JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Simple Description of the Capacitance of the Double Layer of a High Concentration Electrolyte

Douglas Henderson*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States

Stanisław Lamperski

Department of Physical Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

ABSTRACT: Recently, the electrochemical properties of an ionic liquid have received increasing attention. The simplest model of an ionic liquid is a fluid of charged hard spheres, all of which have the same diameter (the restricted primitive model or RPM), and the simplest theory of the double layer formed by an electrolyte is the Gouy−Chapman−Stern (GCS) theory. This theory is moderately useful for a low concentration electrolyte but is incorrect for a high concentration electrolyte, such as an ionic liquid. Among other things, the GCS theory predicts that the capacitance has a minimum at small electrode charge. In contrast, the capacitance of the double layer of an ionic liquid often has a maximum at small electrode charge. This is predicted by simulations and the modified Poisson−Boltzmann (MPB) theory. The mean spherical approximation (MSA) seems to agree with the simulations and MPB but is applicable only for small electrode charge. In this note we graft the MSA onto the GCS result and obtain qualitatively reasonable results for the capacitance that may be of use. This result is identical to the GCS theory at small concentrations and to the MSA at small electrode charge. A maximum is found for small electrode charge and high concentration.

INTRODUCTION

The Gouy−Chapman−Stern (GCS) theory[1−3] is widely used to intrepret experimental results for the electrochemical properties of double layers formed by low concentration electrolytes. For a simple symmetric model electrolyte (called the restricted primitive model) consisting of charged hard sphere ions, all of the same diameter, d, and valence, z, and a solvent represented by a dielectric continuum whose dielectric constant or relative permittivity is ε_r, the GCS expression for the differential capacitance, C_{df}, of the double layer is

$$\frac{1}{C_{df}} = \frac{d}{2\varepsilon_r\varepsilon_0} + \frac{1}{\varepsilon_r\varepsilon_0\kappa\sqrt{1+b^2/4}} \tag{1}$$

where ε_0 is the vacuum permittivity and κ is the Debye screening parameter, whose square is given by

$$\kappa^2 = \frac{\beta z^2 e^2 \rho}{\varepsilon_0\varepsilon_r} \tag{2}$$

where $\beta = 1/kT$, k is the Boltzmann constant, T is the temperature, e is the magnitude of the elementary charge, and ρ is the number density of all of the ions. Further b is a dimensionless measure of the charge density of the electrode

$$b = \frac{\beta z e \sigma}{\varepsilon_0\varepsilon_r\kappa} \tag{3}$$

where σ is the charge density in dimensional units (coulomb·m^{-2}).

Other than for the Stern layer, whose contribution is given by the first term in eq 1, the GCS neglects the size of the ions. In the ion−ion interactions, the ions are treated as charged point ions. Thus, in the GCS theory, the ion size is considered only for the ion-electrode interaction.

The GCS theory has some similarity to the experimental results for the capacitance for the double layer formed by simple symmetric electrolytes at low concentrations. In particular, the GCS differential capacitance has a minimum at small electrode charge that weakens as the concentration is increased. At large concentration and/or large b or σ, $C_{df} = 2\varepsilon_r\varepsilon_0/d$. Under no circumstances can the GCS C_{df} exceed this limiting value, usually called the Stern or inner layer capacitance. In applications, in the inner layer capacitance d can be expressed as a function b or σ or equivalently the potential.

In the past, we have pointed out that the GCS theory fails for systems with a large coupling constant, $z^2e^2/4\pi\varepsilon_0\varepsilon_r dkT$. Unfortunately, such systems (high valence salts or low dielectric constant solvents) pose difficultes for experimental studies. As a result, the GCS theory retains its utility despite its defects. Kornyshev[4] has drawn attention to double layers formed by ionic fluids that are attractive for experimental investigation and are systems in which differences from GCS behavior appear. Before and after Kornyshev's article there have been several theoretical studies of ionic liquid double layers.[5−15] One interesting feature is that the ionic liquid C_{df} often has a maximum (a bell-shaped curve) rather than a minimum. Lamperski and Kłos[16]

Special Issue: John M. Prausnitz Festschrift

Received: October 26, 2010
Accepted: December 1, 2010
Published: January 26, 2011

ACS Publications © 2011 American Chemical Society

have seen a bell-shaped maximum in their simulation of a molten salt. This is not surprising as there is a conceptual similarity between molten salts and ionic liquids. Both are high concentration electrolytes; ionic liquids can be thought of as room temperature molten salts. The shape of the capacitance curve of the double layer of an ionic liquid is not limited to a bell-shaped curve but can have a double hump. Federov et al.[7] have studied, by means of a simulation, a model ionic liquid in which the cations consist of dumbells, and even longer chains, with the positive charge located at one end and with the other end being neutral. They find that the capacitance has a double hump at low electrode potential. In this work, our discussion is directed to the existence of the bell or dome-shaped maximum and not to any specific ionic liquid. We show that a simple modification of the GCS theory can yield this maximum.

■ MEAN SPHERICAL APPROXIMATION

The mean spherical approximation (MSA) is the simplest modern analytic theory of the double layer. The MSA shows that at low electrode charge, the double layer capacitance can, in contradiction to the GCS theory, increase without limit as the concentration increases. The MSA is closely related to the linearized GCS. Perhaps the best way to think about the relation between the GCS theory and MSA is to appeal to the fact that the linearized GCS theory is based on what may be called a ring sum in which ion diameters are ignored. The MSA is also based on a ring sum but with the ion diameters taken into account. If the reader does not know about or care to know about ring sums, this statement can be treated as a qualitative, but still useful, remark. In any case, Blum[17] has shown that the MSA result for C is

$$\frac{1}{C} = \frac{1}{2\varepsilon_r\varepsilon_0\Gamma} \tag{4}$$

where

$$2\Gamma d = \sqrt{1+\kappa d} - 1 \tag{5}$$

is a renormalized screening constant. The MSA is a linearized theory, valid only for small σ, and makes no distinction between differential and integral capacitances. At low concentrations, where ion size is less important, the above MSA expression gives, on expansion in powers of κd, the linearized GCS result

$$\frac{1}{C} = \frac{d}{2\varepsilon_r\varepsilon_0} + \frac{1}{\kappa\varepsilon_r\varepsilon_0} \tag{6}$$

Note that with increasing concentration, κ increases and $2\varepsilon_r\varepsilon_0/d$ is the limiting value for C in the above equation.

Since Γ increases with increasing ρ or concentration, the MSA C can, in contrast to the GCS result, eq 6, exceed $2\varepsilon_r\varepsilon_0/d$. The experiments and analysis of Parsons and Zobel[18] are often taken to provide support for the GCS theory. However, a careful analysis and comparison with the MSA[19,20] indicates that at high concentrations the experimental capacitance exceeds the GCS result and lies close to the MSA result.

■ SIMULATIONS AND SIMPLE DESCRIPTION

Recently, Lamperski et al.[21] have made a Monte Carlo (MC) simulation for a model fluid that has some features of an ionic fluid. They used $d = 0.4$ nm and $T^* = 4\pi\varepsilon_0\varepsilon_r dkT/z^2e^2 = 0.8$ for a range of densities or concentrations and calculated the integral and differential capacitance. They found GCS-like behavior at low densities but found that as the density is increased, the minimum in the capacitance disappears and is replaced by a maximum. Lamperski and Henderson[22] have made further simulations for this same system but used a very large range for the electrode charge. The largest values of σ were used in order to see the full behavior of the capacitance. Their result is plotted in Figure 1. The differential capacitance shows a minimum for $\rho^* = Nd^3/V = 0.04$, a slight minimum for $\rho^* = 0.14$, and a maximum for $\rho^* = 0.24$. In the definition of ρ^*, N and V are the number of all the ions and the volume, respectively. The dimensionless capacitance, C^*, and electrode charge density, σ^* are defined as $C^* = Cd/4\pi\varepsilon_0$ and $\sigma^* = \sigma d^2/e$. Lamperski and Henderson also considered a higher temperature, $T^* = 1.6$ with $d = 0.8$ nm. For simplicity, we confine our attention to the $T^* = 0.8$ electrolyte.

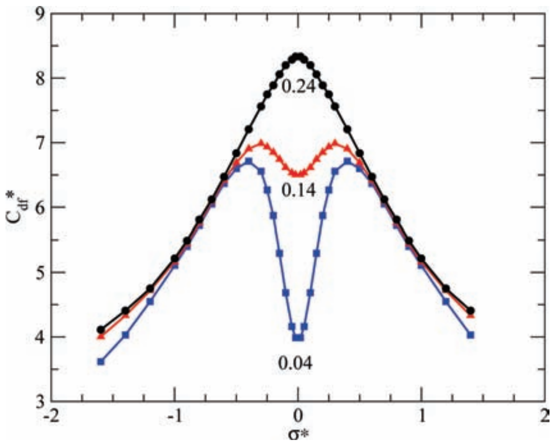

Figure 1. Differential capacitance obtained from MC simulation, plotted as a function of the electrode charge for the system considered by Lamperski et al.[21,22] The curves are, from bottom to top, for $\rho^* = 0.04$, 0.14, and 0.24.

Sometimes the word "camel-like" is used to describe the shape of the capacitance curve.[4] However, both the low and high density capacitance curves are "camel-like". At low density, the shape is that of a bactrian (Central Asia) camel and at high density, the shape is that of a dromedary (Arabia) camel. Because of the ambiguity of the word "camel-like", we prefer to speak of a mimimum and maximum or a well-shaped and bell-shaped or dome-shaped curve. Kornyshev is well aware of this ambiguity and sometimes uses the terms single-humped and double-humped camels.

Note that, in contrast to the GCS theory, in the simulations the capacitance is not a constant when the electrode charge is large. This is because the ions cannot all approach the distance of closest approach, $d/2$. The GCS theory makes this prediction because the ions are assumed to be points. In reality, the adsorption of the ions is analogous to the BET theory (extended Langmuir) adsorption. The first layer becomes saturated and further adsorption takes place at a greater distance.

An interesting further feature seen in simulations, and in the better theories is the phenomenon of overscreening or charge inversion. In the GCS theory the ion profiles are monotonic. The charge profile decays monotonically to zero and the amount of charge in the charge profile is equal, but opposite in sign, to that of the electrode. However, in simulations and in better theories, including the MSA and MPB, the profiles are not monotonic but can change sign. The amount of charge in the first peak exceeds (in magnitude) the charge of the electrode (overscreening). This

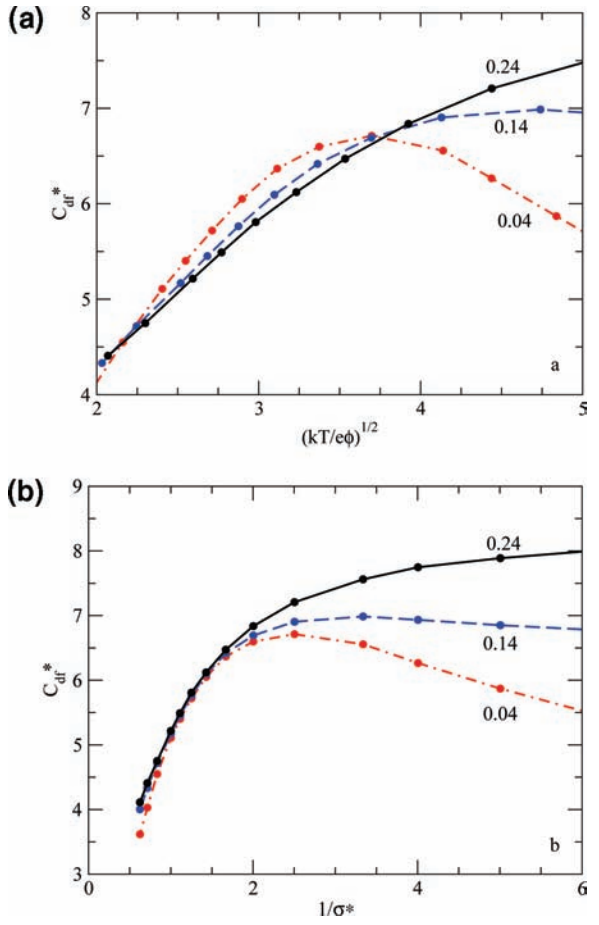

Figure 2. Differential capacitance obtained from MC simulation, plotted as a function of $1/(\phi)^{1/2}$ (part a) and as a function of $1/\sigma$ (part b). The solid, dashed, and dot-dashed curves are for $\rho^* = 0.04$, 0.14, and 0.24, respectively. The system is that considered by Lamperski et al.[21,22]

first peak of counterions is followed by a second peak of co-ions. Further peaks are possible. Of course, the total charge in the charge profile must equal (but be opposit in sign) to that of the electrode. This phenomenon was first observed in the simulations of Torrie and Valleau[23] of the double layer formed by divalent ions and has been observed in subsequent simulations, for example, ref 16, and theory since that time. It is interesting to note the comments of Bazant et al.[24] regarding oversceening in ionic liquids.

On the basis of a simple lattice theory of the double layer Kornyshev[4] has found that the wings of the differential capacitance for the high density electrolyte should decrease inversely with $(\phi)^{1/2}$, where ϕ is the electrical potential of the electrode. This prediction is supported by the simulations of Fedorov and Kornyshev.[5,6] Lamperski et al.[21] considered this prediction using the MPB theory and the related, but simpler, PB + EVT theory. They found that the results of these theories seemed to be consistent with Kornyshev's prediction but it was hard to make a definitive statement because it is difficult to obtain convergent results from these theories when the potential or charge is large. Also, this prediction has been seen experimentally by Islam et al.[25] Since these experimental results are for an actual ionic liquid, and not a model system, this asymptotic dependence of the capacitance on $1/(\phi)^{1/2}$ appears to be universal. It is very likely that the coefficient of $1/(\phi)^{1/2}$ is model and system dependent. This does not detract from the importance of Kornyshev's result. It is easy to show that an equivalent result is an inverse dependence of the wings of the differential capacitance on σ. Our values of the MC capacitance are plotted as a function of $1/(\phi)^{1/2}$ and $1/\sigma$ in Figure 2, part a and part b, respectively. A linear dependence at large $(\phi)^{1/2}$ or σ is consistent with the MC data. However, a linear dependence seems clearer when the capacitance is plotted as a function of $1/(\phi)^{1/2}$. Whether the dependence is exactly linear and not just approximately linear could be established by means of a logarithmic plot. In any case, the values of σ used in our simulations may not be large enough to reach the asymptotic region. For this reason, we regard such a logarithmic plot as overkill and content ourselves with observing that the dependence is close to linear. Note that the Kornyshev asymptotic behavior is seen for both high and low values of ρ. Although there seems to be a slight dependence of the coefficient of $1/(\phi)^{1/2}$ or σ on ρ, the results in Figure 2 show strong support for the asymptotic behavior being universal.

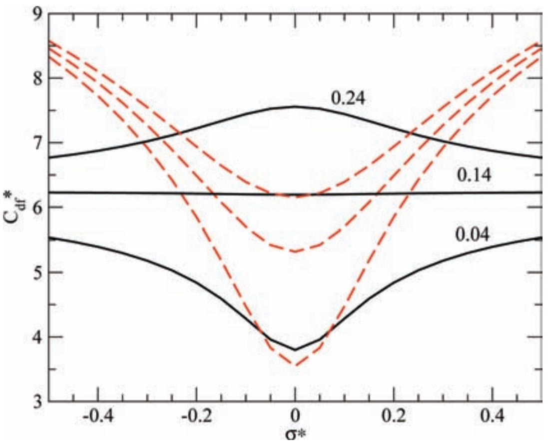

Figure 3. Differential capacitance plotted as a function of the electrode charge for the system considered by Lamperski et al.[21,22] The solid curves are obtained from eq 7 and the dashed curves are obtained from the GCS theory. In each case, the curves are, from bottom to top, for $\rho^* = 0.04$, 0.14, and 0.24.

Henderson et al.[26] have shown that the MSA provides reasonably accurate results for the capacitance of the $T^* = 0.8$ system for zero electrode charge. As the MSA is a linearized theory, it cannot shed any light on the question of whether the capacitance curve has a minimum or maximum. A simple description can be obtained by combining the MSA and GCS approaches, say by grafting the MSA capacitance onto the GCS result for the capacitance. One way of doing this is to write

$$\frac{1}{C_{\mathrm{df}}} = \frac{d'}{2\varepsilon_{\mathrm{r}}\varepsilon_0} + \left(\frac{1}{\Gamma} - d'\right)\frac{1}{2\varepsilon_{\mathrm{r}}\varepsilon_0\sqrt{1+b^2/4}} \tag{7}$$

The parameter d' is not some distance of closest approach but would be related to the distance from the electrode of the center of charge of the adsorbed ions, defined by

$$\langle x\rangle = \frac{\int_{d/2}^{\infty} xq(x)\,\mathrm{d}x}{\int_{d/2}^{\infty} q(x)\,\mathrm{d}x} \tag{8}$$

where $q(x)$ is the charge profile and x is the normal distance from the electrode.

Thus, d' should be greater than d since $\langle x\rangle$ must increase because of the hard cores of the ions. Equation 7 yields the MSA result when b is small and $d'/2\varepsilon_{\mathrm{r}}\varepsilon_0$ when b is large. It is not necessary to require that the capacitance be equal to the MSA result at small b. One could require that it be equal to the somewhat more accurate, but more complex, modified Poisson—Boltzmann (MPB) theory[21,26] or even a MC result at small b.

The results obtained from eq 7 using $d' = 2d$ are plotted in Figure 3. They are qualitatively similar to the MC results. The curves obtained from eq 7 for $\rho^* = 0.04$, 0.14, and 0.24, respectively, have a minimum, a very shallow minimum (although the curve looks flat), and a maximum. Note that the GCS curves always have a minimum. We made no attempt to optimize the value of d' but used a simple value that exceeded the value of d. The results obtained from eq 7 are qualitatively acceptable. However, if one wished to examine large electrode charge, d' should increase with increasing electrode charge. Perhaps, something like $d' = \delta(1 + \sigma)$ would be useful. However, we have not investigated this point. The results in this paper are based on d'=2d and are useful for region of primary experimental interest and cover the region for which the MPB theory converges.

At small electrode charge, the results of this simple graft can be improved by using one MC result for each value of ρ^* at very small electrode charge. It must be at small, but not zero, electrode charge to avoid dividing by zero. Although such an 'improvement' would no longer be fully analytic, the amount of MC simulation would be vastly reduced. As mentioned, the results at large electrode charge could be improved by using an optimized and σ dependent expression for d'. In order to keep our treatment simple and analytic, we have not investigated either modification here but merely indicate their possibity.

■ SUMMARY

A simple description of the capacitance of an electrolyte that yields a dome-like shape at higher concentration has been presented. There is a parameter, d', that is adjustable. However, this is analogous to the application of the GCS theory, where the inner or Stern layer capacitance is parametrized. In any case, this description yields a minimum in the capacitance at low concentrations and a maximum or dome in the capacitance at high concentrations and seems useful. We applied this approach to the other case simulated by Lamperski and Henderson. Qualitatively, the results are similar. However, the MSA seems less accurate for this case. However, the MC results, or perhaps the MPB results, at small b could be used.

The merit of this approach is its simplicity. However, it does not yield charge profiles. For this it is necessary to use more sophisticated approaches, such as simulations and integral equations. Integral equations that may be valuable are the MPB approach for spherical ions and the singlet reference interaction site model (SRISM) approach for spherical and nonspherical ions. Simulations and integral equation approaches are planned.

■ AUTHOR INFORMATION

Corresponding Author

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

Funding Sources

S.L. appreciates the financial support of the Faculty of Chemistry of Adam Mickiewicz University.

■ DEDICATION

John Prausnitz has made important contributions to condensed matter theory. Additionally, he is a gracious host to visitors who come to Berkeley. This article is a modest thank you.

■ REFERENCES

(1) Gouy, M. Sur la constitution de la charge electrique a la surface d'un electrolyte. *J. Phys.(Paris)* **1910**, *9*, 457–468.

(2) Chapman, D. L. A contribution to the theory of electrocapillarity. *Phil. Mag.* **1913**, *25*, 475–481.

(3) Stern, O. Zur theorie der electrolytischen doppelschicht. *Zeit. Elektrochem.* **1924**, *30*, 508–516.

(4) Kornyshev, A. A. Double layer in ionic liquids: paradigm change?. *J. Phys. Chem. B* **2007**, *111*, 5545–5557.

(5) Fedorov, M. V.; Kornyshev, A. A. Ionic liquid near a charged wall: structure and capacitance of electrical double layer. *Phys. Chem. Lett.* **2008**, *112*, 11868–11872.

(6) Fedorov, M. V.; Kornyshev, A. A. Towards understanding the structure and capacitance of electric double layer in ionic liquids. *Electrochim. Acta* **2008**, *53*, 6835–6840.

(7) Federov, M. V.; Georgi, N.; Kornyshev, A. A. Double layer in ionic liquids: the nature of the camel shape of capacitance. *Electrochem. Commun.* **2010**, *12*, 296–299.

(8) Lynden-Bell, R. M. Gas-liquid interfaces of room temperature ionic liquid. *Mol. Phys.* **2003**, *101*, 2625–2633.

(9) Lynden-Bell, R. M.; Kohanov, J.; Del Polpolo, M. G. Simulation of interfaces between room temperature ionic liquids and other liquids. *Faraday Discuss.* **2005**, *129*, 57–67.

(10) Pinilla, C.; Del Polopo, M. G.; Kohanov, J.; Lynden-Bell, R. M. Polarization relaxation in an ionic liquid confined between electrified walls. *J. Phys. Chem. B* **2007**, *111*, 4877–4884.

(11) Kilic, M. S.; Balzant, M. Z.; Ajdari, A. Steric effects in the dynamicsof electrolytes at large applied voltages. 1. Double layer charging. *Phys. Rev. E* **2007**, *75*, 021502.

(12) Oldham, K. B. A Gouy-Chapman-Stern model of the double layer at a(metal)/(ionic liquid) interface. *J. Electroanal. Chem.* **2008**, *613*, 131–138.

(13) Fawcett, W. R.; Ryan, P. J.; Smagala, T. G. Properties of the diffuse double layer at high electrolyte concentration. *J. Phys. Chem. B* **2009**, *113*, 14310–14314.

(14) Fawcett, W. R.; Ryan, P. J. The diffuse double layer in ionic liquids. *Collect. Czech. Chem. Commun.* **2009**, *74*, 1665–1674.

(15) Fawcett, W. R.; Ryan, P. J. An improved version of the Kornyshev-Eigen-Wicke model for the diffuse double layer in concentratated electrolytes. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9816–9821.

(16) Lamperski, S.; Kłos, J. Grand canonical Monte Carlo investigations of electrical double layer in molten salts. *J. Chem. Phys.* **2008**, *129*, 164503.

(17) Blum, L. Theory of electrified interfaces. *J. Phys. Chem.* **1977**, *81*, 136–147.

(18) Parsons, R.; Zobel, F G. R. The interphase between mercury and sodium dihydrogen phosphate. *J. Electroanal. Chem.* **1965**, *9*, 333–346.

(19) Blum, L.; Henderson, D.; Parsons, R. The means spherical approximation capacitance of the double layer for an electrolyte at high concentrations. *J. Electroanal. Chem.* **1984**, *161*, 389–392.

(20) Henderson, D.; Boda, D. Insights on theory and simulation on the electrical double layer. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3822–3830.

(21) Lamperski, S.; Outhwaite, C. W.; Bhuiyan, L. B. The electric double layer differential capacitance at and near zero surface charge for a restricted primitive electrolyte. *J. Phys. Chem. B* **2009**, *111*, 8925–8929.

(22) Lamperski, S.; Henderson. D. Simulation study of capacitance of the electric double layer of an electrolyte near a highly charged electrode. *Mol. Simul.* **2010**, 1−5; published online.

(23) Torrie, G. M.; Valleau, J. P. Electrical Double Layers. 4. Limitations of the Gouy-Chapman theory. *J. Phys. Chem.* **1982**, *86*, 3251–3257.

(24) Bazant, M.; Storey, B.; Kornyshev, A. A. Double layer in ionic liquids: Overscreening versus crowding. Preprint 2010.

(25) Islam, M. M.; Tanzirul, A.; Ohsaka, T. Electrical Double-Layer Structure in Ionic Liquid: A Colloboration of the Theoretical Model by Experimental Results. *J. Phys. Chem. B* **2008**, *112*, 16568–16574.

(26) Henderson, D.; Lamperski, S.; Outhwaite, C. W.; Bhuiyan, L. B. A mean spherical approximation study of the capacitance of an electric double layer formed by a high density electrolyte. *Collect. Czech. Chem. Commun.* **2010**, *75*, 303–312.