

Charged pore matrices prepared with and without template particles by computer simulations

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Recibido el 10 de noviembre de 2003; aceptado el 5 de marzo de 2004

Series of Molecular Dynamics simulations to study the structure of different porous matrices were investigated. Matrices were prepared by two different processes. The first method consisted of charged particles simulated at a fixed density, and after equilibration, the matrix structure was taken from the last configuration. The second method was prepared from a binary mixture of charged particles where one of the components served as the template material and the other as the matrix. The final porous matrix configuration was obtained by removing template particles from the equilibrated mixture, and therefore only the matrix particles remained in the system. The volume distribution, the cluster formation, and the porosity in the pore matrix were investigated. The present results were compared with previous results of pore matrices prepared without electrostatic interactions. Therefore, electrostatic effects were analyzed in terms of the pore matrix preparation method. As a general trend, it was observed that matrices prepared with template presented smaller voids in the structure in comparison with matrices prepared without template. It was also found that porosity was higher in matrices without template than in matrices with template. When comparisons were made between matrices with and without electrostatic interactions, the porosity was higher in matrices with charge than in matrices without charge. Finally, at low and high temperatures, the porosity values were nearly the same.

Keywords: Porous structure; porosity; charged porous matrices; computer simulation.

Se realizaron simulaciones de Dinámica Molecular para estudiar la estructura de matrices porosas. Las matrices fueron preparadas mediante dos métodos. El primer método consistió en simular partículas cargadas a una densidad fija donde su última configuración fué la de la matriz. El segundo método utilizó una mezcla binaria de partículas cargadas donde una especie se consideró como partículas de un sustrato y la otra especie como partículas de la matriz. La configuración final de la matriz se tomó después de congelar al sistema y remover las partículas del sustrato. Se investigó la distribución de volúmenes, la formación de agregados y la porosidad de las matrices. Los resultados de la porosidad obtenidos se compararon con resultados anteriores para sistemas sin interacciones eléctricas. Así entonces, fue posible estudiar el efecto de la interacción electrostática en la preparación de matrices porosas. Los resultados muestran que las matrices preparadas sin partículas sustrato tienen mayores cavidades que aquellas matrices preparadas con sustrato. Las comparaciones entre matrices con y sin cargas muestran que la porosidad es mayor en matrices preparadas con interacciones electrostáticas. Finalmente, a altas y bajas temperaturas las porosidades fueron muy similares.

Descriptores: Estructura de poros; porosidad; matrices porosas cargadas; simulaciones por computadora.

PACS: 61.25.-f; 61.43.Bn; 61.43.Gt

1. Introduction

Over the last years, the study of fluids in confined microporous matrices has been of great interest due to their practical applications. Moreover, it has been of particular interest to find new methods to control the structure of the porous matrices to be used in applications of heterogeneous catalysis, petroleum recovery, membrane separation processes, etc.

From the theoretical point of view, Madden and Glant proposed an extension of the liquid-state theory to study fluids adsorbed in disordered porous materials [1,2]. Other studies have been carried out to understand the structure of disordered fluid systems (e.g. [3–6]). Some other authors have been more interested in studies of porosity and adsorption of fluids in porous matrices [7–10]. Therefore, it is crucial to characterize the porous solid structure in order to understand the properties of fluids inside them.

Some authors have used common models to prepare disordered matrices by computer simulation or theory. These models consist of a system of quenched particles usually in an equilibrium configuration [1, 11–13]. However, more recently, a new method inspired by the actual formation process has been employed [14,15]. This model considers the explicit presence of a template material, *i.e.* the system is composed of a binary system where one specie is the matrix and the other is the template [7, 16]. Once the system is equilibrated at a particular thermodynamic state it is frozen, and the template particles are removed, *i.e.*, the remaining particles form the pore matrix.

The matrix configuration and the porosity using template materials were previously investigated by Van Tassel some years ago [7]. However, he just analyzed the case when the systems were prepared with hard spheres. It was found

that the porosity was higher when matrices were prepared with template particles. More recently, pore matrices prepared with attractive and repulsive potentials were investigated at low and high temperatures [17, 18]. For low temperatures and repulsive potentials, the porosity results agreed with those of hard sphere systems. For attractive forces, at low temperature, the highest porosity was found in matrices prepared without template compared with those prepared with template. In terms of the porous structure, large vacancies were found in matrices prepared with attractive forces at low temperature compare to those prepared at high temperature. Studies of diffusion coefficients were also investigated in the different matrices. It was found that the highest diffusion was obtained for fluids immersed in attractive matrices prepared at low temperatures without template. Therefore, from these results, it was possible to investigate the role of temperature and particle interactions in the final matrix structure.

On the other hand, studies of fluids in disordered porous media composed of charge centers are also very important to understand the dynamic response of nonmetallic materials, ionic glasses and polymeric and glassy conductors. Moreover, some materials such as zeolites that are used for catalytic and separation processes, exhibit a distribution of charged centers. Although there are few works studying fluids on disordered matrices with charged centers [19, 20], there are no systematic studies regarding the characterization of charged matrices themselves, *i.e.* how the structure of the pore is affected by the presence of charge centers, or the role of temperature in the matrix structure. In this paper, we investigate the case when porous matrices are constructed with and without a template charged media.

Knowing the structure of porous matrices will allow us, for instance, to characterize the matrix porosity. In experimental areas this property, for example, is of great importance for studies of adsorption. Moreover, these studies can also give insight about the free volume available in the porous matrix. Therefore, diffusion of adsorbed fluids as in experiments of diffusion of ions through zeolites can be studied. However, due to the parameters used in the present work, there is not a straightforward comparison with real experiments. Nevertheless, simulations with appropriate parameters, and studies of adsorbed ionic fluids are being conducted in our group now.

2. Computational method and model

The model to prepare the porous matrices consisted of particles placed in a cubic box of lengths $X=Y=Z=12.59921\sigma$. There are in total $2N$ charged particles of equal diameter, half of them with charge $+q$, and the other half with charge $-q$, embedded in a structureless solvent with dielectric constant ϵ_m . Therefore, particles are able to interact among each other with short- and long-range forces. The short-range forces were given by the Lennard Jones potential (LJ),

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where σ is the diameter of the particle and ϵ is the well depth of the LJ potential.

The long-range forces were given by the coulomb potential

$$U_{coul}(r) = \frac{1}{4\pi\epsilon_m\epsilon_0} \frac{q_i q_j}{r^2} \quad (2)$$

where ϵ_0 is the vacuum permittivity, q_i and q_j are the charge of particles i and j respectively. Hereafter, it is assumed that $\epsilon_m=80.0$ (water dielectric constant). The total potential energy is the contribution of both terms, *i.e.* $U = U_{LJ} + U_{coul}$. In order to compare the effects of the electrostatic potential on the matrix preparation, we chose the same LJ potential of previous works, and we added the long-range interaction. Periodic boundary conditions (in the X-Y and Z directions) were used in all the simulations. All calculations were given in reduced units defined in terms of the LJ parameters [21], energy $U^* = U/\epsilon$, distance $r^* = r/\sigma$, temperature $T^* = KT/\epsilon$, density $\rho^* = \rho\sigma^3$, etc. with the parameters for argon, $\epsilon/KT = 119.8$ and $\sigma = 3.405 \text{ \AA}$. Simulations were carried out using the Molecular Dynamics (MD) method [21] where the electrostatic interactions were handled by using the Ewald summation. For the short-range potential we used a cutoff of $r = 4.5\sigma$

Then, the preparation of the pore matrices was conducted by two methods.

Method I. In this procedure a template was not used, and we prepared two systems with different densities, *i.e.* $\rho_m^* = 0.3$ and 0.5 . The number of particles were chosen in order to have half of them positive and half of them negative, *i.e.*, the total charge of the system was zero. The total number of particles were 600 and 1000 for $\rho_m^* = 0.3$ and 0.5 , respectively. The chosen densities were the same as those given in a previous paper [17], so we can make comparisons of the present results with the previous ones. Each system was run for 50 000 time steps in an MD simulation after equilibration. The final matrix structure was obtained by stopping all the particles, and by keeping the last configuration.

Method II. In this method template particles were used, and we prepared the matrices with the same densities as described above. However, in this case, the matrices were prepared from a binary mixture of identical components, *i.e.* the two species had the same LJ parameters. In order to differentiate the components of the mixture we used labels where the species 1 was the template fluid and the species 2 was the matrix. In order to have a neutral system, half of the particles of the species 1 were negative and the other half were positive. The same arrangement was imposed for the particles of the species 2. Moreover, the number of particles of the specie 1 was kept constant (the density of this specie was always $\rho_t^*=0.3$) in the box. The initial system configuration consisted of random particles of the species 1 located in the box. Then a different number of particles of the species 2 were randomly added to have two binary mixtures with total densities $\rho^* = 0.8$ and 1.0 . The final porous matrix configuration was obtained by removing the template particles (the

first specie). Therefore, we had two disordered matrices with densities $\rho_m^* = 0.3$ and 0.5 .

Simulations were carried out at different temperatures. In order to compare the results, and to determine the effects of the electrostatic interactions in the matrix preparation, the temperature values were chosen to be the same as those used in previous works [17]. However, in this case the phase diagram of the system is unknown (to the best of our knowledge we did not find any reported data). Therefore, it is not possible to determine where in the phase diagram the chosen temperatures are. In the literature, only the phase diagram of charged hard spheres (primitive model) [22], and the phase diagram of a system with a square well potential and electrostatic interactions [23] were found.

3. Results

In the next subsections we present the results obtained from our simulations. The structure and the porosity of the matrices are analyzed in terms of the preparation method.

3.1. Matrix structure

The matrix structure was analyzed by investigating the voids in the matrix, *i.e.* the vacancies or empty spaces between the matrix particles. For this study, we employed the Voronoi-Delaunay tessellation method using the “*Qhull*” algorithm [24]. This method has been used to study voids (structure), or free volume of LJ and hard spheres fluids [25–27]. As in our previous paper [17], we evaluated the vertices of Voronoi polygons to define all the void centers in the box. The size of a void was calculated by growing up a sphere (increasing its radius) from the void center until it overlapped with a matrix particle. Therefore, the volume of a void (V_{cav}) was expressed in terms of the volumes of spheres of different diameters. The x-axis in most figures is given in terms of $\ln(V_{vac}^*)$ to enhance features.

In Fig. 1, the void size distribution for all the different matrices is shown in terms of the reduced volume V_{cav}^* . From the figure, the formation of very small volumes (less than a particle volume, $V_{\sigma}^* < 0.5$) is observed in the matrix. One possible explanation of this result can be given in terms of the potential interaction. Particles with attractive interactions can approach each other without touching. Consequently, we have pairs of particles which can be slightly separated for more than one particle diameter from their centers leading to small empty spaces between them. Therefore, these spaces can not be considered as real voids or free accessible volumes in the matrix structure. Even more, from our void definition we cannot directly relate those with porous cavities. Nevertheless, the data can give us valuable information about the free volumes, and their distribution in the porous matrices. The figure shows the results for matrices with densities $\rho_m^* = 0.3$ and $\rho_m^* = 0.5$ prepared at temperature $T^* = 0.8$. When matrices of the same density are prepared with and without template, the distributions are quite

different. The percentages of volumes larger than V_{σ}^* are 61.6%, and 10.4% for matrices prepared with and without template, respectively. Nevertheless the matrix without template presents the largest void ($V_{cav}^* = 187$) in contrast with the matrix with template ($V_{cav}^* = 164$). The same trend is observed for matrices with $\rho_m^* = 0.5$, where volumes larger than V_{σ}^* are 13.8%, and 3.0% for matrices prepared with and without template, respectively. Here, the largest volumes are $V_{cav}^* = 82$ and $V_{cav}^* = 6.4$ for matrices without and with template, respectively.

The pore structure of the matrix as a function of the temperature was analyzed in Figs. 2 and 3. Figure 2 corresponds to a matrix ($\rho_m^* = 0.3$) prepared with template. At low temperatures the distribution presents two peaks, while a single

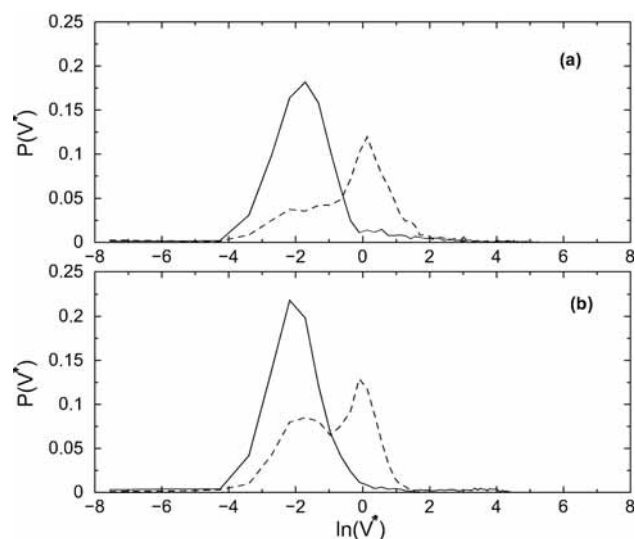


FIGURE 1. Void size distributions of matrices at $T^* = 0.8$ with density a) $\rho_m^* = 0.3$ and b) $\rho_m^* = 0.5$. Solid lines are for matrices without template and dashed lines for matrices with template.

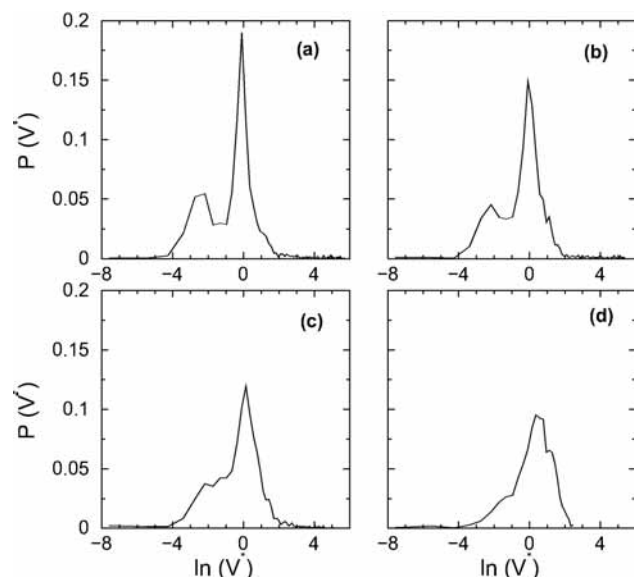


FIGURE 2. Void size distributions of matrices at $\rho_m^* = 0.3$ prepared with template. a) $T^* = 0.3$, b) $T^* = 0.5$, c) $T^* = 0.8$ and d) $T^* = 1.5$.

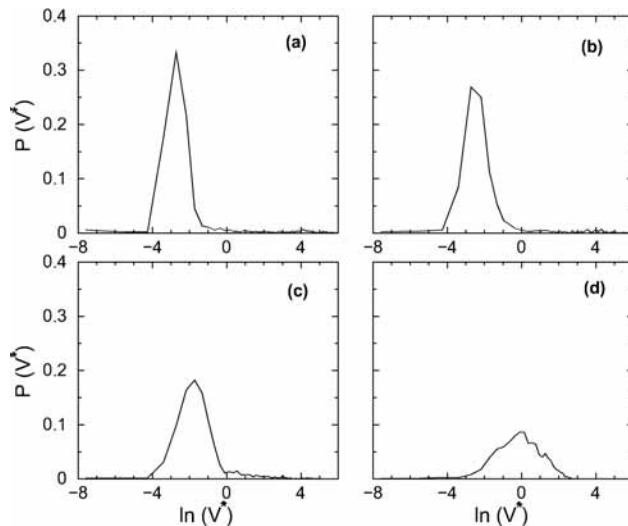


FIGURE 3. Void size distributions of matrices at $\rho_m^* = 0.3$ prepared without template. a) $T^* = 0.3$, b) $T^* = 0.5$, c) $T^* = 0.8$ and d) $T^* = 1.5$.

distribution is observed at higher temperatures. It seems that low temperatures produce small cavities, although they are much smaller than V_σ^* (*i.e.* they are not really accessible volumes). Nevertheless, those matrices also present the largest voids, $V_{cav}^* = 298$ and $V_{cav}^* = 210$ for $T^* = 0.3$ and $T^* = 0.5$, respectively. As the matrix formation temperature increases, the matrix forms a single peak with smaller voids compared to those at lower temperature, $V_{cav}^* = 164$ and $V_{cav}^* = 11.5$ for $T^* = 0.8$ and $T^* = 1.5$, respectively. From the graphs of Fig. 2, it is obvious that changes in temperature form quite different porous structures. If the same matrix (with $\rho_m^* = 0.3$) is prepared without a template different features are observed (Fig. 3). All distributions have one single peak which is located at volumes lower than V_σ^* . The position of the peak becomes shorter, and shifts to a larger volume than V_σ^* as the temperature increases. Larger voids are observed in matrices prepared at low temperature. The volumes are $V_{cav}^* = 446, 392, 185$ and 16 for $T^* = 0.3, 0.5, 0.8$ and 1.5 , respectively. Therefore, the results suggest that at low temperatures the particles of the matrices form compact structures leading to larger voids in the system compared to those matrices prepared at high temperature. At high temperatures the matrix particles present higher mobility (higher kinetic energy), and they are probably more uniformly distributed in the simulation box than those at low temperature. As a consequence, larger voids are present.

The formation of possible clusters of particles were also studied. A cluster was defined as those matrix particles which are close to each other for less than two atomic diameters. In all the cases the matrices form one set of particles, *i.e.*, a single cluster. These results indicate that the main difference of using or not template particles to prepare the matrices is the shape of the final cluster. When a template is not used, the matrix particles are closer to each other leading to large voids. On the other hand, when a template is used, the matrix particles are more uniformly distributed forming smaller cav-

ities in the system. The results are in agreement with those of the volume distribution. In Fig. 4, porous matrix structures are shown for matrices ($\rho_m^* = 0.3$ and $T^* = 0.8$) prepared with charges with and without template. When a template is used particles are more uniformly distributed in the simulation cell.

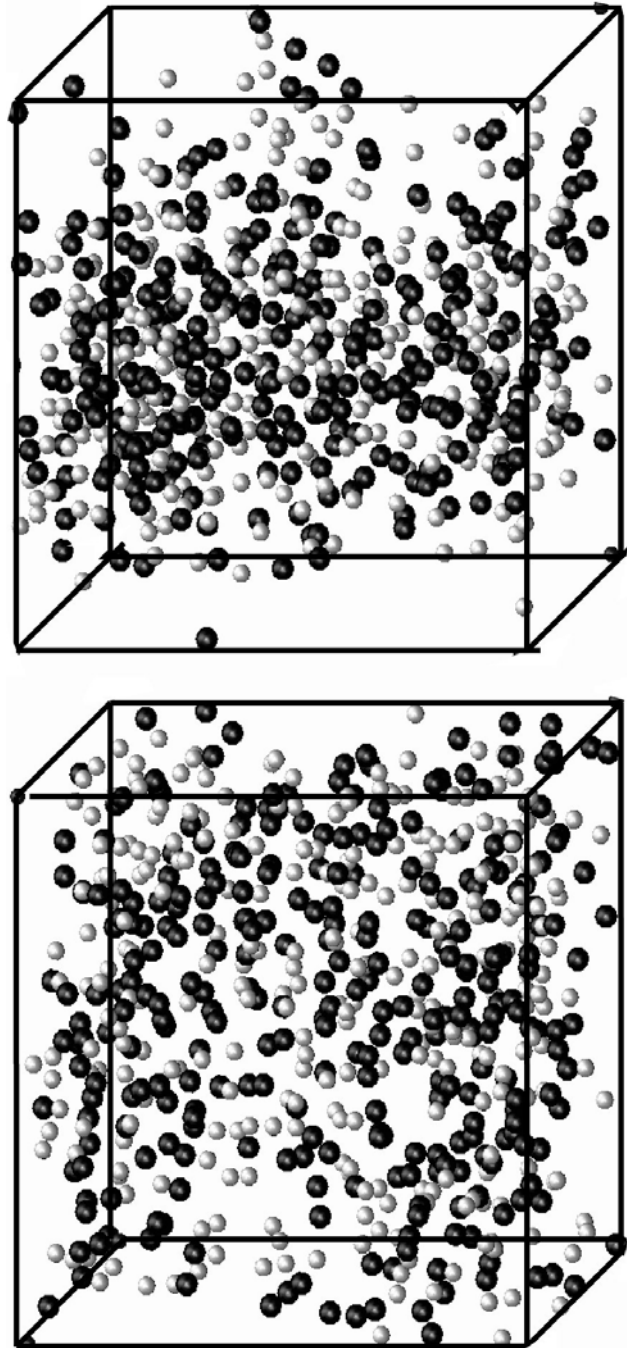


FIGURE 4. Snapshots of two characteristic charged matrix configurations ($\rho_m^* = 0.3$ and $T^* = 0.8$) prepared with (bottom) and without (top) template. Black particles are positive charges and white particles are negative charges.

3.2. Matrix Porosity

A quantity commonly measured in these systems is the porosity. From the previous results, it is expected that the porosity in the matrix might be altered due to the matrix structure, *i.e.* the preparation method. The porosity of the systems was measured by random insertions of a test spherical particle of diameter σ_t into the matrix configuration, and any overlap with the matrix particles was checked. Then, the porosity was calculated as the ratio

$$P = \Phi_0 / \Phi \quad (3)$$

where Φ was the total number of insertions, and Φ_0 was the number of no-overlaps.

It is worth mentioning the importance of porosity in studies of absorption of different fluids in porous matrices. Therefore, the porosity was calculated using different test size particles since different fluids can have distinct molecular diameters. As in previous analyse the matrix particles are completely frozen, *i.e.* we took the last configuration of the particles after a long simulation run as described in previous sections. Figure 5 shows the values of the porosity as a function of the temperature for a matrix (with $\rho_m^* = 0.3$) prepared with template. The general trend in all cases is the reduction of the porosity as the temperature increases as it is expected. The porosity decreases as the test particle diameter increases. However, when the matrix is constructed with template the porosity seems to decay uniformly for the range of temperatures studied. On the other hand, if a template is not used (Fig. 6), the porosity only decreases uniformly up to temperatures around $T^* = 1.0$, then it decreases drastically. It is also interesting to observe in matrices without template a uniform decrease of the porosity as the test particle diameter increases. This is true for temperatures lower than $T^* = 1.0$, whereas for higher temperatures from test particles with $\sigma_t = 0.6$ to $\sigma_t = 1.0$, the porosity changes drastically. The same drastic change in the porosity is observed for test particles from $\sigma_t = 1.0$ to $\sigma_t = 1.4$.

To study the effects of the electrostatic interactions on the matrix porosity, other matrices (with the same density) were prepared but without electrostatic interactions. Figure 5 also shows the results for matrices ($\rho_m^* = 0.3$) prepared with template at different temperatures (solid lines). It is noticed that at low ($T^* = 0.3, 0.5$), and high ($T^* = 1.5$) temperatures the values of the porosity are nearly the same. However, the difference in the matrix porosity of matrices with and without electrostatic interactions increases at intermediate temperatures. Furthermore, independently of the size of the test particle, the porosity is always higher in matrices with electrostatic interactions. In Fig. 6, the same information is shown, but for matrices prepared without template. Similar trend is observed, *i.e.*, the porosity is higher in matrices prepared with electrostatic interactions than in matrices without electrostatic interactions. However, even though the values of the porosity are nearly the same at low and high temperatures, in such case the difference in the porosity at interme-

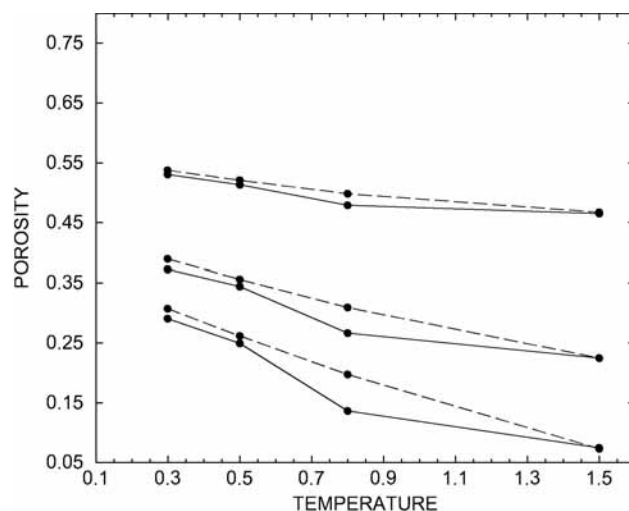


FIGURE 5. Comparison of matrix porosities as functions of temperature for matrices ($\rho_m^* = 0.3$) without (solid lines) and with (dashed lines) electrostatic interactions. Matrices were prepared with template for different test particle diameters, σ_t^* . From top to bottom $\sigma_t^* = 0.6, 1.0$ and 1.4 , respectively. The lines are just given to guide the eye.

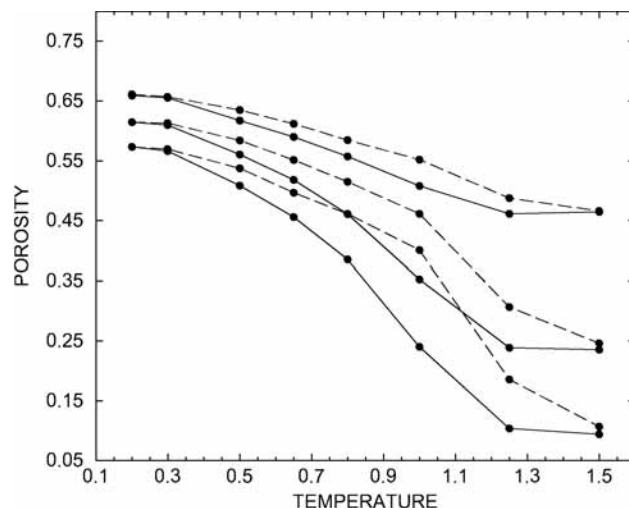


FIGURE 6. Comparison of matrix porosities as functions of the temperature for matrices ($\rho_m^* = 0.3$) without (solid lines) and with (dashed lines) electrostatic interactions. Matrices are prepared without template for different test particle diameters, σ_t^* . From top to bottom $\sigma_t^* = 0.6, 1.0$ and 1.4 , respectively. The lines are just given to guide the eye.

diated temperatures is large compared to that in matrices with template as described in Fig. 5.

3.3. Conclusions

A series of computer simulations to study the structure of porous matrices prepared with and without template particles and with electrostatic interactions was performed.

The structure of the different pore matrices was studied in terms of the cluster formation, and the void volume distributions in the matrices. Simulations were carried out at

different temperatures, and in two different matrix densities. A cluster analysis revealed in all cases that the matrix particles were always connected forming a single cluster. Nevertheless, the form of the cluster seems to be different for each matrix whether a template is used or not. By using template the matrix particles are closer to each other in such a way, that the maximum void size is smaller than in those matrices without template.

As a general trend, matrices prepared without template present higher porosity than those with template regardless of the matrix interaction. It is also observed that as the temperature increases the matrix porosity decreases. All these results indicate that templating plays an important role in the pore matrix structure. An important feature from the results is the comparison of these matrices with those calculated without electrostatic interactions. A series of simulations to study the porosity were conducted to investigate the charge effects in the matrix formation. The results were obtained at different temperatures, and it was observed that the porosities are slightly higher in matrices prepared with electrostatic interactions than in those prepared without electrostatic interactions. However, the porosity of a matrix with and without electrostatic interactions (at the same matrix density) were quite similar at low and high temperatures within our temperature range. We must recall, that the phase diagram of these charged fluids is not known. It could be possible that the high temperatures are too high above the critical point

and therefore, the electrostatic interactions did not play an important role. Consequently, the matrices with and without Coulomb interactions were quite similar. This could explain the results of the porosity at high temperatures. At low temperatures, even though the electrostatic interactions are more important, the temperatures are too low and therefore, the particles might have a solid-like behavior. Therefore, when matrices were prepared with and without electrostatic interactions at low temperature, the particles showed small displacements, and the arrangement was nearly the same (with similar voids), and consequently the porosity is similar for both matrices.

Finally, as it was mentioned before, these studies will help us to understand better the adsorption of ionic fluids. For example, diffusion of ionic fluids in zeolites has shown that changing the charge of the diffusing particles the diffusivity decreases by orders of magnitude. This effect can be explained by possible traps created by matrix particles during the preparation method [19]. Therefore, simulations of adsorbed fluids in that direction are being performed in our group at this time.

Acknowledgments

We acknowledge the support from DGAPA, UNAM through grant IN113201 and CONACyT-Mexico through grant 37323E

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