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# On the calculation of single ion activity coefficients in homogeneous ionic systems by application of the grand canonical ensemble

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The grand canonical ensemble has been used to study the evaluation of single ion activity coefficients in homogeneous ionic fluids. In this work, the Coulombic interactions are truncated according to the minimum image approximation, and the ions are assumed to be placed in a structureless, homogeneous dielectric continuum. Grand canonical ensemble Monte Carlo calculation results for two primitive model electrolyte solutions are presented. Also, a formula involving the second moments of the total correlation functions is derived from fluctuation theory, which applies for the derivatives of the individual ionic activity coefficients with respect to the total ionic concentration. This formula has previously been proposed on the basis of somewhat different considerations.

## I. INTRODUCTION

Single ion activities are important in the theory of various electrochemical phenomena. As an example of significant technical interest, we here just mention the *pH* concept, which is intimately connected to the individual activity of the hydrogen ion. Unfortunately, it appears that no rigorous experimental procedure has yet been devised by which reliable single ion activity coefficients could be measured. This fact strongly motivates a more thoroughly theoretical investigation.

The present work focuses on two aspects associated with the application of the grand canonical ensemble (GCE) to homogeneous ionic fluids. First, the feasibility of estimating single ion activity coefficients from GCE Monte Carlo (GCEMC) calculations is discussed, and numerical results are presented for two primitive model electrolytes. Second, we consider the problem of calculating single ion properties for "infinite" homogeneous systems within the framework of the Kirkwood-Buff theory.<sup>1</sup> In passing, it is noted that these topics have very recently been considered for confined, spherical systems.<sup>2</sup> For the sake of simplicity, the discussion in this paper is restricted to spherical symmetrical ions in a dielectric continuum.

Since the pioneering work of Valleau and Cohen,<sup>3</sup> it has become common to consider only electroneutral configurations in GCEMC calculations of homogeneous ionic systems. By such a procedure, it is not possible, however, to obtain information regarding *individual* ionic activities. In the present paper, it is shown that it is possible to estimate single-ion activity coefficients by GCEMC calculations on homogeneous systems with standard periodic boundary conditions if the Coulombic interactions are truncated according to the minimum image (MI) approximation.

The systems considered in this work consist of ions in a central cubic box of volume  $V$  with side length  $L = V^{1/3}$ . The system is surrounded by periodically repeated images of itself containing "mirror particles" moving like the original ones. In the MI approximation, every ion in the cen-

tral box is assumed to interact only with other ions (including "mirror ions") within a cube of side length  $L$  with the selected ion at the center.

By formally considering such a MI system in the limit  $V \rightarrow \infty$ , an expression is derived for a system containing two ionic species, which applies for the single-ion activity coefficients. This expression is the same as the one previously proposed on the basis of somewhat different considerations.<sup>4</sup> However, the present approach (although so far restricted to a dielectric continuum) might appear to be more appealing from a "physical" point of view. It could be mentioned that the corresponding "Kirkwood-Buff expression" for the *mean* ionic activity coefficient was considered quite some years ago by Rasaiah and Friedman.<sup>5</sup>

## II. THEORY

In the grand canonical ensemble, the electrochemical potentials of the individual species are held fixed. Let  $\bar{\mu}_\alpha$ ,  $\mu_\alpha^\theta$ , and  $a_\alpha$  be the electrochemical potential, the standard chemical potential, and the activity of species  $\alpha$ , respectively, and let  $\Psi$  be the electric potential of the phase. Then  $\bar{\mu}_\alpha$  is given by

$$\bar{\mu}_\alpha = \mu_\alpha^\theta + k_B T \ln a_\alpha + q_\alpha \Psi. \quad (1)$$

In Eq. (1),  $q_\alpha$  is the charge of a particle of species  $\alpha$ ,  $T$  is the absolute temperature, and  $k_B$  is the Boltzmann constant. By Eq. (1), it is assumed that the activity  $a_\alpha$  is a dimensionless quantity. The electric potential  $\Psi$  of the phase is not known *a priori*. Thus, in order to determine the individual activities, it is necessary to evaluate  $\Psi$  *a posteriori*, by some means. This problem is greatly simplified if the ions are placed in a structureless dielectric continuum (e.g., if we consider the primitive model of electrolyte solutions). The value of  $\Psi$  in Eq. (1) is identified with the average electrostatic potential acting on a hypothetical "test ion," of vanishing charge and size, situated in the MC system. In our system, the average electrostatic potential  $\langle \Psi(\mathbf{r}) \rangle$  at any position  $\mathbf{r}$  is generated by ions in the central

box as well as by mirror ions. Since all electrostatic interactions are truncated according to the MI approximation, only ions within a cubic region  $\Omega$  of size  $L^3$ , centered at  $\mathbf{r}$ , contributes to  $\langle \Psi(\mathbf{r}) \rangle$ . Let  $\rho_q(\mathbf{r}')$  be the average electric charge density at  $\mathbf{r}'$  and let  $\epsilon$  be the (uniform) dielectric permittivity. The average electrostatic potential  $\langle \Psi(\mathbf{r}) \rangle$  stemming from the charges inside the closed region  $\Omega$  is then given by<sup>6</sup>

$$\begin{aligned} \langle \Psi(\mathbf{r}) \rangle &= \int_{\Omega} \frac{\rho_q(\mathbf{r}')}{4\pi\epsilon|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ &= \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \frac{\rho_q(x,y,z)}{4\pi\epsilon\sqrt{x^2+y^2+z^2}} \\ &\quad \times dx dy dz. \end{aligned} \quad (2)$$

Since the average distribution of ions (including the mirror ions) is homogeneous, by construction,  $\rho_q(\mathbf{r}') = \rho_q(x,y,z)$  is a constant with the value  $\rho_q = \langle Q \rangle / L^3$ , where  $\langle Q \rangle$  is the net average charge within the central box. Equation (2) then gives

$$\Psi = \langle \Psi(\mathbf{r}) \rangle = \langle Q \rangle K / 16\pi\epsilon L, \quad (3)$$

where  $K$  is a constant given by<sup>7</sup>

$$\begin{aligned} K &\equiv \int_{-1}^1 \int_{-1}^1 \int_{-1}^1 (x^2+y^2+z^2)^{-1/2} dx dy dz \\ &= 2[6 \ln(2+\sqrt{3}) - \pi] \approx 9.52. \end{aligned} \quad (4)$$

Equation (3) provides the desired expression for the effective (uniform) electric potential in our system. Having solved this problem, we are now equipped to proceed with some formal considerations. Let  $\langle \dots \rangle$  denote an average in the GCE and let  $N_\alpha$  be the number of particles of species  $\alpha$  in a given configuration. For given values of  $T$ ,  $V$ , and the electrochemical potentials of the individual species, it is then possible, from a GCCEMC calculation, to obtain values of  $\langle N_\alpha \rangle$  and  $\langle N_\alpha N_\beta \rangle$ , etc. The particle number fluctuations  $\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle$  are related to the derivatives of the individual electrochemical potentials with respect to the average composition of the system. In the present work, we explicitly consider systems with two different kinds of particles only, i.e., one kind of cation (denoted  $+$ ) and one kind of anion (denoted  $-$ ). In this case, it is convenient to express the average composition of a system in terms of  $\langle Q \rangle = \langle q_+ N_+ + q_- N_- \rangle$  and  $\rho \equiv \langle N \rangle / V$ , where  $N = N_+ + N_-$ . For systems which are not too small, the following relations can be obtained:<sup>2,8</sup>

$$\begin{aligned} (q_\alpha - q_\beta) (\partial \bar{\mu}_\alpha / \partial \rho)_{\langle Q \rangle} \\ = k_B T q_+ q_- \xi_\beta / M_{+-} C \quad (\alpha \neq \beta), \end{aligned} \quad (5)$$

$$(\partial \bar{\mu}_\alpha / \partial \langle Q \rangle)_{\langle N \rangle} = k_B T q_\alpha / C \quad (6)$$

with

$$\xi_\alpha = \langle N_\alpha Q \rangle - \langle N_\alpha \rangle \langle Q \rangle, \quad (7)$$

$$C \equiv \sum_{\beta} q_\beta \xi_\beta, \quad (8)$$

$$M_{+-} = \lim_{V \rightarrow \infty} \frac{|q_+ q_-|}{(q_+ - q_-)^2} \frac{\langle N^2 \rangle - \langle N \rangle^2}{V} = \rho_+ \rho_- G_{+-}, \quad (9)$$

$$G_{+-} = 4\pi \int_0^\infty [g_{+-}(r) - 1] r^2 dr. \quad (10)$$

In Eq. (10),  $g_{\alpha\beta}(r)$  is the radial distribution function between species  $\alpha$  and species  $\beta$ . It is possible to obtain a simple, analytical expression for the quantity  $C$ , defined by Eq. (8), in the limit  $V \rightarrow \infty$ . From Eq. (3), it is seen that the charge density vanishes as  $V \rightarrow \infty$  for any given finite value of  $\psi$ . Thus, it can be expected that the calculated activities becomes independent of  $\psi$  as the system becomes large. From Eqs. (1), (3), and (6), we then obtain

$$\begin{aligned} (\partial \bar{\mu}_\alpha / \partial \psi)_{\langle N \rangle} &= (\partial \bar{\mu}_\alpha / \partial \langle Q \rangle)_{\langle N \rangle} (d \langle Q \rangle / d \psi) \\ &= 16\pi\epsilon L k_B T q_\alpha / C K \rightarrow q_\alpha \\ &\Rightarrow C \rightarrow 16\pi\epsilon k_B T L / K \quad (\text{for } V \rightarrow \infty). \end{aligned} \quad (11)$$

It is seen later on that Eq. (11) is consistent with the second moment electroneutrality condition of Stillinger and Lovett,<sup>9</sup> and also with our numerical Monte Carlo results.

From Eqs. (1), (3), (5), and (8), we finally obtain

$$(\partial \ln a_\alpha / \partial \rho)_{\langle Q \rangle} = \frac{|q_\alpha|}{q_+ - q_-} \frac{1 - q_\alpha \xi_\alpha / C}{M_{+-}}. \quad (12)$$

Equation (12) provides an expression for  $(\partial \ln a_\alpha / \partial \rho)_{\langle Q \rangle}$  in terms of  $\xi_\alpha / C$  and  $M_{+-}$ . Here it is noted that any influence of the artificial MI system is expected to be removed when the system becomes infinitely large. Equation (12) might be useful in connection with GCCEMC calculations, but is not directly applicable in connection with, e.g., integral equation approximation calculations. In the following, we shall try to remedy this shortcoming by rewriting the term  $\xi_\alpha / C$ . To do this, we first find an alternative way to express the net charge  $Q$ , of a given configuration, in the central box. Let  $\psi(\mathbf{r})$  be the electric potential at  $\mathbf{r}$  for a given configuration of the system. Integration of  $\psi(\mathbf{r})$  over the central box yields (the prime indicates that the summation is to be taken over the  $N$  ions—including mirror ions—within a cube of edge length  $L$  with  $\mathbf{r}$  at the center)

$$\begin{aligned} \int \Psi(\mathbf{r}) d\mathbf{r} &= \int \sum_k q_k / (4\pi\epsilon|\mathbf{r}-\mathbf{r}_k|) d\mathbf{r} \\ &= (Q/4\pi\epsilon) \int 1/|\mathbf{r}| d\mathbf{r} \\ &= L^2 Q K / 16\pi\epsilon \\ &\Rightarrow \lim_{V \rightarrow \infty} Q/C = (1/V k_B T) \int \Psi(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (13)$$

where the last identity is obtained by application of Eq. (11).

Here, we shall consider only systems which are overall electroneutral, i.e., we shall set  $\langle Q \rangle = 0$ . This relation is fulfilled for a "real" electrolyte bulk system. In passing, it is noted that this amounts to put  $\Psi = 0$ , in the present context, according to Eq. (3). Then, the following identity is obtained from Eqs. (7) and (13) in the limit  $V \rightarrow \infty$ :

$$\xi_\alpha/C = \langle N_\alpha Q \rangle / C = (1/k_B T V) \left\langle N_\alpha \int \Psi(\mathbf{r}) d\mathbf{r} \right\rangle. \quad (14)$$

Let  $U_N$  be the total potential energy of a given configuration and let  $\Xi$  be the grand canonical partition function. Then  $\langle N_\alpha \int \Psi(\mathbf{r}) d\mathbf{r} \rangle$  can be given by

$$\begin{aligned} \left\langle N_\alpha \int \Psi(\mathbf{r}) d\mathbf{r} \right\rangle &= \sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{a_+^{N_+} a_-^{N_-} N_\alpha}{N_+! N_-! \Xi} \int \cdots \int \Psi(\mathbf{r}) d\mathbf{r} \exp(-U_N/k_B T) d\mathbf{r}_1 \cdots d\mathbf{r}_N \\ &= \iint \left[ \sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{a_+^{N_+} a_-^{N_-} N_\alpha}{N_+! N_-! \Xi} \int \cdots \int \Psi(\mathbf{r}) \exp(-U_N/k_B T) d\mathbf{r}_2 \cdots d\mathbf{r}_N \right] d\mathbf{r}_1 d\mathbf{r} \\ &= \iint \left[ \sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{a_+^{N_+} a_-^{N_-} N_\alpha}{N_+! N_-! \Xi} \int \cdots \int \exp(-U_N/k_B T) d\mathbf{r}_2 \cdots d\mathbf{r}_N \psi_\alpha(\mathbf{r}_1, \mathbf{r}) \right] d\mathbf{r}_1 d\mathbf{r} \\ &\Rightarrow \left\langle N_\alpha \int \Psi(\mathbf{r}) d\mathbf{r} \right\rangle = \iint \rho_\alpha(\mathbf{r}_1) \psi_\alpha(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1 d\mathbf{r} \end{aligned} \quad (15)$$

with

$$\psi_\alpha(\mathbf{r}_1, \mathbf{r}) = \frac{\sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{a_+^{N_+} a_-^{N_-} N_\alpha}{N_+! N_-!} \int \cdots \int \Psi(\mathbf{r}) \exp(-U_N/k_B T) d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{a_+^{N_+} a_-^{N_-} N_\alpha}{N_+! N_-!} \int \cdots \int \exp(-U_N/k_B T) d\mathbf{r}_2 \cdots d\mathbf{r}_N}. \quad (16)$$

In Eq. (15),  $\rho_\alpha(\mathbf{r}_1)$  is the local average density of species  $\alpha$  at  $\mathbf{r}_1$ . By examination of Eq. (16), it is seen that  $\psi_\alpha(\mathbf{r}_1, \mathbf{r})$  is the average electrostatic potential at  $\mathbf{r}$ , supposing that an ion of species  $\alpha$  is fixed at  $\mathbf{r}_1$ . In a homogeneous system,  $\rho_\alpha(\mathbf{r}_1)$  is a constant with the value  $\rho_\alpha = \langle N_\alpha \rangle / V$ , and  $\psi_\alpha(\mathbf{r}_1, \mathbf{r})$  is a function of the distance  $r \equiv |\mathbf{r} - \mathbf{r}_1|$  only. In this case, Eq. (15) yields

$$\left\langle N_\alpha \int \Psi(\mathbf{r}) d\mathbf{r} \right\rangle = \langle N_\alpha \rangle \int \psi_\alpha(r) d\mathbf{r}. \quad (17)$$

By combination of Eqs. (14) and (17) (the following equations, in this section, apply for  $V \rightarrow \infty$ ),

$$k_B T \xi_\alpha / C = \rho_\alpha \int \psi_\alpha(r) d\mathbf{r} \quad (18)$$

is obtained. From Eq. (18) and the definition of  $C$ , we obtain

$$\sum_\alpha q_\alpha \rho_\alpha \int \psi_\alpha(r) d\mathbf{r} = k_B T. \quad (19)$$

In the case of a dielectric continuum, the above equation has been shown to be equivalent to the second moment condition.<sup>10</sup> Following the procedure outlined by Outhwaite in Ref. 10, we may show

$$\rho_\alpha \int \psi_\alpha(r) d\mathbf{r} = (\rho_\alpha / \epsilon) \sum_\gamma q_\gamma \rho_\gamma A_{\alpha\gamma} = k_B T \xi_\alpha / C, \quad (20)$$

where

$$A_{\alpha\gamma} \equiv - (4\pi/6) \int_0^\infty [g_{\alpha\gamma}(r) - 1] r^4 dr. \quad (21)$$

Insertion of Eqs. (9) and (20) into Eq. (12) yields

$$\frac{d \ln a_\alpha}{d\rho} = |q_\alpha| \frac{1 - (\rho_\alpha q_\alpha / \epsilon k_B T) \sum_\gamma q_\gamma \rho_\gamma A_{\alpha\gamma}}{\rho_+ \rho_- (q_+ - q_-) G_{+-}}, \quad (22)$$

where  $G_{+-}$  is given by Eq. (10). Equation (22) applies for an "infinite" electroneutral bulk system. Introducing the activity coefficients  $\gamma_\alpha \equiv a_\alpha / \rho_\alpha$ , Eq. (22) can be rewritten as

$$\frac{d \ln \gamma_\alpha}{d\rho} = \frac{1 - \rho_\alpha G_{+-} - (q_\alpha \rho_\alpha / \epsilon k_B T) \sum_\gamma q_\gamma \rho_\gamma A_{\alpha\gamma}}{\rho \rho_\alpha G_{+-}}. \quad (23)$$

The above equation is equivalent to the expression proposed in Ref. 4.

### III. MONTE CARLO RESULTS

In this section, we investigate the GCCEMC method for the primitive model (PM) of electrolyte solutions. The PM is defined by the pair potential functions between a particle of species  $\alpha$  at  $\mathbf{r}_1$  and a particle of species  $\beta$  at  $\mathbf{r}_2$  ( $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ ),

$$u_{\alpha\beta}(\mathbf{r}_{12}) = \begin{cases} \infty, & |\mathbf{r}_{12}| < (d_\alpha + d_\beta)/2 \\ q_\alpha q_\beta / 4\pi\epsilon |\mathbf{r}_{12}|, & |\mathbf{r}_{12}| \geq (d_\alpha + d_\beta)/2. \end{cases} \quad (24)$$

TABLE I. GCEMC results based on computed values of  $\langle N_+ \rangle$  and  $\langle N_- \rangle$  for a 1:1-electrolyte with  $B=1.681$ ,  $d_+/d_-=3$ , and  $\exp(\Delta\bar{\mu}_+/k_B T) = \exp(\Delta\bar{\mu}_-/k_B T) = 0.048\ 34$ . A total number of 1 million configurations was generated for  $L/a=5$  and  $L/a=10$ . In the case of the larger systems, a total number of 1.5 million configurations was generated in each run. The first 20 000 configurations were neglected in all of the runs.

$L/a$	$\rho_s^*$	$\ln y_+$	$\ln y_-$	$-e_0\Psi/k_B T$
5	0.0469	0.260	-0.198	0.207
10	0.0467	0.263	-0.195	0.223
15	0.0464	0.272	-0.190	0.228
17.5	0.0466	0.264	-0.190	0.225
20	0.0463	0.273	-0.188	0.229

Here,  $d_\alpha$  is the hard core diameter of a particle of species  $\alpha$ . GCEMC calculations have been performed for a 1:1 electrolyte with  $d_+/d_-=3$  and for a 2:1 electrolyte with  $d_+/d_-=1$ . The GCEMC procedure applied here is similar to the one described in Ref. 11. It is convenient to introduce a length scale in terms of the distance of contact between a cation and an anion  $a = (d_+ + d_-)/2$ . Then we have the dimensionless densities  $\rho_\alpha^* \equiv \rho_\alpha a^3$  and the dimensionless activities  $a_\alpha = \rho_\alpha^* y_\alpha$ . From Eqs. (1) and (3), we obtain the relation

$$\Delta\bar{\mu}_\alpha \equiv \bar{\mu}_\alpha - \mu_\alpha^\theta = k_B T \ln \rho_\alpha^* y_\alpha + q_\alpha \langle Q \rangle K / 16\pi\epsilon L$$

or

$$\exp(\Delta\bar{\mu}_\alpha/k_B T) = \rho_\alpha^* y_\alpha \exp[q_\alpha \langle Q \rangle BK / |q_+ q_-| 4(L/a)], \quad (25)$$

where  $B$  is the Bjerrum parameter defined by  $B \equiv |q_+ q_-| / 4\pi\epsilon k_B T a$ .

For given values of  $\Delta\bar{\mu}_\alpha$ ,  $B$ , and  $L/a$ , it is possible to obtain  $\rho_\alpha^* = \langle N_\alpha \rangle a^3 / V$  and  $\langle Q \rangle$  from a GCEMC calculation, and eventually the individual ionic activity coefficients  $y_\alpha$  by application of Eq. (25). Here it is noted that for the relatively small systems used in Monte Carlo calculations, the calculated values of  $y_\alpha$  might depend on  $\langle Q \rangle$  to some extent. We shall return to this aspect later on.

The 1:1 electrolyte, considered in this work, is specified by  $B=1.681$  and a mean ionic activity  $a_\pm = \sqrt{a_+ a_-} = 0.048\ 34$ . Similarly, the 2:1 electrolyte is specified by  $B=3.400$  and  $a_\pm = \sqrt[3]{a_+ a_-^2} = 0.034\ 37$ . These parameters correspond to hypothetical aqueous electrolyte solutions at room temperature with molar concentrations around 1 mol/dm<sup>3</sup>, supposing that  $a=4.25$  and 4.2 Å, respectively. Monte Carlo results for the logarithm of the single-ion

TABLE II. GCEMC results based on computed values of  $\langle N_+ \rangle$  and  $\langle N_- \rangle$  for a 2:1-electrolyte with  $B=3.400$ ,  $d_+/d_-=1$ ,  $\exp(\Delta\bar{\mu}_+/k_B T) = 0.021\ 65$ , and  $\exp(\Delta\bar{\mu}_-/k_B T) = 0.043\ 31$ . A total number of 1 million configurations was generated in each run. The first 20 000 configurations were neglected in all of the runs.

$L/a$	$\rho_s^*$	$\ln y_+$	$\ln y_-$	$e_0\Psi/k_B T$
5	0.0490	-2.400	-0.025	0.766
10	0.0470	-2.205	-0.060	0.709
15	0.0469	-2.180	-0.068	0.701
20	0.0467	-2.176	-0.065	0.702

TABLE III. GCEMC results based on fluctuation theory for the systems defined in the heading to Table I.

$L/a$	$(\partial \ln y_+ / \partial \rho^*)_{\langle Q \rangle}$	$(\partial \ln y_- / \partial \rho^*)_{\langle Q \rangle}$	$C/[e_0^2(L/a)]$
5	9.0	1.3	0.235
10	9.8	1.9	0.247
15	8.2	2.8	0.249
17.5	9.1	2.9	0.247
20	8.1	4.0	0.251

activity coefficients, the electric potential, and the dimensionless salt densities  $\rho_s^* = (\rho_+^* + \rho_-^*) / (v_+ + v_-)$  ( $v_\alpha$  being the stoichiometric coefficient of species  $\alpha$ ) are presented in Tables I and II for different values of  $L/a$ . The results in Tables I and II were obtained by (quite arbitrarily) setting  $\exp(\Delta\bar{\mu}_+/k_B T) = \exp(\Delta\bar{\mu}_-/k_B T) = 0.048\ 34$  in the case of the 1:1 electrolyte, and by setting  $\exp(\Delta\bar{\mu}_+/k_B T) = 0.021\ 65$  and  $\exp(\Delta\bar{\mu}_-/k_B T) = 0.043\ 31$  in the case of the 2:1 electrolyte. It should be emphasized that the results of a MC run are to be considered as “experimental data” and as such are subject to some uncertainty. In general, the GCEMC results in Tables I and II are in satisfactory agreement with results obtained by the hypernetted chain (HNC) approximation.<sup>12</sup> Also, the results in Table I are in good agreement with the corresponding GCEMC results for confined spherical systems obtained in Ref. 2.

In Tables III and IV, we show the results for the  $(\partial \ln y_\alpha / \partial \rho^*)_{\langle Q \rangle}$  coefficients as well as the values obtained for  $C/[e_0^2(L/a)]$  ( $e_0$  being the charge of a proton). The values of  $(\partial \ln y_\alpha / \partial \rho^*)_{\langle Q \rangle}$  were estimated by  $(\rho^* = \rho_+^* + \rho_-^*)$ ,

$$\begin{aligned} (\partial \ln y_\alpha / \partial \rho^*)_{\langle Q \rangle} &= (\partial \ln a_\alpha / \partial \rho^*)_{\langle Q \rangle} - (\partial \ln \rho_\alpha^* / \partial \rho^*)_{\langle Q \rangle} \\ &= \frac{|q_\alpha|}{q_+ - q_-} \frac{1 - q_\alpha \xi_\alpha / C}{M_{+-}^\#} \\ &\quad - \frac{q_\alpha}{(q_\alpha - q_\beta) \rho_\beta^*} \quad (\alpha \neq \beta) \end{aligned} \quad (26)$$

with

$$M_{+-}^\# \equiv \frac{|q_+ q_-|}{(q_+ - q_-)^2} \frac{\langle N^2 \rangle - \langle N \rangle^2}{(V/a)}. \quad (27)$$

At this point, we just note that the values of  $(\partial \ln y_\alpha / \partial \rho^*)_{\langle Q \rangle}$  are subject to rather large uncertainties. From Tables III and IV, it is seen that the values of  $C/[e_0^2(L/a)]$ , for the larger systems, are very close to the limiting values

TABLE IV. GCEMC results based on fluctuation theory for the systems defined in the heading to Table II.

$L/a$	$(\partial \ln y_+ / \partial \rho^*)_{\langle Q \rangle}$	$(\partial \ln y_- / \partial \rho^*)_{\langle Q \rangle}$	$C/[e_0^2(L/a)]$
5	-0.28	5.1	0.254
10	-0.15	4.3	0.248
15	-0.11	4.8	0.246
20	1.2	5.1	0.247

TABLE V. Various GCEMC results for a 1:1-electrolyte with  $B=1.681$ ,  $d_+/d_-=3$ ,  $\exp(\Delta\bar{\mu}_+/k_B T)=0.06078$ , and  $\exp(\Delta\bar{\mu}_-/k_B T)=0.03845$ . A total number of 1.5 million configurations was generated in each run except for  $L/a=20$ , in which case, a total number of 2 million configurations was generated. The first 20 000 configurations were neglected in all of the runs.

$L/a$	$\rho_s^*$	$\ln y_+$	$\ln y_-$	$(\partial \ln y_+ / \partial \rho^*)_{\langle Q \rangle}$	$(\partial \ln y_- / \partial \rho^*)_{\langle Q \rangle}$
5	0.0465	0.265	-0.188	9.2	2.2
10	0.0466	0.264	-0.190	8.5	2.0
15	0.0467	0.261	-0.192	8.8	3.4
20	0.0466	0.267	-0.192	8.7	4.3

given by Eq. (11), which are 0.250 and 0.247, respectively. This indicates that the results for  $\ln y_\alpha$  becomes independent of  $\langle Q \rangle$ .

A "real" bulk electrolyte is electroneutral. In order to examine to what extent the (artificial) MC system disturbs the results in cases where  $\langle Q \rangle \neq 0$  additional runs were carried out for the 1:1 electrolyte with  $\exp(\Delta\bar{\mu}_+)=0.06078$  and  $\exp(\Delta\bar{\mu}_-)=0.03845$ . These values were chosen on the basis of the results in Table I to correspond to  $\langle Q \rangle \simeq 0$ . Results for these runs are reported in Table V. The results for  $\rho_s^*$  are remarkably independent of the size of the system in contrast to the corresponding results in Table I. This indicates (as one could expect) that the result of a MC run on a finite system is closer to the thermodynamic value if  $\langle Q \rangle \simeq 0$ . The results for the  $\partial \ln y_\alpha / \partial \rho^*$

coefficients in Table V are in good agreement with the corresponding results in Table III. The results for  $(\partial \ln y_+ / \partial \rho^*)_{\langle Q \rangle}$  are fairly independent of the size of the system, whereas the values of  $(\partial \ln y_- / \partial \rho^*)_{\langle Q \rangle}$  seem to increase with  $L/a$ . Thus, in order to estimate  $(\partial \ln y_- / \partial \rho^*)$  in the thermodynamic limit, computations for larger systems should probably be carried out. However, the present GCEMC method might not be practical/efficient for the calculation of more precise values of the  $(\partial \ln y_\alpha / \partial \rho)$  coefficients. A reason for this is that the  $\xi_\alpha$  values are obtained as small differences between two large quantities and are thus expected to be subject to quite some uncertainty. The values of  $C$  seem here to be determined rather accurately, though.

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<sup>8</sup>Although the discussion in Ref. 2 is especially concerned with confined systems, these equations are also valid in the present context.

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