

Scientific paper

# Adsorption of Electrolyte Mixtures in Disordered Porous Media. A Monte Carlo Study<sup>†</sup>

Gregor Trefalt<sup>1</sup> and Barbara Hribar-Lee<sup>1,\*</sup>

<sup>1</sup> Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia;

\* Corresponding author: E-mail: barbara.hribar@fkk.uni-lj.si

Received: 29-05-2007

<sup>†</sup>Dedicated to Prof. Dr. Jože Škerjanc on the occasion of his 70<sup>th</sup> birthday

## Abstract

The adsorption of electrolyte mixtures with a common anion in a disordered porous media containing charges was studied using the grand canonical Monte Carlo method. The porous media (matrix) was prepared by a sudden quench of a model +1 : -1 electrolyte. A mixture of +1 : -1, +1 : -1 model electrolytes with ion sizes that correspond to HCl and NaCl water solutions was then allowed to penetrate such a material for a thermal equilibrium with an external bulk solution to be established. The systems were studied at different ionic strengths of the annealed electrolyte mixture and at different matrix concentrations. The results show similar trends as for electrolyte mixture adsorption in charged cylindrical micropores. At low matrix and annealed electrolyte mixture concentration the sorption of the ions is observed while at high concentrations the electrolytes get excluded from the matrix. As expected, the exclusion is stronger for the HCl solutions as a result of a weaker electrostatic attraction between H<sup>+</sup> and matrix ions.

**Keywords:** Electrolyte mixtures, primitive model electrolyte, random porous media, separation factors, Donnan exclusion coefficients, ion-exchange isotherm, Monte Carlo simulation

## 1. Introduction

The partition of electrolyte solutions between an isotropic bulk phase and a microporous material is important for understanding many chemical and engineering processes, desalination of water, ion exchange resins equilibria, and membrane equilibria being just few of them.<sup>1</sup> In all these processes the selectivity of the adsorption of different kinds of ions plays a crucial role. In the softening of water, for example, the “hard” water is passed through cation exchange resins in which calcium ions are replaced by sodium ones. In the process of deionization of water, on the other hand, the sodium ions from water are adsorbed in the ion exchanger and replaced by hydrogen ions. Due to different level of adsorption, the concentration ratio of competing ions in the adsorbent is different from that in the bulk solution, in other words, the adsorbent “selects” one species in preference to the other. This selectivity is usually measured by the so-called separation factor,  $\alpha_{A'}^B$ , defined as<sup>2</sup>:

$$\alpha_{A'}^B = \frac{c_A^{\text{out}} \cdot c_B^{\text{in}}}{c_B^{\text{out}} \cdot c_A^{\text{in}}} \quad (1)$$

Here, A and B are the competing ions, the subscript *out* denotes the concentration of the ion in the external solution, and the subscript *in* denotes the concentration of the ion in the adsorbent.

Because of their great practical importance, these systems have been extensively studied experimentally and theoretically, for more recent reviews see for example Ref. 3–4. While most of the earlier theories are based on the empirical or semiempirical equations, in the last few decades theories have been developed that provide the correct description of the phenomena based on the physical chemistry of these systems.<sup>1</sup> One of the first such theories is based on the classical Donnan equilibrium<sup>5</sup> where the rejection of an electrolyte from the adsorbent is measured conveniently by the so-called Donnan exclusion coefficient, which is for a certain ion A defined by<sup>6</sup>:

$$\Gamma_A = \frac{c_A^{\text{out}} - c_A^{\text{in}}}{c_A^{\text{out}}} \quad (2)$$

A more detailed model of electrolyte exclusion is based on the Poisson – Boltzmann (PB) equation.<sup>7–9</sup>

Although the PB theory has successfully described various experimental results it contains several statistical-thermodynamical approximations that can lead to unphysical results in some cases. In the last few years some better theories have been developed.<sup>10–11</sup>

The method that, when properly applied, provides the exact calculation for the thermodynamic properties of a chosen model, is the Monte Carlo computer simulation. When phase equilibria are involved in the calculation, the grand canonical Monte Carlo method (GCMC) proves particularly useful since its methodology already provides the equivalency of the chemical potentials of two phases involved, the condition that needs to be fulfilled for the chemical equilibrium to be established.<sup>12</sup> The method was successfully used in several studies of electrolyte adsorption in charged microporous materials.<sup>6, 13–17</sup>

In this paper a slightly different model of adsorbent is used. A random microporous material is considered that, in spite containing positive and negative charges, is electroneutral as a whole.<sup>18</sup> Adsorption of single electrolyte solutions in such materials has been previously studied by Monte Carlo computer simulations and integral equation theories.<sup>19–20</sup> Here we were interested in the preferential adsorption of an electrolyte mixture with a common anion in which the cations differ in size. The model was studied using the grand canonical Monte Carlo simulations. The paper is organized as follows. After this brief Introduction, the Model and the Method used are described in Section 2. The results are presented and discussed in Section 3 and the Conclusion are summarized in Section 4.

## 2. The Model Description and the Simulation

The model system under consideration consists of two subsystems. The first subsystem, the adsorbent (also called matrix), was modeled as an equilibrium distribution of a primitive model +1 : -1 electrolyte with ion diameters  $\sigma_+^0 = \sigma_-^0 = 4.25 \text{ \AA}$  (the upper index 0 indicates the matrix particles). After the equilibration the electrolyte was subject to a sudden quench and the ions were frozen in their positions. The second subsystem, a mixture of two +1 : -1 primitive model electrolytes with a common anion, was then allowed to come in the thermal equilibrium with the matrix, not influencing the matrix subsystem. The whole system was treated on the McMillan-Mayer level of approximation: the solvent was treated as a dielectric continuum with the dielectric constant  $\epsilon_0$  or  $\epsilon_1$ , respectively, and the pair potential between ions of different species was:

$$\beta U_{ij}^{00} = \begin{cases} \infty & r < \frac{\sigma_i^0 + \sigma_j^0}{2} \\ \frac{z_i^0 z_j^0 e_0^2}{4\pi \epsilon_0 \epsilon k_B T_0 r} = \frac{L_{B,0} z_i^0 z_j^0}{r} & r \geq \frac{\sigma_i^0 + \sigma_j^0}{2} \end{cases}$$

$$\beta U_{ij}^{01} = \begin{cases} \infty & r < \frac{\sigma_i^0 + \sigma_j^1}{2} \\ \frac{z_i^0 z_j^1 e_0^2}{4\pi \epsilon_1 \epsilon k_B T_1 r} = \frac{L_{B,1} z_i^0 z_j^1}{r} & r \geq \frac{\sigma_i^0 + \sigma_j^1}{2} \end{cases} \quad (3)$$

$$\beta U_{ij}^{11} = \begin{cases} \infty & r < \frac{\sigma_i^1 + \sigma_j^1}{2} \\ \frac{z_i^1 z_j^1 e_0^2}{4\pi \epsilon_1 \epsilon k_B T_1 r} = \frac{L_{B,1} z_i^1 z_j^1}{r} & r \geq \frac{\sigma_i^1 + \sigma_j^1}{2} \end{cases}$$

As before, the upper index 0 denotes matrix particles, while the index 1 denotes fluid particles. Although in general, the temperature of the quench of the matrix,  $T_0$ , can differ from the annealed fluid equilibration temperature,  $T_1$ , both temperatures were taken to be the same throughout this study, and namely 298 K, which corresponds to the Bjerrum length,  $L_{B,0} = L_{B,1} = L_B = 7.14 \text{ \AA}$ .  $\beta = (k_B T_1)^{-1}$ , where  $k_B$  is the Boltzmann constant,  $e_0$  is the proton charge, and  $\epsilon$  is the permittivity of the vacuum.

As already stated, the parameters for the matrix were  $z_+^0 = 1$ ,  $z_-^0 = -1$ , and  $\sigma_+^0 = \sigma_-^0 = 4.25 \text{ \AA}$ . The annealed fluid adsorbed in the matrix was a mixture of two +1 : -1 electrolytes with a common anion,  $z_{+,A}^1 = z_{+,B}^1 = 1$ ,  $z_-^1 = -1$ . The sizes of the ions were chosen to correspond to the mixture of HCl and NaCl in water<sup>21</sup>:  $\sigma_{H^+}^1 = 5.04 \text{ \AA}$ ,  $\sigma_{Na^+}^1 = 3.87 \text{ \AA}$ , and  $\sigma_{Cl^-}^1 = 3.62 \text{ \AA}$ .

The matrix configuration was obtained using the canonical Monte Carlo simulation. After the equilibration, the matrix ions were frozen in their positions. The annealed electrolyte ions were then distributed within the matrix and the system was studied by the grand canonical Monte Carlo method. The methodology of the method is well established and extensively described in several previous papers and is therefore not repeated here.<sup>6, 12, 17, 22</sup> The details of the simulations are as follows. The number of matrix particles used was from 1000 to 5000, depending on the concentration. The average number of a fluid cation species distributed within the matrix varied from 50 to 1500. The ions within the matrix were first equilibrated over at least  $10^6$  grand canonical Monte Carlo steps. After the equilibration, the production run of  $2 \times 10^7$  attempted configurations was carried out to obtain the average concentration of the adsorbed electrolyte species.

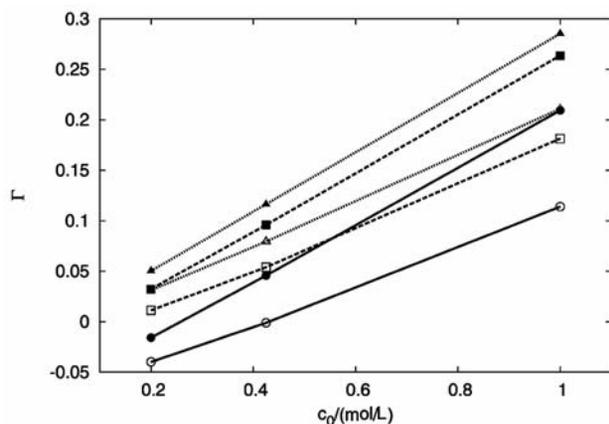
To calculate the mean activity coefficient of the annealed electrolyte from the equilibrium relation  $a_{\pm}^1 = \gamma_{\pm}^1 \sqrt{c_+^1 c_-^1} = a_{\pm}^{out} = \gamma_{\pm}^{out} \sqrt{c_+^{out} c_-^{out}}$ , where index + refers to one of the cation species, and *out* to the properties of the bulk electrolyte mixture, the activity coefficient of the bulk electrolyte mixture,  $\gamma_{\pm}^{out}$ , has to be known in advance. The values used were obtained using hypernetted-chain (HNC) theory which has proved to be very successful in describing the properties of ionic fluids.<sup>23</sup>

### 3. Results and Discussion

We begin this section by presenting the Donnan exclusion coefficients,  $\Gamma$ , for both electrolytes in the mixture at a constant mole fraction of HCl in the external solution,

and namely,  $x_{\text{H}}^{\text{out}} = \frac{c_{\text{H}}^{\text{out}}}{c_{\text{H}}^{\text{out}} + c_{\text{Na}}^{\text{out}}} = 0.5$ , as a function of the ma-

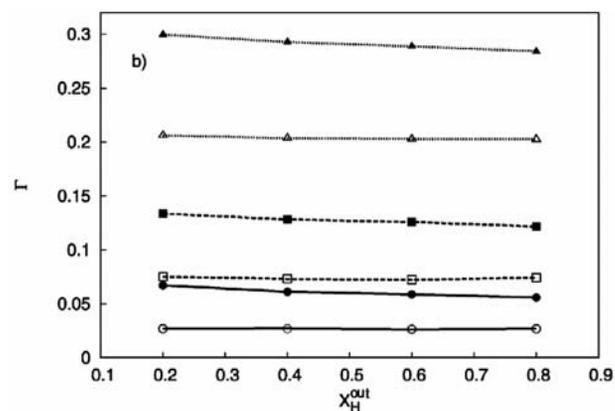
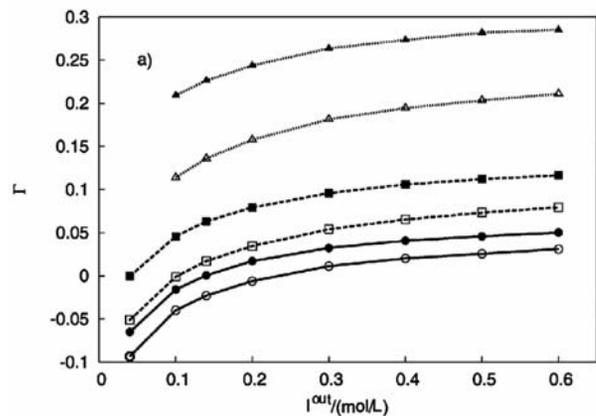
trix concentration. The exclusion coefficients are for several ionic strength of the external solution ( $I^{\text{out}} = 0.1 \text{ M}$  – full lines,  $I^{\text{out}} = 0.3 \text{ M}$  – dashed lines, and  $I^{\text{out}} = 0.6 \text{ M}$  – dotted lines) presented in Figure 1. The symbols represent the Monte Carlo results while the lines are here only to guide the eye.



**Figure 1.** The Donnan exclusion coefficient,  $\Gamma$ , as a function of matrix concentrations,  $c_0$ .  $x_{\text{H}}^{\text{out}} = 0.5$  and  $I^{\text{out}} = 0.1 \text{ M}$  (full lines),  $0.3 \text{ M}$  (dashed lines), and  $0.6 \text{ M}$  (dotted lines). The full symbols show the exclusion coefficients for  $\text{H}^+$  ions and empty symbols for  $\text{Na}^+$  ions.

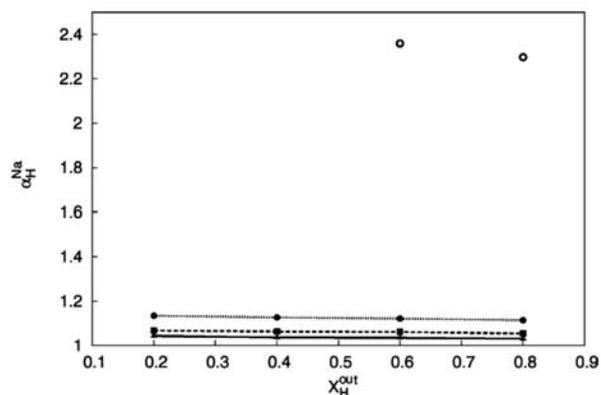
One can clearly see that in all cases studied the exclusion coefficients for HCl model solution (full symbols) are higher than the corresponding ones for NaCl (empty symbols). Due to larger radius of the  $\text{H}^+$  model ion, its charge density is smaller than the one of  $\text{Na}^+$  model ion. The electrostatic attraction between matrix anions and  $\text{H}^+$  model ions is therefore weaker, and the excluded volume effect of the matrix larger, both effects causing more intensive adsorption of the NaCl solution.

Very similar effects are seen in Figure 2 where the Donnan exclusion coefficients are shown as a function of the ionic strength of the external solution at a fixed mole fraction of HCl,  $x_{\text{H}}^{\text{out}} = 0.5$  (Figure 2a), and as a function of the mole fraction of HCl at a constant ionic strength of the external solution,  $I^{\text{out}} = 0.5 \text{ M}$  (Figure 2b), in both cases, for several matrix concentrations ( $c_0 = 0.2 \text{ M}$  – full lines,  $c_0 = 0.425 \text{ M}$  – dashed lines, and  $c_0 = 1.0 \text{ M}$  – dotted lines). Again, the full symbols apply to the HCl and empty symbols to the NaCl solutions.



**Figure 2:** a) The Donnan exclusion coefficient,  $\Gamma$ , as a function of the ionic strength of the external electrolyte,  $I^{\text{out}}$ .  $x_{\text{H}}^{\text{out}} = 0.5$  and  $c_0 = 0.2 \text{ M}$  (full lines),  $0.425 \text{ M}$  (dashed lines), and  $1.0 \text{ M}$  (dotted lines). The full symbols show the exclusion coefficients of  $\text{H}^+$  ions and empty symbols for  $\text{Na}^+$  ions. b) The Donnan exclusion coefficient,  $\Gamma$ , as a function of  $x_{\text{H}}^{\text{out}}$ .  $I^{\text{out}} = 0.5 \text{ M}$ , the rest as for Figure 2a.

At low ionic strengths and low matrix concentrations one actually observes the sorption of the electrolyte into the matrix, the concentration of the electrolyte is



**Figure 3.** The separation factor,  $\alpha_{\text{Na}}^{\text{NaCl}} = \frac{c_{\text{H}}^{\text{out}} \cdot c_{\text{Na}}^{\text{in}}}{c_{\text{Na}}^{\text{out}} \cdot c_{\text{H}}^{\text{in}}}$ , as a function of  $x_{\text{H}}^{\text{out}}$  at  $I = 0.5 \text{ M}$ , and  $c_0 = 0.2 \text{ M}$  (full lines),  $0.425 \text{ M}$  (dashed lines),  $1.0 \text{ M}$  (dotted lines), and  $5.0 \text{ M}$  (empty symbols).

higher in the matrix than in the external solution of the same activity ( $\Gamma < 0$ ). At these conditions the excluded volume due to the matrix is small and the matrix charges are only poorly screened, causing the attractive forces between matrix anions and fluid cations to “pull” the external solution into the adsorbent. Again, the attraction is stronger for the  $\text{Na}^+$  ions (Figure 2a). No such sorption is observed in the adsorbents containing no charges.<sup>24</sup>

At a given ionic strength of the external electrolyte, the exclusion coefficient shows very little dependence on the electrolyte composition (Figure 2b).

To see more clearly the difference between the adsorption of the HCl and NaCl solution in the matrix, the separation factors,

$$\alpha_H^{\text{Na}} = \frac{c_H^{\text{out}} \cdot c_{\text{Na}}^{\text{in}}}{c_{\text{Na}}^{\text{out}} \cdot c_H^{\text{in}}}$$

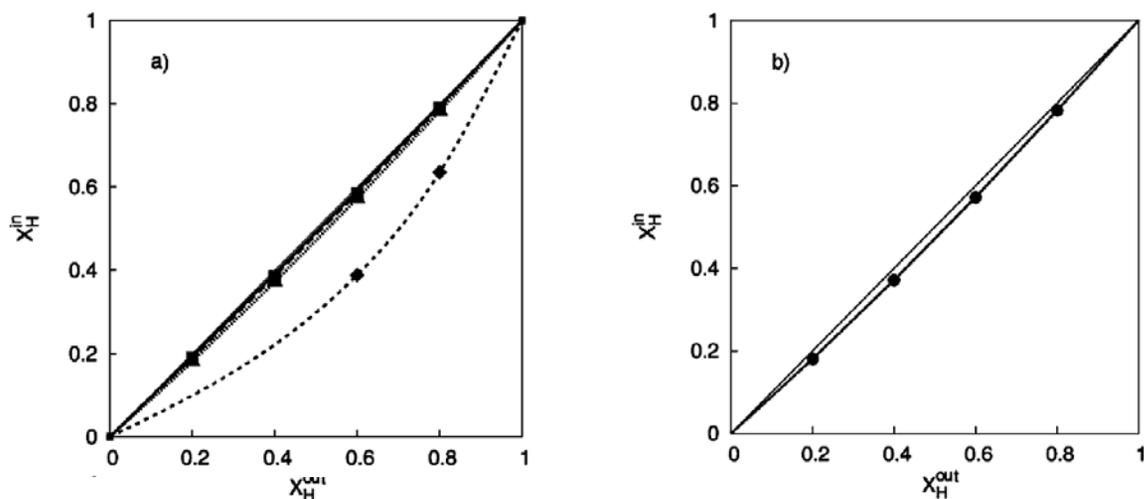
are for several matrix concentrations ( $c_0 = 0.2$  M – full lines,  $c_0 = 0.425$  M – dashed lines,  $c_0 = 1.0$  M – dotted lines, and  $c_0 = 5.0$  M – empty symbols) presented in Figure 3. The ionic strength of the external electrolyte in this case was  $I^{\text{out}} = 0.5$  M. At low matrix concentrations the separation factors do not vary substantially with the mole fraction  $X_{\text{H}}$ . This is consistent with previous observations for the preferential adsorption in charged cylindrical micropores<sup>6</sup>, as well as with the experimental results.<sup>2</sup> As expected, the selectivity coefficients are much larger at higher matrix concentrations where both, the excluded volume effect, and the electrostatic effect favor smaller  $\text{Na}^+$  model ions with higher charge density.

Another convenient form of showing the selectivity of the adsorbent is the ion-exchange isotherm presenting the mole fraction of one competing ion within the adsorbent,  $x_A^{\text{in}}$ , as a function of the mole fraction of the same ion in the external solution,  $x_A^{\text{out}}$ . Some of the

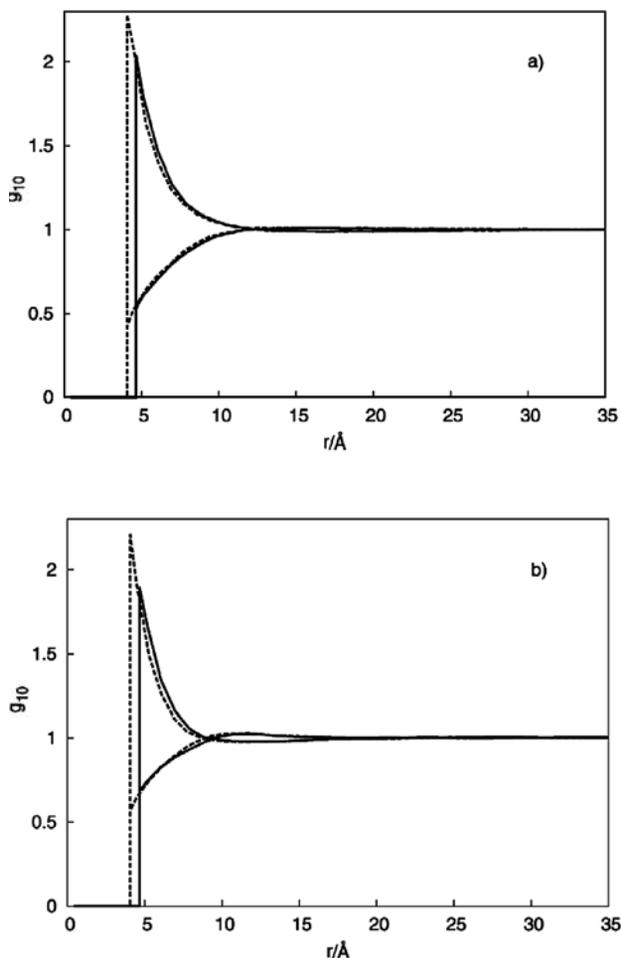
ion-exchange isotherms for the cases studied are shown in Figure 4. In a system in which the adsorbent would show no preference for one or the other ion, the ion-exchange isotherm would be linear, while the curvature signifies the selectivity. In our case the negatively curved ion-exchange isotherms show the characteristic of the adsorbent to prefer  $\text{Na}^+$  ions to the  $\text{H}^+$  ones. Here the rombs (short-dashed line) show the results for  $c_0 = 5.0$  M, the triangles (dotted line) show the results for  $c_0 = 1.0$  M, squares (long-dashed line) show the results for  $c_0 = 0.425$  M, and circles (full line) show the results for  $c_0 = 0.2$  M. The error-bars not shown in the figure are smaller than the size of the symbols. In all cases,  $I^{\text{out}} = 0.5$  M.

Consistently with our previous observations, the selectivity of the matrix increases with its concentration (Figure 4a). In Figure 4b the ion-exchange isotherms in the matrix with the concentration  $c_0 = 1.0$  M are presented. The results for  $I^{\text{out}} = 0.05$  M are shown with full lines, for  $I^{\text{out}} = 0.2$  M with dashed lines, and for  $I^{\text{out}} = 0.5$  M with dotted lines. The results for all the cases studied visually coincide showing almost no dependence of the matrix selectivity on the external electrolyte ionic strength (Figure 4b).

To further support our explanation of the results presented above, we show some fluid-matrix radial pair distribution functions (pdfs) for the competing ions. Figure 5 shows the pdfs for the case where the ionic strength of the external solution was 0.5 M, and  $x_{\text{H}}^{\text{out}} = 0.5$ . At these conditions, the corresponding equilibrium fluid concentrations in the matrix with  $c_0 = 0.2$  M were  $c_{\text{NaCl}} = 0.244$  M and  $c_{\text{HCl}} = 0.239$  M (Figure 5a), and in the matrix with  $c_0 = 1.0$  M,  $c_{\text{NaCl}} = 0.199$  M and  $c_{\text{HCl}} = 0.180$  M (Figure 5b). The full lines show the H-matrix ion pdfs and the dashed



**Figure 4.** Ion-exchange isotherms ( $x_{\text{H}}^{\text{in}}$  as a function of  $x_{\text{H}}^{\text{out}}$ ) for the mixture of HCl + NaCl in +1 : -1 electrolyte matrix. a)  $I^{\text{out}} = 0.5$  M;  $c_0 = 5.0$  M (rombs, short-dashed line),  $c_0 = 1.0$  M (triangles, dotted line),  $c_0 = 0.425$  M (squares, long-dashed line), and  $c_0 = 0.2$  M (circles, full line) b)  $c_0 = 1.0$  M;  $I^{\text{out}} = 0.05$  M (full line),  $I^{\text{out}} = 0.2$  M (dashed line), and  $I^{\text{out}} = 0.5$  M (dotted line). The solid line without symbols is showing the diagonal.



**Figure 5.** Fluid-matrix radial pair distribution functions  $g_{10}(r)$  for  $\text{H}^+$  – matrix (full lines) and  $\text{Na}^+$  matrix (dashed lines). The upper curves correspond to the matrix anion and the lower ones to the matrix cation.  $\Gamma^{\text{out}} = 0.5 \text{ M}$  and  $x_{\text{H}}^{\text{out}} = 0.5$ . a)  $c_0 = 0.2 \text{ M}$  and b)  $c_0 = 1.0 \text{ M}$ .

lines show the Na-matrix ion pdfs. The figures corroborate our previous findings. The  $\text{Na}^+$  model ions come closer to the matrix ions. The height of the peaks is showing that the probability of finding a  $\text{Na}^+$  ion in contact with a matrix anion is higher than the corresponding probability for a  $\text{H}^+$  ion.

Another interesting observation are the shapes of the described pdfs. In both cases ( $c_0 = 0.2 \text{ M}$  – Figure 5a, and  $c_0 = 1.0 \text{ M}$  – Figure 5b) the cross-over of the ++ and +- pdfs is observed. At a certain distance the interaction between fluid and matrix cations (anions) becomes attractive, and the interaction between oppositely charged ions becomes repulsive. In the case of low matrix concentrations this cross-over occurs at relatively large distances (Figure 5a), allowing the sorption of the electrolyte in the matrix (Figure 2a). At higher matrix concentrations the cross-over is shifted to much shorter distances (Figure 5b) causing the desorption of the electrolyte from the matrix (Figure 2a).

## 4. Conclusions

In this work the preferential adsorption of an electrolyte mixture with a common anion, and in which the cations differ in the size alone, in a disordered porous media containing charges was studied using the grand canonical Monte Carlo simulation. The parameters of the model were chosen to mimic a mixture of HCl and NaCl water solution, while the adsorbent was chosen to be a frozen configuration of an equilibrated symmetric  $+1 : -1$  electrolyte.

The separation factors and the ion-exchange isotherms show the ability of the adsorbents to filter the electrolyte mixture. The adsorbents considered in this work prefer the  $\text{Na}^+$  ions to the  $\text{H}^+$  ones. This is the result of two effects combined. Due to the larger size of the  $\text{H}^+$  model ion the excluded volume effect is more pronounced for these ions, especially at higher matrix concentrations. At low matrix concentrations the electrostatic effect is more important. Again, due to smaller charge density, the electrostatic attraction between  $\text{H}^+$  model ions and the oppositely charged matrix ions is smaller than for the  $\text{Na}^+$  model ions.

To see the influence of the adsorbent structure on the ability of the adsorbent to filter the mixtures of electrolytes, a comparison with the results for the adsorption of mixed electrolytes in charged cylindrical micropores studied previously is of some interest. Although due to the differences in the models no direct comparison is possible, our observations show qualitatively similar trends as those for the preferential adsorption in the cylindrical micropores: While the separation factor depends strongly on the density and/or the charge density of the adsorbent, it shows almost no dependence on the adsorbing mixed electrolyte composition at its constant ionic strength. Our conclusion was that the selectivity of the matrix shows very little dependence on the actual microstructure of the adsorbent.

Our observations are also consistent with the experimental results. To get an even more direct comparison with the experiment, we hope to investigate the preferential adsorption of the mixtures in the charged random matrices in our future work.

## 5. Acknowledgement

B. H. L. appreciates the support of the Ministry of Science and Education of Slovenia under grants P1-0201 and J1-6553.

## 6. References

1. V. Vlachy, A. D. J. Haymet, *Aust. J. Chem.* **1990**, *43*, 1961–1982.
2. F. Helfferich, *Ion Exchange*; McGraw Hill, New York, **1962**.
3. M. L. Rosinberg, In *New Approaches to Problems in Liquid State Theory*; Ed. by C. Caccamo, J. P. Hansen, G. Stell; Kluwer, Dordrecht, Holland, **1999**, 245–278.

4. O. Pizio, In *Computational Methods in Surface and Colloid Chemistry*; Ed. by M. Borowko, Marcel Dekker, New York, **2000**, 293–345.
5. F. Donnan, *Z. Elektrochem.* **1911**, *17*, 572–581.
6. B. Jamnik, V. Vlachy, *J. Am. Chem. Soc.* **1995**, *117*, 8010–8016.
7. M. Lozada-Cassou, In *Fundamentals of Inhomogeneous Fluids*; Ed. by D. Henderson; Marcel Dekker, New York, **1992**, 303–323.
8. D. Dolar, V. Vlachy, *Vestn. Slov. Kem. Drus.* **1981**, *28*, 327–338.
9. L. Dresner, K. A. Kraus, *J. Phys. Chem.* **1963**, *67*, 990–996.
10. X. Lefebvre, J. Palmeri, *J. Phys. Chem. B* **2005**, *109*, 5525–5540.
11. A. Szymczyk, P. Fievet, *J. Membrane Sci.* **2005**, *252*, 77–88.
12. M. P. Allen, D. J. Tildesley, *Computer Simulation of Liquids*; Clarendon Press, Oxford, **2006**.
13. V. Vlachy, A. D. J. Haymet, *J. Electroanal. Chem.* **1990**, *283*, 77–85.
14. B. Jamnik, V. Vlachy, *J. Am. Chem. Soc.* **1993**, *115*, 660–666.
15. V. Vlachy, A. D. J. Haymet, *J. Am. Chem. Soc.* **1989**, *111*, 477–481.
16. B. Hribar, V. Vlachy, L. B. Bhuiyan, C. W. Outhwaite, *J. Phys. Chem. B* **2000**, *104*, 11522–11527.
17. M. Lukšič, B. Hribar-Lee, V. Vlachy, *J. Phys. Chem. B* **2007**, *in press*.
18. D. Bratko, A. K. Chakraborty, *J. Chem. Phys.* **1996**, *104*, 7700–7712.
19. B. Hribar, V. Vlachy, O. Pizio, *J. Phys. Chem. B* **2001**, *105*, 4727–4734.
20. H. Dominguez, B. Hribar-Lee, V. Vlachy, O. Pizio, *Physica A* **2003**, *324*, 469–483.
21. J. P. Simonin, O. Bernard, L. Blum, *J. Phys. Chem. B* **1998**, *102*, 4411–4417.
22. J. P. Valleau, L. K. Cohen, *J. Chem. Phys.* **1980**, *72*, 5935–5941.
23. D. M. Duh, A. D. J. Haymet, *J. Chem. Phys.* **1992**, *97*, 7716–7729.
24. G. Trefalt, *Diploma*, **2007**, Ljubljana.

## Povzetek

V tem delu smo s pomočjo metode računalniške simulacije Monte Carlo v velekanoničnem ansamblu študirali adsorpcijo mešanic modelnih elektrolitov v neurejeni porozni snovi. Adsorbent smo pripravili z zamrznjenjem uravnovežene raztopine simetričnega +1 : -1 elektrolita. Adsorbentu, mešanici dveh modelnih +1 : -1 elektrolitov, ki ustrežata vodnim raztopinam HCl in NaCl, smo dovolili, da se v tako pripravljenem adsorbentu porazdeli in pride z njim v termično ravnotežje. Ravnotežja smo študirali pri različnih ionskih jakosti elektrolitskih mešanic in različnih koncentracijah adsorbenta. Rezultati kažejo podobne trende kot za adsorpcijo elektrolitskih mešanic v nabitih cilindričnih mikroporah. Pri nizkih koncentracijah adsorbenta in adsorbata pride do sorpcije elektrolita v adsorbent, pri višjih koncentracijah pa je koncentracija elektrolita v adsorbentu nižja kot v nemoteni raztopini enake aktivnosti. Kot pričakovano je stopnja adsorpcije višja za Na<sup>+</sup> ione, kar je posledica njihove manjše velikosti in večje gostote naboja.