[2] Department of Physics, Universidad Autónoma Metropolitana, Apartado Postal 55–534, 09340 México, DF, México

[3] Molecular Engineering Research Program, Instituto Mexicano del Petroleo, Apartado Postal 14–805, 07730 México DF, México

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Bhuiyan, Outhwaite, and Henderson, *J. Electroanal. Chem., 2007,* **607***, 54*, have studied the electric double layer formed by a symmetric electrolyte in the restricted primitive model and suggested that an examination of the product of the coion and counterion profiles, normalized to the one when the distance of an ion from the electrode is large, is an interesting and useful test of a theory. This product is identically one in the Poisson-Boltzmann theory but simulation results show that, at contact, this product can be greater or smaller than one at small electrode charge but always seems to tend to zero at large electrode charge. In this study we report the results of the hypernetted chain approximation (HNC/MSA version) for this product and find that, at contact, for this theory this product is always greater than the one at small electrode charge but tends to zero at large electrode charge.

Key words: *double layer, ion profiles, integral equations, hypernetted chain approximation*

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1. Introduction

The authors are pleased to join with the journal in honouring Fumio Hirata on the occasion of his birthday and in recognizing his accomplishments.

The theory of ions near an electrode (the electric double layer or EDL) is an interesting application of statistical mechanics because of the long range of the Coulomb forces. It can be even more interesting if the electrons of the electrode are taken into consideration, which makes it a mixed classical/quantum statistical mechanical problem. However, this latter aspect of the EDL is beyond our consideration here. The earliest work is the classic study of Gouy [1], Chapman [2], and Stern [3], which is often referred to as the Poisson-Boltzmann (PB) or Gouy-Chapman-Stern (GCS) theory. There is a widely accepted view that at higher concentrations, where the PB/GCS might need revision, the capacitance is dominated by the contribution of the 'inner' layer (the region between the electrode and the distance of closest approach of an ion) and any inadequacies in the PB/GCS theory may safely be ignored and, as a result, the theory is in a satisfactory state. This is not true. At best, the PB/GCS theory gives qualitatively reasonable results for integrated quantities, such as the potential difference across the EDL but is much less satisfactory for the ion profiles themselves. Even if the inner layer often dominates the capacitance, the profiles are of interest for the study of the electrochemical reactions. The inadequacies of the PB/GCS theory are especially evident for higher valence ions. Some years ago, Torrie and Valleau [4] made Monte Carlo (MC) simulations for the EDL. They found that the PB/GCS theory is not too bad for monovalent salts but not at all satisfactory for divalent and higher valence salts. However, a comment is required; the PB/GCS theory is fairly satisfactory for monovalent ions only if the electrode

*E-mail: doug@chem.byu.edu

charge is used as the independent variable. It is not satisfactory if the electrode potential is used as the independent variable. This is a nontrivial point since the potential is the natural independent variable in the PB/GCS theory (and indeed most theories) as well as in experiment. It is only in simulations that the electrode charge is used as the independent variable.

The PB/GCS theory is based on the *primitive model* of an electrolyte, where the ions are treated as charged hard spheres and the solvent is treated as a dielectric continuum. Almost all theories are based on the primitive model. In addition, in this note we assume that the ions are all of equal diameter, d, (this is called the *restricted primitive model*) (RPM). We use the RPM here. Further, we assume, for simplicity, that the electrolyte is binary and all the ions have the same valence, $z=|z_i|$, so that the charge of an ion of species i is $z_i e$, where e is the magnitude of the electronic charge. Because of the intrinsic symmetry of this system, we can assume without any loss of generality that the electrode is negatively charged.

Recently, there has been a renewed interest in the simulation and theory of the EDL. Boda et al. [5,6] have examined the capacitance of the EDL when the coupling is large (high valence, low temperature, low dielectric constant, small ion diameter, or any combination thereof) and found that, in this regime, the capacitance decreases as the temperature is decreased. At smaller coupling, the more usual behavior of an increasing capacitance with decreasing temperature is seen. This is in contrast to the PB/GCS theory that shows an always increasing capacitance with decreasing temperature. This finding accounts for the anomalous behavior of molten salt EDLs that previously had been thought to be a result of the high density (concentration) of molten salts. In addition, nonaqueous low concentration experimental systems can exhibit this behavior [7]. In the past few years, this anomalous behavior has been found in some of the better theories [8–10].

Another interesting test of a theory of the EDL has been recently proposed by Bhuiyan et al. [11]. They observed that the PB/GCS approximation is based on the assumption that the $g_i(x) = \exp[\pm\beta ze\phi(x)]$, where $g_i(x)$ is the density profile of an ion of species i as a function of the distance x from the electrode, normalized so that $g_i(\infty)$ is one, and $\phi(x)$ is the electric potential as a function of x. This means that in the PB/GCS theory $g_+(x)g_-(x) = 1$, identically. Their simulations showed that the contact value of this product can be greater or smaller than one when the electrode is uncharged but this contact product always seems to tend to zero at a large electrode charge. This contact product can tend to zero monatonically or first increase and pass through a maximum before tending to zero. Of course, any decent theory will predict that $g_+(x)g_-(x) = 1$ when x is large. Thus, the contact product is of most interest. Also, they showed that the PB/GCS theory failed to predict the correct behavior for $g_+(d/2)g_-(d/2)$ (as noted, it gives one) but that the modified Poisson-Boltzmann (MPB) theory did predict that this product tends to zero as the electrode charge is increased and can show a maximum, but could be in error when the electrode is zero. Another theory of interest is the hypernetted chain (HNC) approximation. The behavior of this contact product in this theory (HNC/MSA version) is considered here.

2. Theoretical preliminaries

First it is useful to consider the exact sum rule or contact value condition (CVC), found by Henderson et al. [12] for the profiles at contact $x = d/2$. The CVC is

$$g_s(d/2) = \frac{1}{2}\left[g_+(d/2) + g_-(d/2)\right] = a + \frac{b^2}{2}\,, \tag{1}$$

where

$$a = \frac{p}{\rho kT}\,, \tag{2}$$

p is the osmotic pressure of the ions of the electrolyte, k is Boltzmann's constant, T is the temperature, and ρ is the number density of all of the ions (N/V). Although equation (1) was derived rigorously, it is a force balance relation and was first obtained intuitively [13]. Thus, the first term on the RHS of equation (1) is the momentum transfer at the electrode and the second term is the

Maxwell stress. The quantity b is defined by

$$b = \frac{4\pi\beta z e\sigma}{\epsilon\kappa}, \tag{3}$$

where ϵ is the dielectric constant, κ is the Debye parameter,

$$\kappa^2 = \frac{4\pi\beta z^2 e^2 \rho}{\epsilon} \tag{4}$$

and $\beta = 1/kT$.

There is no known expression for a that is fully reliable but the mean spherical approximation (MSA) result,

$$a = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{\Gamma^3}{3\pi\rho}\,, \tag{5}$$

is useful. In equation (5), $\eta = \pi\rho d^3/6$ and Γ is a renormalized decay parameter that is related to κ by

$$\Gamma d = \frac{1}{2}\sqrt{1+2\kappa d} - \frac{1}{2}\,. \tag{6}$$

Thus, the pressure, given by a, consists of a positive term that results from the ionic hard cores and a negative electrostatic term. Hence, a can be greater or smaller than one. Of course, in a fully satisfactory theory a would always be positive. However, an approximate theory, such as the MSA, might give negative values for a.

The PB/GCS theory satisfies equation (1) but with $a = a_{\mathrm{PB}} = 1$. Thus, the PB/GCS approach approximates the pressure by the ideal gas result but completely neglects the electrostatic term in a. It does yield the b^2 term. The HNC/MSA theory also satisfies equation (1) but with a given by [14]

$$a = a_{\mathrm{H/M}} = \frac{1}{2}\left(1 + \frac{(1+2\eta)^2}{(1-\eta)^4}\right). \tag{7}$$

The HNC/MSA does obtain the b^2 term in equation (1) but completely neglects the electrostatic contribution to a. The HNC/MSA hard core part of a is an improvement over the ideal gas result; the hard core contribution to a is approximate but is not too bad as long as the concentration is not too large. However, the HNC/MSA gives a poor result, even for the hard sphere part, for molten salts.

Note that $g_s(d/2)$ becomes small when the electrostatic coupling $\beta z^2 e^2/(\epsilon d)$, is large (multivalent ions, low dielectric constant, low tempertaure, small ions, or some combination thereof). This leads to negative adsorption of the ions at large coupling. Low values of $g_s(d/2)$ are a symptom, but not a cause, of the capacitance anomaly that has been mentioned. A low value of the difference function, $g_d(x) = [g_+(x) - g_-(x)]/2$ is more directly related to this anomaly. Holovko et al. [15] have obtained an exact contact value theorem for $g_d(d/2)$. In addition, from their simulation studies, Boda and Henderson [16] concluded that at small electrode charge,

$$g_d(d/2) = ab, \tag{8}$$

was a useful result. In other words, at large coupling not only is there negative adsorption of the total number of ions but there is a negative adsorption of the charge as well. This is still not quite enough for the capacitance anomaly for which there should be a fairly broad region in which the ions have withdrawn from the electrode and this region should increase in width, leading to an increasing potential difference across the EDL, as the temperature is decreased. Such a phenomenon can be refered to as drying. Note that negative adsorption and drying apply only to the ions. The solvent continues to wet the electrode. Even less is known about $g_-(d/2)$ for large b. However, the small b behavior is probably most important for the capacitance since the potential of the inner layer between $x = 0$ and $x = d/2$ seems to dominate at large electrode charge.

Both the PB/GCS and HNC/MSA theories yield $g_d(d/2) = b$ at small b. In other words, the PB/GCS theory *possibly* satisfies equation (8) in a selfconsistent sense with $a = a_{\mathrm{PB}} = 1$ but the

HNC/MSA does not satisfy equation (8) in any sense. Since there is a close connection between the PB/GCS and HNC/MSA approximations, it is probably best to say that neither theory satisfies equation (8) and that neither theory can predict the capacitance anomaly. It is known that the PB/GCS theory does not predict the capacitance anomaly [5]. As the HNC/MSA theory has been applied at only one temperature one cannot directly verify that the HNC/MSA fails to predict a capacitance anomaly. However, we expect that it does not. In any case, there is no reason to believe that it is worth making additional HNC/MSA calculations to investigate this point.

It is of interest to see what various theories predict for $g_+(x)g_-(x)$, and more particularily for $g_+(d/2)g_-(d/2)$. In this paper, we consider this question for the HNC/MSA. We have already mentioned that the PB/GCS theory fails this test.

3. Results

The HNC/MSA yields an integral equation that has been solved numerically by Lozada-Cassou et al. [17]. It is not necessary to repeat these calculations because the results of that study have been stored. Regretably, they were stored only on paper so that it is really convenient only to confine an examination of $g_+(x)g_-(x)$ to $x = d/2$. However, this is the most interesting region. In principle, other values of x could be retrieved but this would be a great deal of work and probably not worth the effort. By good fortune, the parameters used in the HNC study are identical to those used by Alawneh and Henderson [18] in a recent simulation study so that a comparison with simulation results can be made. Since we make reference to the Alawneh and Henderson results, we mention that we use only their simulation results for the case where the electrode has a dielectric constant equal to that of the electrolyte.

This study is made for 0.1M and 1M monovalent and divalent ions with $d = 4.25$ Å, $\epsilon = 78.5$, and $T = 298$ K. The reduced densities corresponding to 0.1M and 1M are $\rho d^3 = 0.00925$ and 0.0925, respectively. The reduced temperature, $T^* = (kT\epsilon d)/z^2e^2)$, is equal to 0.595 and 0.159, respectively, for monovalent and divalent ions. The divalent ion regime is near the region for which anomalous capacitance results can be expected.

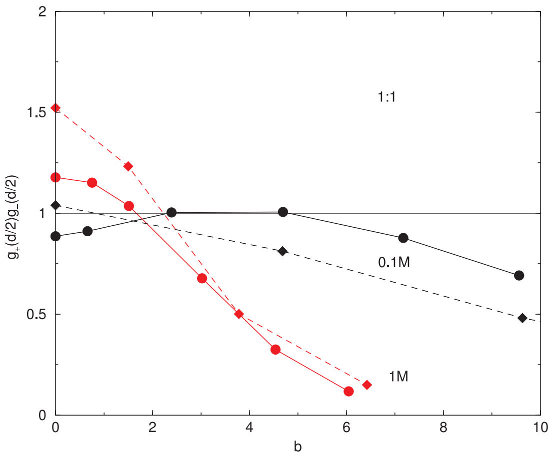

Figure 1. MC and HNC/MSA contact products as a function of b for a 1:1 0.1M and 1M restricted primitive model electrolyte. The MC and HNC/MSA results are given by circles and diamonds, respectively. The only purpose of the lines through the MC and HNC/MSA data is to aid the reader in connecting the points. The PB/GCS result is the straight horizontal line.

The HNC/MSA and simulation results for the contact product, $g_+(d/2)g_-(d/2)$, for 1:1 and 2:2 electrolytes are shown in figures 1 and 2. The points give the actual MC and HNC/MSA results. The lines are plotted only to help the reader connect the points. The PB/GCS result (a horizontal straight line at one) is also shown. These results are plotted as a function of b. This dimensionless parameter is a convenient measure of the electrode charge not only because it is dimensionless but

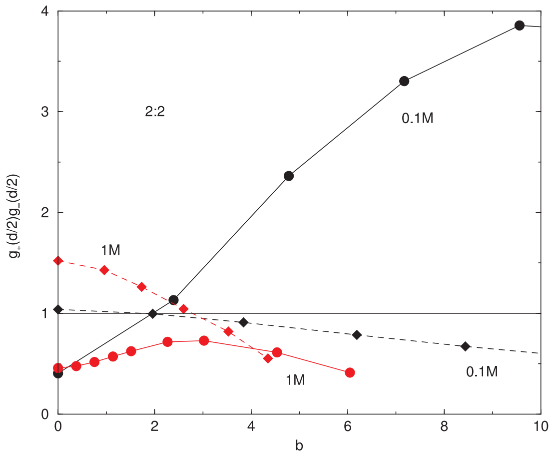

Figure 2. MC and HNC/MSA contact products as a function of b for a 2:2 0.1M and 1M restricted primitive model electrolyte. The points and lines have the same meaning as in figure 1.

also because in the PB/GCS theory various properties scale with b. Conversion to electrode charge density, σ in physical units (coul/m^2) can be made using $\sigma = b/(0.0586(\mathrm{conc})^{1/2})$. It is difficult to obtain accurate contact values for $b > 10$ because the counterion contact value becomes huge and difficult to obtain accurately. The results for 1M are not plotted beyond $b = 5$ or 6 because beyond these values, the corresponding values of σ are rather large and possibly unphysical.

The MC contact product at $b = 0$ can be greater ($z = 1$) or less ($z = 2$) than one. The 1:1 0.1M and 2:2 1M MC results pass through a maximum as b is increased. In the case of $z = 1$ at 1M, the values of the contact product are monotonic. In all cases, the MC results for the contact product tend to zero at large b although in some cases the value of b may be large before this is seen.

On the other hand, the HNC/MSA values of the contact product are always greater than one at $b = 0$. This is because of equation (7). The HNC/MSA expression, $a_{\mathrm{H/M}}$, lacks an electrostatic component; the hard sphere component always exceeds one. However, it is pleasing that the HNC/MSA values of the contact product do tend to zero. However, they always do this monotonically.

4. Summary

Both the MC and HNC/MSA results for the contact value tend to zero as b becomes large. In contrast to the MC results, the HNC/MSA results for the contact product at $b = 0$ are never less than one. The HNC/MSA results never show a maximum in the contact value as a function of b. This is easily understood. Equation (1) is exact. Equation (8) is accurate to order b^2. In fact, recent simulations [19] have shown that equation (8) is probably exact to order b^2. Equation (8) can have only odd powers of b as it should be symmetric under a change of sign of the electrode charge. Thus, accepting equation (8) as exact to order b^2,

$$g_i(d/2) = a + \frac{b^2}{2} \pm ab. \tag{9}$$

This result is accurate (probably exact) up to order b^2. Multiplication yields,

$$g_+(d/2)g_-(d/2) = a^2 + (a - a^2)b^2 \tag{10}$$

to order b^2.

Thus, at $b = 0$, the contact product is greater or less than one, depending on the value of a. As b is increased, the initial slope of the contact product is negative if a exceeds one but positive if a is less than one. If a=1, the initial slope is zero and curve is initially flat. Since $a = 1$ in the PB/GCS theory, the contact product is one at small b. Of course, we already know this.

On the other hand, the HNC/MSA contact values at small b satisfy

$$g_+(d/2)g_-(d/2) = a^2_{\mathrm{H/M}} - b^2. \tag{11}$$

Since $a_{\mathrm{H/M}} > 1$, the initial value of the HNC/MSA contact product always exceeds one and its initial slope is always negative.

We hypothesize that the small b behavior is related to the capacitance anomaly. Without a factor in front of b in the small b expression for $g_d(d/2)$ that can become increasingly smaller than one as T is decreased, a capacitance anomaly is improbable. It is this factor that produces equation (9) and the low b behavior of the contact product. The PB/GCS and HNC/MSA theories lack such a factor and does not produce (in the case of the PB/GCS theory) or is unlikely (in the case of the HNC/MSA theory) to produce a capacitance anomaly. On the other hand, the HNC/MSA theory does produce a contact product that tends to zero at large b. It is possible, perhaps probable, that any satisfactory modern theory will produce a vanishing contact product at large b. The PB/GCS theory is unsatisfactory in this regard.

Equation (8) gives insight not only into the capacitance anomaly but also into the behavior of the contact product at small b.

These conclusions are valid only for the HNC/MSA theory. There have been few HNC/HNC studies due to the more lengthy numerical computations that are required. In addition, the values of $a_{\mathrm{H/H}}$ would be numerical, making conclusions less certain.

The relation between equation (8) and the result of Holovko et al. [15] is the subject of a study that is presently in progress and will be the subject of a forthcoming paper.

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Застосування нещодавно запропонованого тесту для подвійного електричного шару до гіперланцюжкового наближення

Д.Гендерсон[1], М.Алавнег[1], Р.Сааведра-Барера[2], М.Лозада-Касу[3]

[1] Факультет хімії та біохімії, Брігмен Юнг університет, Прово, штат Юта, США
[2] Факультет фізики, Автономний Метрополітана університет, Мехіко, Мексика
[3] Дослідницька програма молекулярної інженерії, Мексиканський інститут нафти, Мехіко, Мексика

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Бгуян, Аутбайт і Гендерсон (*J. Electroanal. Chem., 2007,* **607**, *54*), вивчаючи електричний подвійний шар, сформований симетричним електролітом в рамках спрощеної примітивної моделі, показали, що дослідження добутку нормованих на одиницю на великих відстанях профілів ко-іона і контр-іона є цікавим та корисним тестом теорії. Цей добуток є тотожно рівним одиниці в теорії Пуассона-Больцмана, але результати комп'ютерного моделювання показують, що на контакті цей добуток може бути більшим, або меншим від одиниці при малому заряді на електроді, проте завжди прямує до нуля при великому заряді на електроді. В роботі для згаданого добутку представлено результати гіперланцюжкового наближення (версія HNC/MSA) і показано, що в цій теорії цей добуток є завжди більший за одиницю для малих величин заряду на електроді та прямує до нуля при великих значеннях заряду на електроді.

Ключові слова: *подвійний шар, іонні профілі, інтегральні рівняння, гіперланцюжкове наближення*

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