Monte-Carlo simulation of mixed electrolytes next to a plane charged surface

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ABSTRACT

Monte-Carlo simulations of the electric double layer are performed for two electrolyte mixtures next to a plane, uniformly charged, surface. Simulations are made at parameters corresponding to a Poisson–Boltzmann theory which is corrected to include the excluded volume effects of the ions. The corrected Poisson–Boltzmann theory is found to have some deficiencies. The structural properties disagree with simulation results while the theory can be adjusted to give agreement with experiment for the relative concentration excesses of small univalent counterions.

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1. Introduction

An electrolyte in the neighbourhood of a charged surface gives rise to an electric double layer. Double layers play a central role in understanding phenomena arising in a variety of fields such as electrochemistry, solution chemistry, biophysics and colloid science. Increasing theoretical interest is now being paid to electrolyte mixtures rather than single electrolytes [1–11]. The classical approach to treat the electric double layer is via the Poisson–Boltzmann (PB) theory which models the ions as point charges moving in a medium of constant permittivity. In general the complexity of the physical situation restricts the classical approach to low concentration, single, univalent electrolytes against a low charged surface.

The deficiencies of the classical approach are, to a greater or lesser extent, being overcome by improved modelling, simulation techniques, and theoretical work based on density functional approaches, integral equations and PB modifications. Here we will use Monte-Carlo (MC) simulations to check some recent work on electrolyte mixtures by Biesheuvel and Soestbergen [9] who used a volume corrected PB equation. The theoretical work of [9] was developed to explain the unexpected adsorption behaviour of cations from the binary mixtures LiCl + CsCl, MgCl$_2$ + CsCl or BaCl$_2$ + CaCl$_2$ on negatively charged Langmuir monolayers of the surfactant behenyl sulphate observed by Shapovalov et al. [12,13] using X-ray reflectivity and total reflection X-ray fluorescence techniques. Experimentally it was found that at high surface charge the classical PB theory could not explain the relatively high concentration of the smaller monovalent counterion in the double layer. The PB

failure was particularly pronounced for the case in which the solution contained a larger divalent counterion. Analogous results have been noted by Valiskó et al. [8] but at higher bulk electrolyte concentrations. Our MC calculations of ion excesses are in qualitative agreement with experimental results [12] while the MC ion concentration profiles disagree with those of [9].

2. Model and simulation

The electric double layer is modelled by a primitive model electrolyte in the neighbourhood of a uniformly charged plane surface. In the primitive model the ions are treated as hard spheres with a point electric charge embedded at the centre. The ions are immersed in a homogeneous medium of relative electrical permittivity ε_r. Two electrolyte mixtures are considered: 1 mM CsCl with 9 mM LiCl and 5 mM CsCl with 5 mM MgCl$_2$. Two models are chosen for comparison with the work of Biesheuvel and Soestbergen [9]. In the first model the counterions Cs$^+$, Li$^+$ and Mg^{2+} have diameters $d = 0.66$, 0.76, and 0.86 nm, respectively with the coion Cl$^-$ having the value 0.1 nm. The cation diameters correspond to [9] and approximate to the hydrated values [14]. The electrical permittivity ε_r is taken to be 78.5 and the temperature $T = 298.15$ K. In their analysis of the Langmuir film, Biesheuvel and Soestbergen took Cl$^-$ to have zero size and the centres of the two counterions to have identical distances of closest approach to the surface. Thus the nearest approach of the charge of both cations to the Langmuir film is located on the same plane. To mimic their model the value of 0.1 nm for the diameter of Cl$^-$ was used to avoid simulation problems, with the two counterions having the same contact value of the radius of the larger cation (Li$^+$ or Mg^{2+}). We refer to this model as the Langmuir case. The second model we consider is the primitive model electrolyte against a hard wall so that the counterions have different distances of closest approach. The ma-

jority of results are presented for a hard wall as it is a standard model in electric double layer theory. In this model the diameters of Cs^+, Li^+ and Mg^{2+} are 0.66, 0.754286, 0.858 nm respectively. The diameters for Li^+ and Mg^{2+} are slightly different than those used by Biesheuvel and Soestbergen due to the MC programme restrictions, while Cl^- takes the realistic value of 0.66 nm (0.664 nm by Nightingale [14]).

The pioneering simulations of the electrode/electrolyte interface were carried out by Torrie and Valleau [15] in the grand-canonical ensemble (GCMC), this technique being recognised as the most suitable for inhomogeneous systems [16]. An alternative approach is to use simulations in the canonical ensemble. In this ensemble the required bulk electrolyte concentration is obtained by small adjustments to the box length or to the number of ions [16]. The adjustment technique can be successfully applied to a single salt electrolyte, but its application to the mixture of salts would be onerous. This problem does not exist in the GCMC technique applied in the present investigations.

We considered the simulation box as a rectangular prism with the dimensions $W \times W \times L$. The two opposite square walls were impenetrable to ions and were charged with the same electric surface charge density, σ. A system of two electrodes was used as the ions were of different diameters. Another advantage of a two charged electrode system is that in practice two simulations are carried out simultaneously and the results can be averaged. Periodic boundary conditions were applied in the directions parallel to the electrode surfaces while the electrostatic and hard core interactions between ions in the simulation box and ions with the electrodes were calculated explicitly. The long-range electrostatic interactions due to ions outside the box were estimated with the method of equi-distanced charged planes with a square hole for the simulation box [15].

In the GCMC technique the initial number of ions is not significant as it fluctuates and is adjusted by the programme. The important number is the excess number of counterions needed to neutralise the electrode charge. We assumed that when the charge at the electrolyte side (corresponding to this excess number) amounted $400|e|$ C (e—the elementary charge), the electrode surface charge was -0.1 C/m². This gave $W = 17.900709$ nm. We also took $L \approx 50$ nm as the treatment of the electrolyte at fairly low concentrations ($\sim$0.01 M) required a relatively large separation between the electrodes.

The MC simulation in the GC ensemble consists of three moves: displacement, insertion and removal. In the first move an ion selected at random is displaced to a new random position. This move is accepted with the probability

$$\text{acc(displace)} = \min\{1, \exp[-(u_n - u_m)/kT]\}, \tag{1}$$

where u_m and u_n are the potential energies of a configuration before and after the ion displacement, respectively, T is the temperature, and k is the Boltzmann constant.

The next two moves cannot break the condition of electrical neutrality of a system. So in the case of a salt M_pX_q a group of p cations and q anions is inserted at random positions or is selected at random from the ions present in a box and removed. These steps are accepted with the probability

$$\text{acc(insert)} = \min\left\{1, \exp\left[-\Delta u_i/kT + \ln\frac{(\gamma_+ c_+ V_+)^p}{\prod_{\nu=1}^{p}(N_+ + \nu)} \right.\right.$$
$$\left.\left. + \ln\frac{(\gamma_- c_- V_-)^q}{\prod_{\nu=1}^{q}(N_- + \nu)}\right]\right\}, \tag{2}$$

$$\text{acc(remove)} = \min\left\{1, \exp\left[-\Delta u_r/kT + \ln\frac{\prod_{\nu=1}^{p}(N_+ + 1 - \nu)}{(\gamma_+ c_+ V_+)^p} \right.\right.$$
$$\left.\left. + \ln\frac{\prod_{\nu=1}^{q}(N_- + 1 - \nu)}{(\gamma_- c_- V_-)^q}\right]\right\}, \tag{3}$$

Table 1
The ion activity coefficients in a mixture of Cs^+, Li^+ and Cl^- for the Langmuir case (column 4) and the standard model (column 6).

Ion	c (M)	d (nm)	$\ln\gamma$	d (nm)	$\ln\gamma$
Cs^+	0.001	0.66	−0.095487	0.66	−0.077544
Li^+	0.009	0.76	−0.097653	0.754286	−0.076161
Cl^-	0.01	0.1	−0.101721	0.66	−0.077994

Table 2
The ion activity coefficients in a mixture of Cs^+, Mg^{2+} and Cl^- for the Langmuir case (column 4) and the standard model (column 6).

Ion	c (M)	d (nm)	$\ln\gamma$	d (nm)	$\ln\gamma$
Cs^+	0.005	0.66	−0.131006	0.66	−0.106709
Mg^{2+}	0.005	0.86	−0.524766	0.858	−0.455924
Cl^-	0.015	0.10	−0.143671	0.66	−0.108506

where Δu_i and Δu_r are the potentials of insertion and removal, respectively, N_i is the current number of ions of species i before the insertion or removal attempts, c_i is the bulk concentration in mole/m³, γ_i is the ion activity coefficient, and V_i is the volume available for ions i, namely

$$V_i = (L - d_i)W^2. \tag{4}$$

In the case of the Langmuir model d_i was equal to the diameter of the largest ion. The individual activity coefficients were calculated from the inverse GCMC technique [17] and the results collected in Tables 1 and 2.

As we considered the mixture of two salts, the insertion and removal moves were carried out independently for each salt. The kind of salt and move were selected at random, but the applied algorithm allowed an increase in the number of insertion and removal procedures for the low concentration salt to improve its statistics.

The number of configurations applied in the simulations depended on the electrode charge and hence on the number of ions. We used from 15 to 40 million of configurations to equilibrate the system and the next 40–100 million of configurations was applied to compute the profile of the density number of each kind of ion against the electrode surface. The contact values were calculated by extrapolation of the logarithm of the density results to the contact distance [18]. The calculation of a singlet distribution function and concentration profile from the ion density number is straightforward. Concentration profiles were required to make a comparison with the results of Biesheuvel and Soestbergen [9].

3. Results and discussion

We first consider a mixture of 1 mM CsCl and 9 mM LiCl with varying negative surface charge. Fig. 1 shows the singlet counterion distribution functions in the neighbourhood of the hard wall at a surface charge of -0.2 C/m². The following Fig. 2 demonstrates the counterion concentration profiles derived from the singlet distributions. The higher bulk concentration of Li^+ implies that at $\sigma = -0.2$ C/m² it has a higher contact value than the smaller Cs^+. However the roles are reversed as the surface charge is increased due to the packing ability of the smaller ion next to the surface (Figs. 2b and 2c). Moreover the concentration profiles by -0.6 C/m² reflect the counterion layering in the solution at a distance of 1.5 ionic diameters from the surface. Fig. 3 shows the corresponding Langmuir film model at the highest surface charge -0.6 C/m². In this case the contact value of both counterions is nearly identical, with again the beginnings of a layering in the solution. Although there are obvious differences near contact, the predictions of the Langmuir model are qualitatively similar to those of the hard sphere model for the treated range of surface
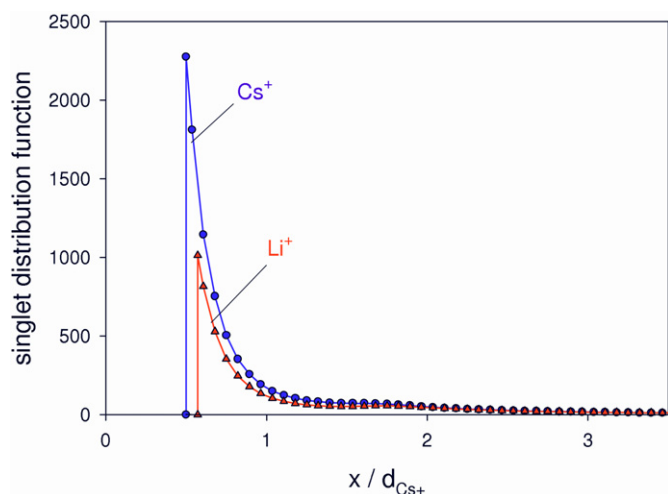
Fig. 1. Singlet distribution functions of Cs^+ ($d = 0.66$ nm, $c = 0.001$ M, $\ln\gamma = -0.077544$, circles, blue colour) and Li^+ ($d = 0.754286$ nm, $c = 0.009$ M, $\ln\gamma = -0.076161$, triangles, red colour) in the mixture with Cl^- ($d = 0.66$ nm, $c = 0.01$ M, $\ln\gamma = -0.077994$) against a hard wall electrode at $\sigma = -0.2$ C/m^2, $\varepsilon_r = 78.5$, $T = 298.15$ K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

charge. Our results in Figs. 2 and 3 disagree with Fig. 1 of Ref. [9]. Their Li^+ concentration exhibits a maximum near contact, which becomes more pronounced as the surface charge increases, while its contact value tends to zero as the surface charge increases. Also in [9] the concentration contact value of Cs^+ is underestimated.

A measure of ion adsorption is given by the individual excess ion concentrations over the double layer

$$\Gamma_i = \int_{a_i}^{\infty} (n_i - n_{ib})\, dx, \qquad (5)$$

where x is the normal distance from the surface, n_i, n_{ib} are the mean number density of ion i at x and in bulk respectively, a_i is the radius of ion i while for the Langmuir situation the counterion a_i is 0.38 nm for the univalent case or 0.43 nm in the divalent case. The individual ion excesses of Cs^+ and Li^+ are given in Fig. 4 with the relative excess of Cs^+ in the mixture in Fig. 5. Very similar graphs were found for the Langmuir case. As expected at small electrode charge the rate of the individual excesses of Cs^+ to Li^+ corresponds approximately to the ratio of bulk concentrations. At high surface charge the rate of the excesses of the two counterions with surface charge is nearly equal, leading to an approximate constant value of 40% for the relative excess of Cs^+. Biesheuvel and Soestbergen did not predict a levelling off of the relative excess of Cs^+ at high surface charge. The relative excess value of 40% at -0.6 C/m^2 is lower than the experimental value which amounts to 50–60% at $\sigma = -0.64$ C/m^2 [12]. In contrast, Biesheuvel and Soestbergen found good agreement.

Fig. 6 gives the concentration profiles of the counterions against a hard wall for the mixture 5 mM CsCl and 5 mM MgCl$_2$ at the 3 surface charges -0.2, -0.4, -0.6 C/m^2. The singlet distributions corresponding to -0.6 C/m^2 are given in Fig. 7. At the two lower surface charges the concentration profiles are as expected with the interface predominately populated by the divalent counterion. However, on increasing the surface charge in the approximate range -0.4 to -0.6 C/m^2, the smaller univalent counterion concentration rises rapidly until its contact value is greater than the divalent counterion, Figs. 6b and 6c. Thus at low surface charge the electrical term of the divalent ion dominates, then as the surface charge increases, a subtle interplay occurs between the electrostatic and volume terms resulting in the eventual
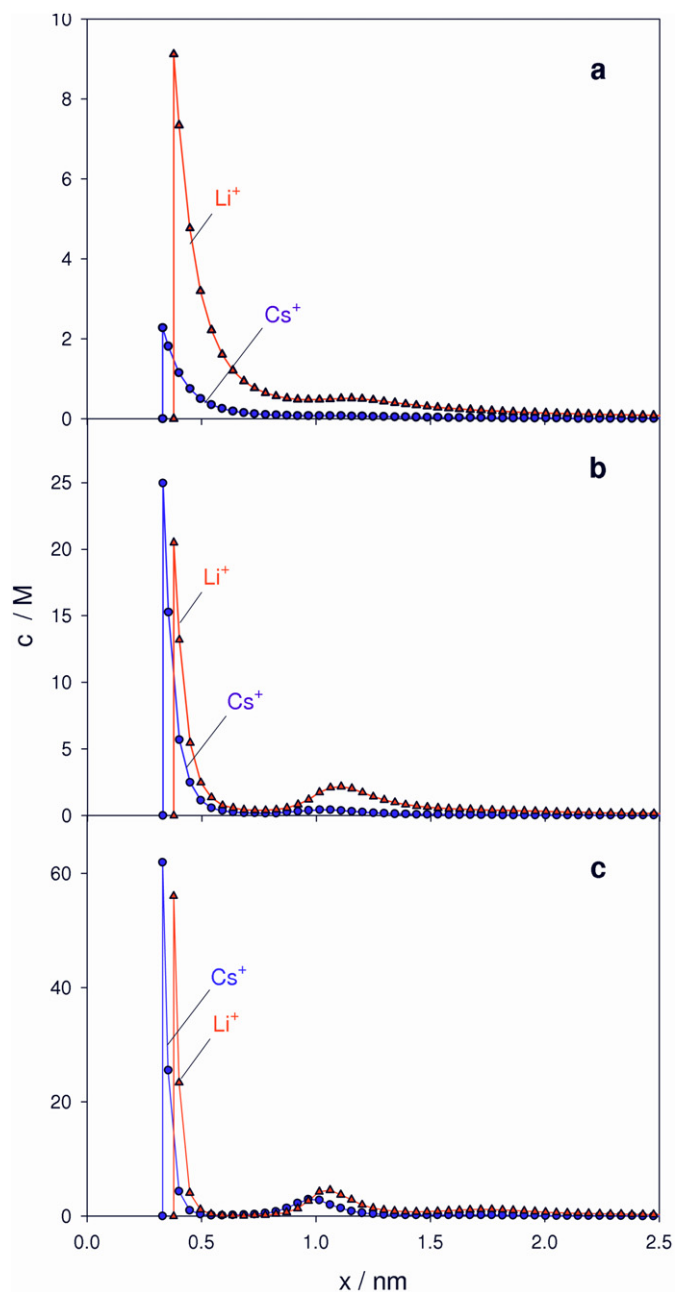

Fig. 2. Concentration profiles of Cs^+ and Li^+ in the mixture with Cl^- against a hard wall electrode at (a) $\sigma = -0.2$ C/m^2, (b) $\sigma = -0.4$ C/m^2, (c) $\sigma = -0.6$ C/m^2. The symbols and other physical parameters as in Fig. 1.

dominance of the smaller univalent ion due to its entropic advantage. The Langmuir model concentration profiles at -0.6 C/m^2 in Fig. 8 demonstrate that the volume advantage of the smaller counterion is greatly reduced when both counterions have the same distance of closest approach to the surface. The corresponding individual excesses and the relative excess of Cs^+ in the mixture are given in Figs. 9, 10. Qualitative similar MC profiles are given by the Langmuir model. The individual excesses reflect the trend seen in the concentration profiles. Up to -0.4 C/m^2 the Cs^+ excess is extremely small while that of Mg^{2+} steadily increases. Between -0.4 and -0.6 C/m^2 the Mg^{2+} excess falls slightly while that of Cs^+ rises steeply to a value not far below that of Mg^{2+}. Above -0.6 C/m^2 both excesses increase at the same rate with surface charge. Biesheuvel and Soestbergen similarly found that the relative excess of Cs^+ initially fell as the surface charge increased
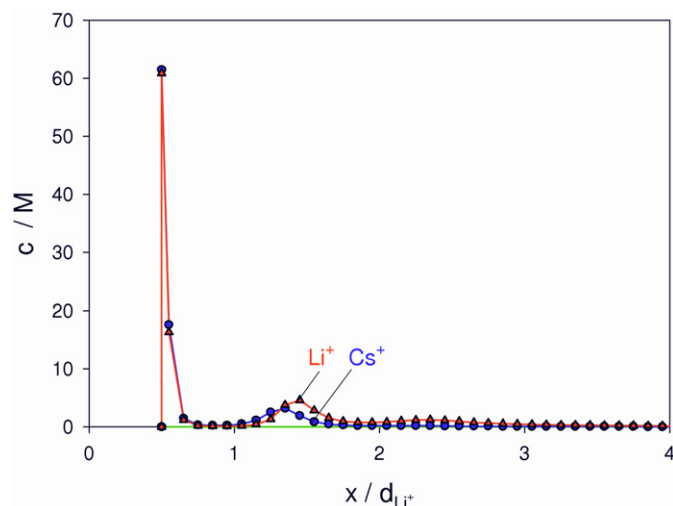
Fig. 3. Concentration profiles of Cs^+ ($\ln\gamma = -0.095487$) and Li^+ ($d = 0.76$ nm, $\ln\gamma = -0.097653$) in the mixture with Cl^- ($d = 0.10$ nm, $\ln\gamma = -0.101721$) against a charged Langmuir film at $\sigma = -0.6$ C/m^2. The symbols and other physical parameters as in Fig. 1.
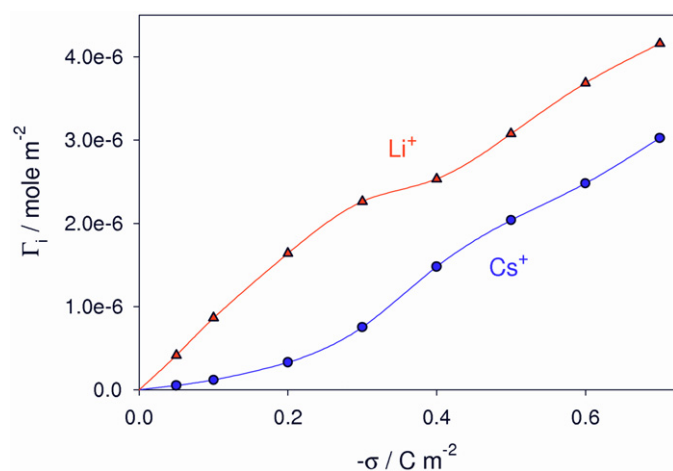

Fig. 4. Individual ion excess of Cs^+ and Li^+ against a hard wall electrode surface charge. The symbols and physical parameters as in Fig. 1.
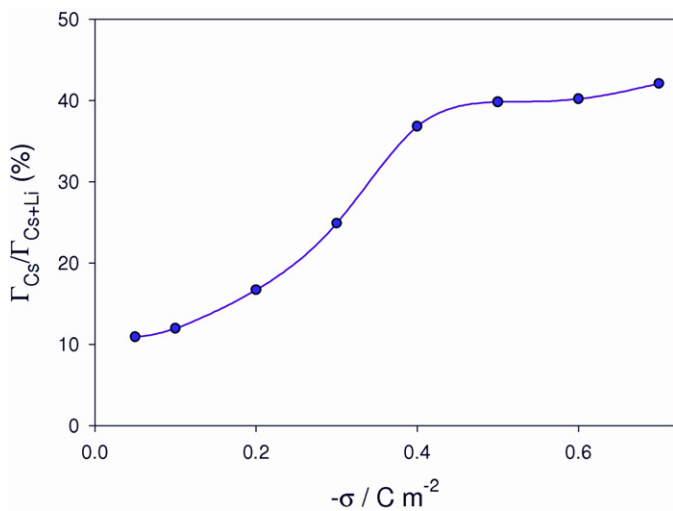

Fig. 5. The relative excess of Cs^+ in a mixture with Li^+ and Cl^- against a hard wall electrode surface charge. The symbols and physical parameters as in Fig. 1.
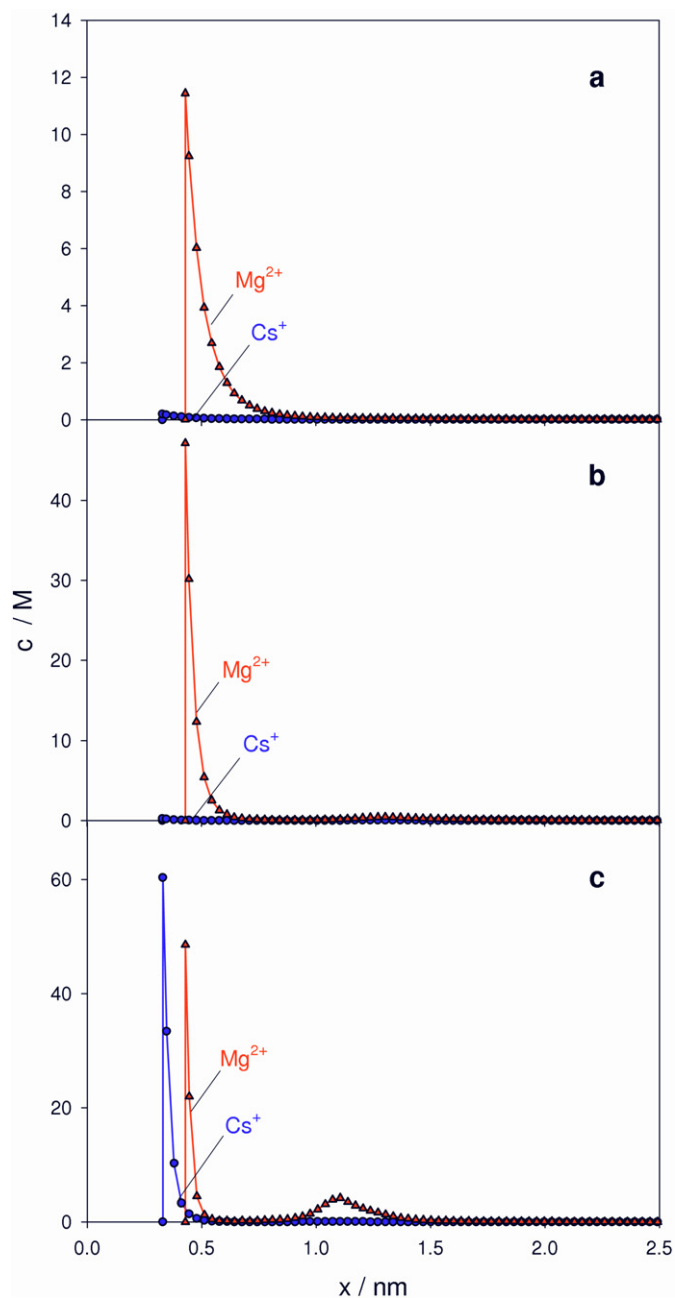

Fig. 6. Concentration profiles of Cs^+ ($d = 0.66$ nm, $c = 0.005$ M, $\ln\gamma = -0.106709$, circles, blue colour) and Mg^{2+} ($d = 0.858$ nm, $c = 0.005$ M, $\ln\gamma = -0.455924$, triangles, red colour) in the mixture with Cl^- ($d = 0.66$ nm, $c = 0.015$ M, $\ln\gamma = -0.108506$) against a hard wall electrode with $\varepsilon_r = 78.5$, $T = 298.15$ K at (a) $\sigma = -0.2$ C/m^2, (b) $\sigma = -0.4$ C/m^2, (c) $\sigma = -0.6$ C/m^2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

from zero but could only obtain a noticeable rise at the higher surface charge by substantially increasing the diameter of Mg^{2+}. To obtain agreement with the relative excess experimental value at -0.6 C/m^2 required a 20% increase in the radius of Mg^{2+}. Our relative excess value of ∼43% at -0.6 C/m^2 is again lower than the experiment value of 57–67% at $\sigma = -0.64$ C/m^2 determined by Shapovalov and Brezesinski [12]. Clearly model improvements such as an adequate treatment of the solvent and polarisation effects are required to obtain better MC agreement with experiment. Again the MC concentration profiles are at odds with those of Ref. [9].
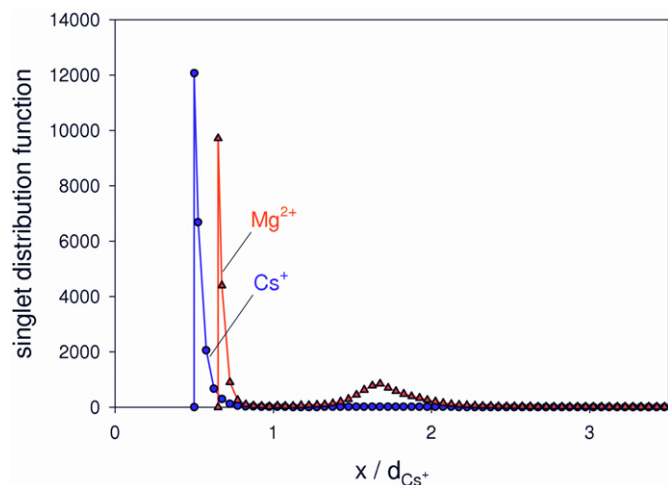
Fig. 7. Singlet distribution functions of Cs^+ and Mg^{2+} in the mixture with Cl^- against a hard wall electrode at $\sigma = -0.6$ C/m². The symbols and other physical parameters as in Fig. 6.
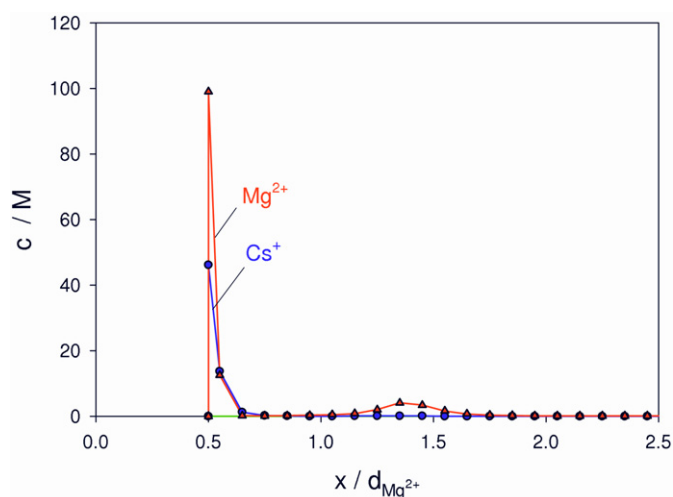

Fig. 8. Concentration profiles of Cs^+ ($\ln \gamma = -0.131006$) and Mg^{2+} ($d = 0.86$ nm, $\ln \gamma = -0.524766$) in the mixture with Cl^- ($d = 0.10$ nm, $\ln \gamma = -0.143671$) against a charged Langmuir film at $\sigma = -0.6$ C/m². The symbols and other physical parameters as in Fig. 6.

4. Conclusion

MC simulations for the electrolyte mixtures considered here indicate that care is required in analysing the mixtures by an exclusion volume corrected PB theory. This theory can be adjusted to account for the ion excesses of the smaller counterion in both the $LiCl + CsCl$ and $MgCl_2 + CsCl$ mixtures, but fails in its prediction of the structural properties. Since simulations accurately treat a specific model, the present electric double layer model results indicate that corrections to the PB theory require a simultaneous treatment of both the exclusion volume and ion–ion correlations (fluctuation) terms. Furthermore the MC simulations imply that a better modelling of the electrolyte mixtures and Langmuir film is necessary for closer agreement with experiment.
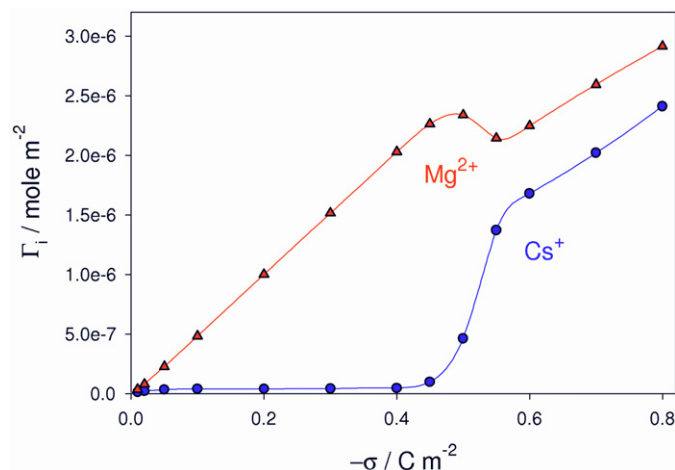
Acknowledgment

Fig. 9. Individual ion excess of Cs^+ and Mg^{2+} against a hard wall electrode surface charge. The symbols and physical parameters as in Fig. 6.
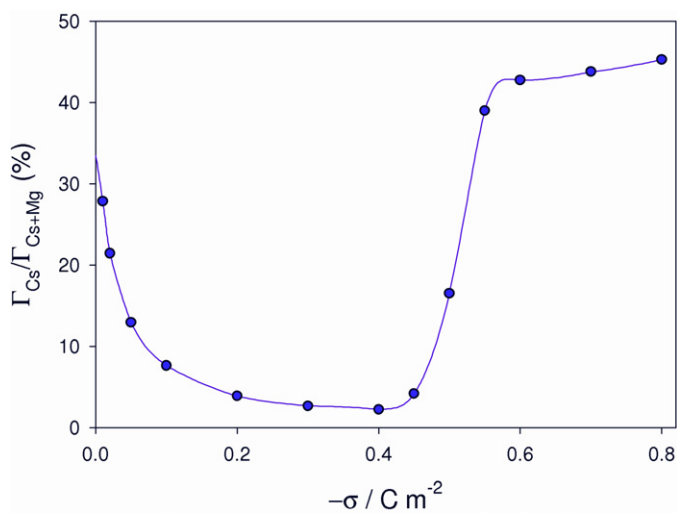

Fig. 10. The relative excess of Cs^+ in a mixture with Mg^{2+} and Cl^- against a hard wall electrode surface charge. The symbols and physical parameters as in Fig. 6.

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