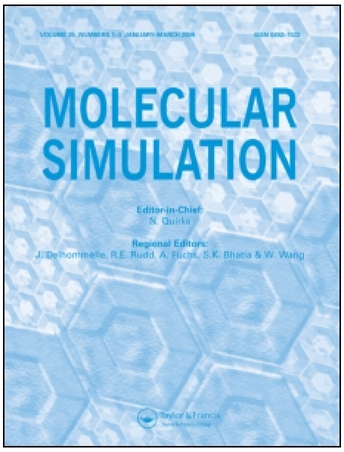

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The individual and mean activity coefficients of an electrolyte from the inverse GCMC simulation

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To cite this Article Lamperski, S.(2007) 'The individual and mean activity coefficients of an electrolyte from the inverse GCMC simulation', Molecular Simulation, 33: 15, 1193 — 1198

To link to this Article: DOI: 10.1080/08927020701739493

URL: http://dx.doi.org/10.1080/08927020701739493

Molecular Simulation, Vol. 33, No. 15, December 2007, 1193–1198

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Research Article

The individual and mean activity coefficients of an electrolyte from the inverse GCMC simulation

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(Received August 2007; in final form October 2007)

The grand-canonical Monte Carlo (GCMC) technique, which is primarily used to calculate the concentration of a solute for a given activity coefficient, can be inverted and applied to calculate the activity coefficients corresponding to a given concentration of a solute. The changes needed to be introduced in the GCMC algorithm are discussed in the paper. The new method called the inverse GCMC (IGCMC) technique is applied to calculate the mean activity coefficient of 1:1, 2:2, 2:1, 3:1 salts with equal and unequal ion sizes and over a wide range of the electrolyte concentrations. The results for equal ion sizes are compared with the corresponding data obtained from the GCMC of Valleau and Cohen. It is shown that the IGCMC technique, after some extensions, can be used to compute the individual ionic activity coefficients. A comparison is made with the Sloth and Sørensen individual activity results and with the theoretical predictions for the 1:1 electrolyte with unequal ion sizes.

Keywords: Individual activity coefficients; Mean activity coefficients; Primitive model of electrolyte; GCMC simulation; IGCMC method

1. Introduction

Since the formulation of the Debye–Hückel theory [1] the activity coefficients of an electrolyte have been the subject of different theoretical approximations. Recent works are based on the mean spherical approximation [2–7], the hypernetted chain equations [8] and the Poisson–Boltzmann theory [9–11]. The molecular simulation methods are complementary to the theory and give exact results for an assumed model. The chemical potential and other entropy-related thermodynamic functions cannot be evaluated directly from the Monte Carlo (MC) simulation of the canonical ensemble [12]. The problem can be relatively simply overcome by application of the Gibbs–Helmholtz equation [12]. According to it, the Gibbs energy (related to temperature) can be obtained by integrating the enthalpy of a system determined at different temperatures. The integration should start from the temperature at which the Gibbs energy is known exactly and the method requires a large set of enthalpy results. To our best knowledge, this method has not been applied to electrolytes yet.

The Widom's "test particle" formula [13] used in the canonical ensemble MC simulation is a simple method for calculating the chemical potential. It has been applied by Sloth and Sørensen [7,14,15] to calculate the individual activity coefficients assuming the primitive model (PM) of electrolyte. However, the results quite strongly depended on the number of particles in the simulation box and the extrapolation to the thermodynamic limit was needed. The method has been improved by Svensson and Woodward [16] and by Sloth and Sørensen [17,18] by neutralising the charge of the test particle.

The activity coefficient can also be calculated from a grand-canonical MC (GCMC) simulation. In the grand-canonical ensemble, the volume, V, temperature, T, and the chemical potential, μ, are constant, while the number of molecules, N, fluctuates. For a given activity coefficient, one calculates the average number of molecules and then the bulk concentration. Valleau and Cohen [19,20] applied the GCMC technique to evaluate the mean activity coefficient of electrolyte.

The disadvantage of the GCMC method is that the concentration is calculated for a given activity, while

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020701739493

we would like to know the activity coefficient corresponding to the concentration in question. In this paper, we describe the changes needed to be introduced into the standard GCMC program to invert the problem and to calculate the activity coefficient for a given electrolyte concentration. To distinguish this method from the standard GCMC method, and from the reverse MC technique introduced by McGreevy and Pusztai [21] to generate molecular configurations from a radial distribution function or structural factor, we will call it the inverse GCMC (IGCMC). We will show that the IGCMC technique allows us to calculate not only the mean activity coefficient but also the individual ionic activity coefficients.

2. The model

In the present paper, we consider the PM of electrolyte. The ions are represented by hard spheres of diameter d_s [s = + (cations), − (anions)] with the electric charge $z_s e$ embedded at the centre (e is the elementary charge and z_s—its charge number). The hard spheres are immersed in a homogeneous medium of relative electrical permittivity, ε_r. Its value is typical of the solvent considered. The potential of interaction between the ion i and j is given by

$$V_{ij} = \begin{cases} \infty & \text{for } r_{ij} \le (d_i + d_j)/2 \\ \dfrac{z_i z_j e^2}{4\pi\varepsilon_0\varepsilon_r r_{ij}} & \text{for } r_{ij} > (d_i + d_j)/2 \end{cases}, \tag{1}$$

where r_{ij} is the distance between the centres of interacting ions.

Although in the PM the short-range interactions are reduced to the hard sphere interactions and the solvent molecules are not considered, the model is frequently used both in theoretical studies and molecular simulations. This allows verification of theoretical predictions by simulations.

3. Inverse grand-canonical MC simulation

3.1 Mean activity coefficient

In GCMC simulation, there are three equallyprobably moves of a molecule: displacement, creation (insertion) and destruction (removal). When considering an electrolyte a compound M_pX_q is dissolved to give p cations and q anions. Thus the molar concentrations of anions and cations are $c_- = qc$, and $c_+ = pc$, respectively, where c is the molar concentration of a compound. Let us introduce the reference number N_s^o of species s (s = +, −) which depends on the concentration c_s and the volume $V$of the simulation box

$$N_s^o = 1000 c_s N_A V, \tag{2}$$

where N_A is the Avogadro constant.

The first move is analogous to that of an electrically neutral molecule: an ion selected at random is displaced to a new random position in the box. The displacement is accepted with the probability

$$\mathrm{acc}(m \rightarrow n) = \min\{1, \exp[-(u_n - u_m)/kT]\} \tag{3}$$

where u_i is the potential energy of the ith configuration, indexes m and n indicate the configurations before and after the ion displacement, and k is the Boltzmann constant. Creation and destruction moves require a group of p cations and q anions to satisfy the condition of overall electrical neutrality. All these ions are inserted at random positions or they are selected at random from the ions present in a box and removed. Expressions for the probability of acceptance of creation and destruction are given in the work of Valleau and Cohen [19]. After some transformations these expressions take the following form convenient for numerical coding:

$$\mathrm{acc}(N_+ + N_- \rightarrow N_+ + N_- + p + q) = \min\left[1, \exp\left(-\Delta u_c/kT + \ln\frac{(\gamma_\pm N_+^o)^p}{\prod_{v=1}^{p}(N_+ + v)} + \ln\frac{(\gamma_\pm N_-^o)^q}{\prod_{v=1}^{q}(N_- + v)}\right)\right] \tag{4}$$

and

$$\mathrm{acc}(N_+ + N_- \rightarrow N_+ + N_- - p - q) = \min\left[1, \exp\left(-\Delta u_d/kT + p\ln\frac{N_+}{\gamma_\pm N_+^o} + q\ln\frac{N_-}{\gamma_\pm N_-^o}\right)\right]. \tag{5}$$

In these expressions, Δu_c and Δu_d are the potentials of creation and destruction, respectively, N_+ and N_- are the current numbers of ions before the insertion or removal attempts, and $\gamma_\pm$ is the mean activity coefficient defined by the individual coefficients γ_+ and γ_-:

$$\gamma_\pm = \left(\gamma_+^p \gamma_-^q\right)^{\frac{1}{p+q}}. \tag{6}$$

The replacement of the individual by the mean activity coefficient means that all the deviations from ideality are shared equally by anions and cations.

3.2 The heart of inverse grand-canonical MC technique

The solution to the problem of finding the mean activity coefficient for a given electrolyte concentration is similar to the procedure for the automatic adjustment of the maximum displacement of a molecule [22]. After each m_{adj} configurations the average $\langle N_s \rangle$ of the current number of ions N_s of the type s is calculated. It is unimportant whether it is the average of anions or cations. If the average $\langle N_s \rangle$ is lower than N_s^o then the value of the activity coefficient $\gamma_\pm$ is increased by a small amount, $\exp(k_1)$. Otherwise, it is decreased by $\exp(-k_1)$. The value of the parameter k_1 is close to 0, but positive. The total

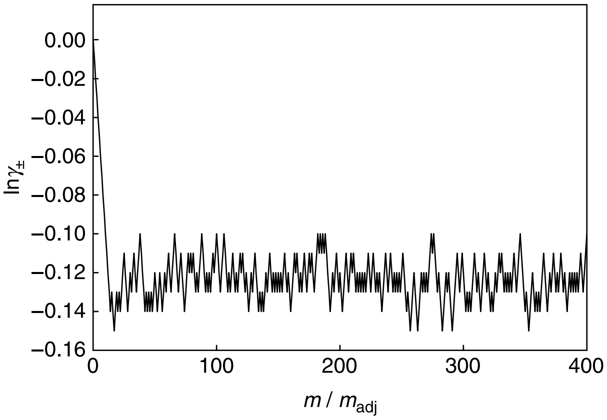

Figure 1. Evolution of the mean activity coefficient during the simulation (1:1 electrolyte, $c = 1\,\mathrm{M}$, $d_- = d_+ = 425\,\mathrm{pm}$, $\varepsilon_{\mathrm{r}} = 78.65$, $T = 298.15\,\mathrm{K}$, $k_1 = 0.01$, $m_{\max} = 4{,}000{,}000$ and $m_{\mathrm{adj}} = 10{,}000$).

number of configurations, $m_{\max}$, must be much greater than m_{adj}, so that the adjustment of $\gamma_{\pm}$ could be performed for many times. The $\ln\gamma_{\pm}$ results obtained after each adjustment are averaged to give the final mean activity coefficient. The work of this procedure is illustrated in figure 1. We start from any reasonable value of the activity coefficient. One is a good choice. In our case, at the beginning of the simulation $\ln\gamma_{\pm}$ linearly decreases. After about 100,000 configurations the linear plot changes into oscillations of $\ln\gamma_{\pm}$. These data are used to calculate the mean value of the activity coefficient.

Precision of the results and efficiency of the method depend on the parameters used in the simulation. After checking the influence of the parameters on the standard deviation of $\ln\gamma_{\pm}$ and assuming the reasonable time of computations we established the following values for the parameters: $k_1 = 0.005$, $m_{\mathrm{adj}} = 20{,}000$ and $m_{\max} = 45{,}000{,}000$.

3.3 *Individual activity coefficient*

In the previous method, the creation and destruction moves required insertion or deletion of the group of p cations and q anions, so that the system was electrically neutral. Now, let us assume that only one type of ions, s, can be exchanged between the system and its reservoir. Parallel to this the electric charge is exchanged, so that the system as well as the reservoir are usually not neutral. These charge fluctuations give some attraction interactions, u_{a}, between the system and the reservoir. The local charge fluctuations in an electrolyte are physically acceptable. The problem is with the assessment of u_{a}. We can expect that its value is much smaller than the interaction energy between two neighbouring ions, so we assume that $u_{\mathrm{a}} = 0$. We will return to this problem in the next section.

The displacement move is exactly the same as described above, while in the creation and destruction moves one ion of the species s is involved. The acceptances of these two moves are given respectively by

$$\mathrm{acc}(N_{\mathrm{s}}\rightarrow N_{\mathrm{s}}+1)=\min\left[1,\exp\left(-\Delta u_{\mathrm{c}}/kT+\ln\frac{\gamma_{\mathrm{s}}N_{\mathrm{s}}^{\mathrm{o}}}{N_{\mathrm{s}}+1}\right)\right] \tag{7}$$

and

$$\mathrm{acc}(N_{\mathrm{s}}\rightarrow N_{\mathrm{s}}-1)=\min\left[1,\exp\left(-\Delta u_{\mathrm{d}}/kT+\ln\frac{N_{\mathrm{s}}}{\gamma_{\mathrm{s}}N_{\mathrm{s}}^{\mathrm{o}}}\right)\right]. \tag{8}$$

The procedure of adjusting an individual activity coefficient to a given concentration is analogous to that described for the mean activity coefficient.

4. Results and discussion

In this section, we are concentrated mainly on testing the correctness of the new technique, however some new results are presented, too. The first tests were very simple. We calculated the mean activity coefficient for the 1:1 electrolyte at $c = 1.003\,\mathrm{M}$, $d_- = d_+ = 425\,\mathrm{pm}$, $T = 298.15\,\mathrm{K}$, $\varepsilon_{\mathrm{r}} = 78.65$ and $N^{\mathrm{o}} = 256$. The logarithm of the mean activity coefficient was -0.12422. Using this value and the same physical parameters, we calculated the electrolyte concentration applying our version of the GCMC computer program analogous to that written by Valleau and Cohen [19]. We obtained $c = 1.003299\,\mathrm{M}$. This result is very close to the input concentration. Alternatively, the mean value of ions in the simulation box amounted to 256.0764 while the reference number N^{o} was 256.

In the calculation of the individual activity coefficient, the fluctuations of the total charge of the whole system take place. The mean number $\langle N_{\mathrm{s}}\rangle$ of ions of type s compared to $N_{\mathrm{s}}^{\mathrm{o}}$ shows whether or not the average of the system charge is zero. The calculations carried out for the above electrolyte with the same physical parameters gave $\langle N_{\mathrm{s}}\rangle = 128.000577$ at $N_{\mathrm{s}}^{\mathrm{o}} = 128$. Let us add that the lowest and the highest N_{s} were 120 and 135, respectively.

The second test concerned the influence of the number of ions, N^{o}, on the mean and individual activity coefficient for the 1:1 electrolyte with the same physical parameters as in the first test. The results are collected in table 1. We see that apart from the results for $N^{\mathrm{o}} = 32$, the mean activity coefficient shows a small increasing tendency with increasing N^{o}, while the individual activity exhibits a decreasing tendency. At large N^{o}, the values of both coefficients are very similar. The change in the logarithm

Table 1. The influence of the number of ions, N^{o}, on the mean and individual activity coefficient for the 1:1 electrolyte with $d_- = d_+ = 425\,\mathrm{pm}$, $\varepsilon_{\mathrm{r}} = 78.65$, $T = 298.15\,\mathrm{K}$ and $c = 1.003\,\mathrm{M}$.

N^o	$\ln\gamma_{\pm}$	$\ln\gamma_{-}$	$u_a/\mathrm{J\,mol}^{-1}$
32	−0.12421	−0.11312	−27.492
108	−0.12498	−0.12040	−11.354
256	−0.12422	−0.12230	−4.7962
500	−0.12410	−0.12273	−3.3962
864	−0.12363	−0.12339	−0.5950
1372	−0.12377	−0.12333	−1.0908
2048	−0.12376	−0.12325	−1.2643

Table 2. The activity coefficient results for the 1:1 electrolyte with $d_- = d_+ = 425$ pm, $\varepsilon_r = 78.65$, $T = 298.15$ K at different molar concentrations, c. The superscript "VC" denotes the results of Valleau and Cohen [19] while "ind"—the mean from the individual activity coefficients.

c/M	$\ln \gamma_{\pm}^{VC}$	$\ln \gamma_{\pm}$	$\ln \gamma_-$	$\ln \gamma_+$	$\ln \gamma_{\pm}^{ind}$
0.01158	−0.087	−0.10481	−0.10425	−0.10410	−0.10417
0.1002	−0.232	−0.22491	−0.22419	−0.22349	−0.22384
0.4950	−0.249	−0.24881	−0.24696	−0.24621	−0.24659
1.0030	−0.127	−0.12407	−0.12039	−0.12229	−0.12134
1.9940	0.271	0.27284	0.27363	0.27069	0.27216
3.0450	0.849	0.85799	0.86096	0.85323	0.85709
3.0520	0.847	0.86451	0.86436	0.86505	0.86471
4.0900	1.661	1.62873	1.60099	1.64136	1.62118
4.7500	2.235	2.22982	2.22878	2.24726	2.23802

Table 3. The activity coefficient results for the 2:2 electrolyte with $d_- = d_+ = 420$ pm, $\varepsilon_r = 78.55$, $T = 298.15$ K at different molar concentrations, c. The superscript "VC" denotes the results of Valleau and Cohen [19] while "ind"—the mean from the individual activity coefficients.

c/M	$\ln \gamma_{\pm}^{VC}$	$\ln \gamma_{\pm}$	$\ln \gamma_-$	$\ln \gamma_+$	$\ln \gamma_{\pm}^{ind}$
0.01025	−0.896	−0.89450	−0.89310	−0.89061	−0.89186
0.0456	−1.437	−1.42627	−1.42685	−1.42904	−1.42795
0.2490	−2.146	−2.13334	−2.13011	−2.13073	−2.13042
0.5920	−2.476	−2.47256	−2.47216	−2.47329	−2.47273
0.9710	−2.635	−2.61315	−2.61211	−2.61187	−2.61199
1.5970	−2.679	−2.65334	−2.65195	−2.65109	−2.65152
1.9290	−2.630	−2.62423	−2.61988	−2.62153	−2.62071
2.9840	−2.487	−2.36181	−2.36137	−2.35637	−2.35887
3.6910	−2.413	−2.07223	−2.06322	−2.06192	−2.06257

of the mean activity coefficient is relatively small (about 1%) and it is perhaps due to the neglect of the interaction with ions being outside the simulation box, which becomes important when the size of the box is small. Usually, the Ewald sum [23] is applied to overcome this problem. The Ewald sum needs the system to be neutral. This condition is not satisfied in the calculation of the individual activity coefficients. That is why instead of applying the Ewald sum we try to determine the minimum number of ions which gives stable and credible results. Analysis of table 1 data suggests that this minimum number could be 500, or even 256, which would be in agreement with the Adams [24] result. The influence of N^{o} on the individual activity coefficient is more distinct and the difference between the lowest and the largest value amounts to about 8%. As the electrolyte is symmetrical, the mean activity coefficient should be equal to the individual one. The difference between these coefficients at the same N^{o} can be used to assess the value of the parameter u_a

$$u_a = RT(\ln \gamma_{\pm} - \ln \gamma_-). \tag{9}$$

The results are collected in table 1. The values of u_a are small which justifies the correctness of our earlier assumption that $u_a = 0$.

The literature MC activity coefficient results for unequal ion sizes are scarce. We make use of those of Sloth and Sørensen ones [15] evaluated by means of the Widom's "test particle" method [13]. The authors considered the 1:1 electrolyte at $d_- = 106.25$, $d_+ = 318.75$ pm, $c = 1.96737$ M, $T = 298.15$ K, $\varepsilon_r = 78.5$, and obtained $\ln \gamma_- = 0.064$ and $\ln \gamma_+ = 1.29$ while our results for the same physical parameters and $N^{\mathrm{o}} = 500$ are 0.08322 and 1.38379, respectively. The theoretical predictions for the same system are: 0.124 and 1.54 (symmetric Poisson–Boltzmann theory [9]), 0.087 and 1.47 (modified Poisson–Boltzmann theory [10,11]) and 0.092 and 1.48 (hypernetted chain equations [8]). The agreement is satisfactory, but it is seen that different simulation techniques and theories give slightly different results.

Finally, we compare our mean activity coefficients, $\ln \gamma_{\pm}$, and the mean activity coefficients, $\ln \gamma_{\pm}^{\mathrm{ind}}$, calculated from the individual coefficients $\ln \gamma_-$ and $\ln \gamma_+$ with the Valleau and Cohen [19] mean coefficients, $\ln \gamma_{\pm}^{\mathrm{VC}}$. We consider the same 1:1, 2:2, 2:1 and 3:1 aqueous electrolytes with equal ion diameters $d_- = d_+ = 425$ pm for the 1:1 electrolyte and 420 pm for other cases. The temperature is 298.15 K and the relative electrical permittivity, ε_r, amounts 78.65 for the 1:1 electrolyte and 78.55 for the others. The concentrations are exactly the same as reported by Valleau and Cohen [19]†. The reference number of ions, N^{o}, is 256 (255 for the 2:1 electrolyte). All the simulations were carried out for 15 million of initial and 45 million of main configurations. The results are shown in tables 2–5. Additionally, in table 6, we present the results for the 1:1 electrolyte with $d_- = 300$ and $d_+ = 425$ pm at the same values of other parameters as for the 1:1 equal-size system. Our mean activity coefficients, $\ln \gamma_{\pm}$, are very similar to those obtained by Valleau and Cohen [19]. Some discrepancies, observed mainly at high electrolyte concentrations, are due perhaps to the smaller number of ions (50–130) and configurations used by these authors in their simulations, performed in the early 1980s. The concentration

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†Strictly speaking we have selected some of the most representative concentrations.

Table 4. The activity coefficient results for the 2:1 electrolyte with $d_- = d_+ = 420\,\mathrm{pm}$, $\varepsilon_r = 78.55$, $T = 298.15\,\mathrm{K}$ at different molar concentrations, c. The superscript "VC" denotes the results of Valleau and Cohen [19] while "ind"—the mean from the individual activity coefficients.

c/M	$\ln\gamma_\pm^{VC}$	$\ln\gamma_\pm$	$\ln\gamma_-$	$\ln\gamma_+$	$\ln\gamma_\pm^{ind}$
0.01009	−0.343	−0.32979	−0.62721	−0.17961	−0.32881
0.0477	−0.582	−0.57387	−1.10965	−0.30528	−0.57340
0.1002	–	−0.70816	−1.40116	−0.36016	−0.70716
0.2590	−0.878	−0.85873	−1.79432	−0.38790	−0.85671
0.5780	−0.913	−0.89602	−2.08334	−0.29697	−0.89243
1.1280	−0.734	−0.73263	−2.16644	−0.01445	−0.73178
1. 4030	−0.602	−0.59553	−2.11621	0.16923	−0.59258
1.9640	−0.206	−0.22761	−1.88971	0.61637	−0.21899
2. 3960	0.087	0.14145	−1.60695	1.02836	0.14992
2.7800	0.501	0.53872	−1.29193	1.42718	0.52081

Table 5. The activity coefficient results for the 3:1 electrolyte with $d_- = d_+ = 420\,\mathrm{pm}$, $\varepsilon_r = 78.55$, $T = 298.15\,\mathrm{K}$ at different molar concentrations, c. The superscript "VC" denotes the results of Valleau and Cohen [19] while "ind"—the mean from the individual activity coefficients.

c/M	$\ln\gamma_\pm^{VC}$	$\ln\gamma_\pm$	$\ln\gamma_-$	$\ln\gamma_+$	$\ln\gamma_\pm^{ind}$
0.01008	−0.252	−0.25059	−0.68573	−0.10433	−0.24968
0.0100	−0.654	−0.65151	−1.76192	−0.27952	−0.65012
0.0468	−1.058	−1.06569	−2.95901	−0.43207	−1.06381
0.2390	−1.540	−1.52309	−4.63578	−0.48434	−1.52220
0.5700	−1.655	−1.63702	−5.65244	−0.29722	−1.63603
1.0640	−1.488	−1.48317	−6.28628	0.11708	−1.48376
1.3170	−1.355	−1.33187	−6.44484	0.37502	−1.32995
1.6340	−1.020	−1.08264	−6.55127	0.74290	−1.08064

dependence of the mean activity coefficients, $\ln\gamma_\pm$, is shown in figure 2. The course of the curves is well known and does not need explanation. Perhaps, it is worth noting that the curve for the 1:1 equal-size electrolyte goes above the unequal-size curve and the discrepancy increases with increasing electrolyte concentration. This behaviour can be explained by a lower packing effect due to the smaller size of anions.

In the symmetrical electrolyte, the individual activity coefficients of anions and cations are the same and are equal to the mean activity coefficient. This is not the case when considering a non-symmetrical electrolyte. The result of charge asymmetry in ions is shown in figures 3 and 4. The effect of unequal ion size is shown in figure 5. Note that Valleau and Cohen [19] did not consider an electrolyte with unequal ion sizes. When looking at the results shown in figures 3–5 it is evident that anions and cations do not share equally the deviations from ideality due to the electrostatic and hard-core interactions.

Table 6. The activity coefficient results for the 1:1 electrolyte with $d_- = 300\,\mathrm{pm}$, $d_+ = 425\,\mathrm{pm}$, $\varepsilon_r = 78.65$, $T = 298.15\,\mathrm{K}$ at different molar concentrations, c. The superscript "ind" denotes the mean from the individual activity coefficients.

c/M	$\ln\gamma_\pm$	$\ln\gamma_-$	$\ln\gamma_+$	$\ln\gamma_\pm^{ind}$
0.01158	−0.10896	−0.10873	−0.10815	−0.10844
0.1002	−0.25144	−0.25109	−0.24782	−0.24945
0.4950	−0.35215	−0.36092	−0.33965	−0.35029
1.0030	−0.32485	−0.34998	−0.29435	−0.32217
1.9940	−0.14970	−0.21938	−0.07280	−0.14609
3.0450	0.12709	−0.00883	0.27236	0.13177
3.0520	0.12956	−0.00987	0.27108	0.13061
4.0900	0.47754	0.25398	0.71498	0.48448
4.7500	0.73965	0.44227	1.03442	0.73834

5. Conclusions

The new simulation technique, called the IGCMC method, allows calculation of the mean and individual activity coefficients for a given electrolyte concentration. We have shown in this paper that the application of the new technique to a single-salt PM gives correct results. The new method can be simply extended to the mixtures of salts and also to more realistic models of electrolyte

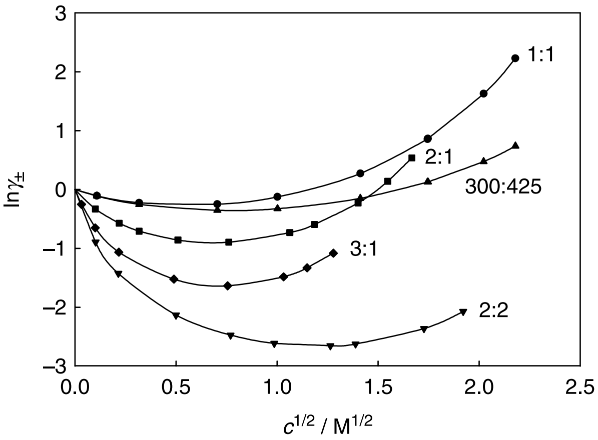

Figure 2. The mean activity coefficient as a function of concentration for the 1:1 electrolyte with $d_- = d_+ = 425\,\mathrm{pm}$, $\varepsilon_r = 78.65$, for 2:2, 2:1, 3:1 electrolyte with $d_- = d_+ = 420\,\mathrm{pm}$, $\varepsilon_r = 78.55$ and for the 1:1 electrolyte with $d_- = 300\,\mathrm{pm}$, $d_+ = 425\,\mathrm{pm}$, $\varepsilon_r = 78.65$. In all cases $T = 298.15\,\mathrm{K}$.

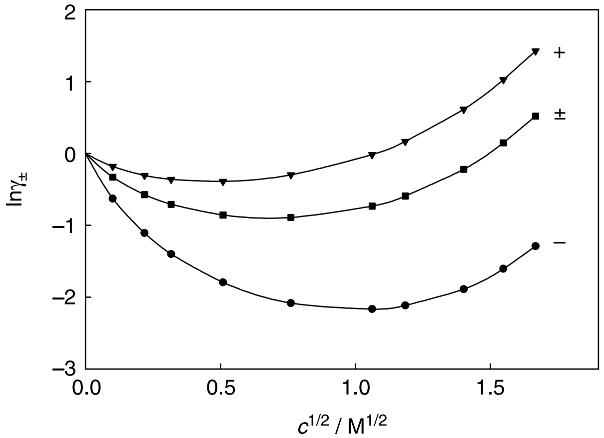

Figure 3. The individual and mean activity coefficients as a function of concentration for the 2:1 electrolyte with $d_- = d_+ = 420$ pm, $\varepsilon_r = 78.55$ and $T = 298.15$ K.

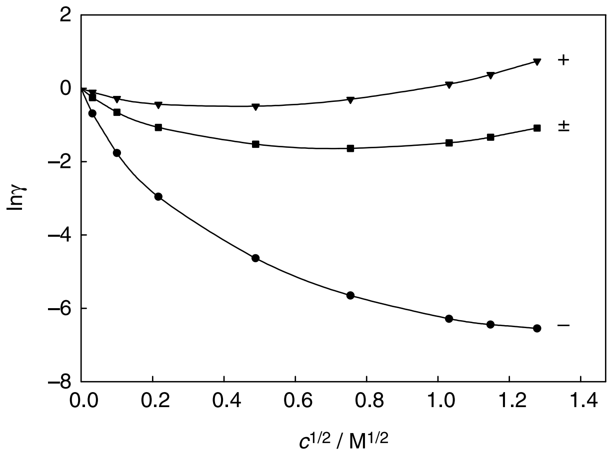

Figure 4. The individual and mean activity coefficients as a function of concentration for the 3:1 electrolyte with $d_- = d_+ = 420$ pm, $\varepsilon_r = 78.55$ and $T = 298.15$ K.

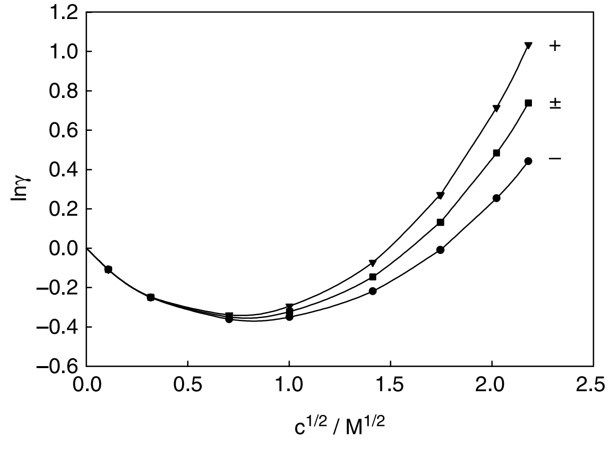

Figure 5. The individual and mean activity coefficients as a function of concentration for the 1:1 electrolyte with $d_- = 300$ pm, $d_+ = 425$ pm, $\varepsilon_r = 78.65$ and $T = 298.15$ K.

which take into account the solvent molecules. We hope that this technique can be applied to more extreme systems like molten salts in which the temperature and ion density are high.

Acknowledgements

The author is very grateful to Professor C. W. Outhwaite, University of Sheffield for his comments and suggestions. Financial support from Adam Mickiewicz University, Faculty of Chemistry, is appreciated.

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