

Estimation of the effective diffusion coefficients in open zeolite coatings

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Abstract

The effective medium theory (EMT), describing diffusion in random composite media, was tested for its suitability to be used in the estimation of the effective diffusion coefficient of water in the inhomogeneous open zeolite 4A coatings prepared by the substrate heating method. The solid zeolite matrix and the void regions distributed in the matrix were taken as the two different phases in the system. The diffusion coefficient values obtained were compared to those determined in a previous study by the help of an experimental method involving the coupled use of thermogravimetric analysis and mathematical modeling. The estimated diffusivities, which increased with increasing void fraction, were in good agreement with the experimentally determined values.

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1. Introduction

Zeolite coatings are potentially useful in various application areas, such as adsorption, separation, catalysis, sensing, etc. [1–3]. An outstanding feature of the zeolite coatings is that they provide compact systems that may eliminate possible heat and mass transfer limitations. Adsorption heat pumps, which may be used for heat management, is one example where the employment of zeolite coatings can improve the performance of the system significantly [4]. The heat transfer limitations originating from the lack of good physical contact at the metal–adsorbent interface and the generally low thermal conductivity values of the adsorbent beds in conventional adsorption heat pumps may be removed to a great extent by using zeolite coatings synthesized on metal supports. Resistance to mass transfer, depending on the magnitude of the diffusion coefficient value of the adsorbate in the adsorbent and the thickness of the adsorbent bed, may be avoided by using the optimum coating thickness, which maximizes the useful effect obtained from the adsorption heat pumps. The optimum thickness of the zeolite 4A coatings grown on metal heat exchanger tubes was determined to be in the range of 25–150 μm , depending on the wall thickness of the heat exchanger tubes and the operating conditions employed [5,6]. The thicknesses in

this range may be regarded to be quite thin when compared to the height of the conventionally used beds of adsorbent in powder form [7] but they are too thick to be prepared by using the commonly employed one step direct synthesis methods.

Zeolites are metastable and their phase transformations make the preparation of relatively thick zeolite coatings difficult. This difficulty may be overcome by using the substrate heating method, which suppresses the reaction in the bulk and promotes that on the substrate by applying a temperature difference between the reaction mixture and the substrate [8]. In this method, the substrate is heated directly while the bulk of the reaction mixture is kept at a lower temperature. As a result of suppressed activity in the bulk, the composition of the solution remains nearly constant. The phase transformations are, therefore, delayed for extremely long periods of time and growth of zeolite coatings of various thicknesses on metal supports may be achieved. An interesting observation was that the coatings prepared by the substrate heating method exhibited differences in their nature originating from their growth under a thermal gradient. The inhomogeneities in the coating thickness at earlier times of synthesis resulted finally in an accessible sponge-like structure. No difficulty was observed for the desorption of water vapor out of even the relatively thick zeolite 4A layers prepared by using the substrate heating method [9]. This observation was further confirmed by the measurements carried out to estimate the effective diffusion coefficients of the coatings [10]. An increase of about four folds was determined in the effective

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diffusion coefficient values of the zeolite 4A coatings, as the equivalent layer thickness was increased from 20 to 140 μm .

Homogeneous and compact coatings are generally expected to be obtained when conventional synthesis methods are employed. As a result, in general, continuous coatings are assumed in modeling studies. In case an inhomogeneous open texture exists, though, effective thermal conductivity and diffusion coefficient values different than those pertaining to continuous coatings may be obtained. In this study, the EMT equation, which may describe diffusion in random composite media, was tested for its suitability to be used in the estimation of the effective diffusion coefficient values of water in the inhomogeneous open zeolite 4A coatings, containing non-zeolite macrovoids, prepared by the substrate heating method. The solid zeolite and the void regions were taken as the two different components of the system investigated. The effective diffusion coefficient values estimated were compared to those obtained experimentally in a previous study by the help of a method involving the coupled use of thermogravimetric analysis and mathematical modeling. The possible effects of pressure and temperature on the effective diffusion coefficient values of water in the zeolite 4A coatings were also investigated.

2. Theoretical

Different theoretical models exist for predicting the permeation or diffusion behavior of molecules in composite materials [11]. In some of these models, analogies are made to electrical circuits, in which resistances may be placed in different arrangements, in series, in parallel or as a combination of the two. The series and parallel models represent limiting cases where the dispersed and continuous phase resistances are assumed to be arranged in series and in parallel, respectively. The Maxwell model represents an arrangement involving a dilute suspension of spheres in a matrix and generally estimates a permeability/diffusivity value in between those determined by the series and the parallel models. The geometrical mean model is an exponential fit of the diffusivity versus zeolite volume fraction plot, and may be a simple alternative to describe effective diffusivity.

2.1. EMT model for the estimation of effective diffusivity in composite materials

The effective medium theory (EMT) has been developed by Landauer [12] for the estimation of the overall conductivity of a multiphase material. It assumes a random distribution of the different phases and replaces the actual inhomogeneous medium with a homogeneous effective medium. EMT may be applied to a variety of situations, including conduction in inhomogeneous binary metallic mixtures [12], in disordered metal–nonmetal solutions [13], in random networks [14], etc. Davis extended the effective medium theory to account for mass transfer in the presence of possible concen-

tration gradients between the distinct phases of a composite material [15]. According to the EMT model, the effective diffusivity may be expressed as:

$$D_e = \left(\frac{D_2}{k} \right) \left(\frac{1}{(1 + \varepsilon(1 - k)/k)} \right) \left(a + \left(a^2 + \frac{1}{2}kx \right)^{1/2} \right) \quad (1)$$

where

$$a = \frac{1}{4}(3\varepsilon - 1 + kx(2 - 3\varepsilon)) \quad (2)$$

$$x = \frac{D_1}{D_2} \quad (3)$$

$$k = \frac{C_1}{C_2} \quad (4)$$

D_e , D_1 and D_2 represent the effective diffusivity and the diffusivities in the two distinct components in the system, respectively. ε_1 and ε_2 denote the volume fractions of the different components in the multiphase material and may be replaced by $1 - \varepsilon$ and ε , respectively. k is a measure of the distribution of the diffusing species between the components of the composite material. C_1 and C_2 denote the concentrations of the species in the different regions. When k is equal to 1, a uniform distribution of the diffusing species exists in the material. A significant assumption of EMT is that the neighborhood of a certain region in a mixture can be treated as a uniform medium having a conductivity or diffusivity that characterizes the mixture [12]. In other words, there should exist no correlation between the positions of the different types of regions.

It has been shown that the evolution of zeolite coatings prepared by the substrate heating method can be simulated quite reasonably when it is assumed that the process of nucleation takes place in a random manner, initially on the substrate and later at the available immediate top, bottom, right or left of an existing particle (or growing nuclei). Thus, in this study, the effective medium theory, which assumes a random distribution of the phases constituting a multiphase material, was used to estimate the effective diffusion coefficient of water in the zeolite 4A coatings prepared by using the substrate heating method. The zeolite coatings were assumed to consist of the solid zeolite matrix and void regions distributed in the matrix. The subscripts 1 and 2 in the equations were used to indicate the solid zeolite and void regions, respectively. Due to the very open natures of the zeolite coatings, totally closed void regions were assumed to be of negligible amount in these materials. In other words, the void regions were assumed to have a connection to the atmosphere and to consist of air and water vapor. The intracrystalline diffusion coefficient of water at 300 K in zeolite 4A was taken from the literature ($D_1 = 6.2 \times 10^{-7} \text{ cm}^2/\text{s}$) [16] while the molecular diffusivity of water vapor at 300 K in air was calculated by using the Chapman–Enskog equation ($D_2 = 0.212 \text{ cm}^2/\text{s}$) [17]. The effective diffusion coefficients

were calculated by using Eqs. (1)–(4) and the results obtained were compared to those determined experimentally in a previous study, in which the TGA method, involving the use of TGA and a mathematical model, had been used to determine the diffusivities of zeolite coatings [10]. In that study [10], the diffusivities of coatings with different nature and thickness had been investigated but no theoretical analysis of the data had been carried out.

2.2. The TGA method

The effective diffusivities of zeolite coatings may be determined by using the TGA method. In this method, as a first step, the amount of water loss in the zeolite coatings is determined as a function of time by using a thermogravimetric analyzer. Then, the operation of the thermogravimetric analyzer is simulated by the help of a simple mathematical model, consisting of energy and mass balances, as well as the initial and boundary conditions corresponding to the experimental operating conditions in the system investigated. The operating conditions in the model should be the same as those used in the experiments.

The system consists of a metal (stainless steel) plate plus the zeolite layer synthesized on the metal surface, placed vertically in the oven of the thermogravimetric analyzer. The energy balances for the metal plate and zeolite layer are represented by the following differential equations, respectively:

$$\frac{\partial^2 T}{\partial z^2} = \left(\frac{1}{\alpha_m} \right) \frac{\partial T}{\partial t} \quad (5)$$

$$\frac{\partial^2 T}{\partial z^2} - \Delta H_{\text{ad}} \left(\frac{\partial C_A}{\partial t} \right) \frac{\rho_{\text{dz}}}{k_z} = \left(\frac{1}{\alpha_z} \right) \left(\frac{\partial T}{\partial t} \right) \quad (6)$$

In these equations, α represents the thermal diffusivity while ρ_{dz} and ΔH_{ad} denote the density of the dry zeolite and the heat of adsorption, respectively. C_A is the concentration of water in the zeolite. The boundary conditions pertaining to the energy balance assume that at both the metal–TGA ambient and the zeolite–TGA ambient interfaces, the amount of heat transferred by conduction is equal to that transferred by convection while at the zeolite–metal interface, conduction fluxes and the temperatures of the adsorbent and the metal plate are equal. The mass balance for the zeolite layer is expressed as follows:

$$\frac{\partial^2 C_A}{\partial z^2} = \left(\frac{1}{D_e} \right) \left(\frac{\partial C_A}{\partial t} \right) \quad (7)$$

D_e represents the effective diffusivity value of the adsorbate in the zeolite. The boundary conditions pertaining to the mass balance assume that the concentration gradient for the adsorbate is zero at the zeolite–metal interface while the equilibrium concentration value exists at the zeolite–ambient interface.

The energy and mass balances together with the initial and boundary conditions are solved to determine both the

temperature and concentration gradients across the zeolite layer and the temperature gradient across the metal plate in the direction representing the thickness of the zeolite coating. As a result, the amount of adsorbate in the zeolite coating may be predicted as a function of the temperature of the TGA ambience and the operation time. A certain heating rate (e.g. 20 °C/min) should be used to raise the temperature of the zeolite samples from ambient (20 °C) to a higher temperature (350 °C) in the model similar to the experiments performed with TGA. In the calculations, the temperature dependencies of the effective diffusion coefficients pertaining to different samples are assumed to be similar to that of the intracrystalline diffusivity of water in zeolite 4A.

The concentration values, obtained as a function of time and temperature from the TGA measurements by using a relatively thin zeolite 4A film of up to 20 µm thickness, for which diffusion limitations are negligible, may be employed as the equilibrium surface concentration values at different operation times and temperatures for the different cases investigated.

In the procedure carried out for the determination of the diffusion coefficient, first, the amounts of adsorbate desorbed from the relatively thicker zeolite coatings (44–140 µm) are determined by TGA measurements. Then, the variation of the concentration values with respect to time is computed for the same coatings for different effective diffusivity values by using the mathematical model. Finally, the effective diffusion coefficient of water in the zeolite coatings is determined from the model by taking into consideration the diffusivity value that allows the theoretical determination of the experimentally observed variation of water concentration with time. The portion of the TGA curves corresponding to a water concentration range of 0.18–0.28 g/g zeolite, exhibiting relatively high dehydration rates, should be employed in the estimations to reduce possible effects that may originate from experimental errors.

When zeolite coatings of very open and inhomogeneous natures, are taken into consideration, it is difficult to represent their thickness by a single value. One good approach seems to be using an equivalent thickness for these coatings. The zeolite 4A coatings prepared by using the substrate heating method are very open, hardly allowing for totally closed void regions in the system. Thus, in the previous study mentioned above [10], the equivalent thickness of the coatings, which may be determined as (mass of zeolite deposited per coated area of the substrate)/(density of zeolite 4A), had been employed in the mathematical model.

2.3. Properties of the coatings utilized

Zeolite coatings prepared at various synthesis times on stainless steel substrates and in some cases, with an additional treatment which involves the application of a ramp in the solution temperature at the end of the synthesis experiments, were employed in the TGA measurements

performed previously [10]. The synthesis conditions utilized corresponded to 18, 48 and 72 h of synthesis without treatment and 27, 48 and 72 h of synthesis with the additional treatment (t). The thicknesses of the coatings prepared under different conditions increased in the order: 18, 48, 27(t), 48(t), 72 and 72(t). The details of the preparation of the zeolite 4A coatings had been given in the related study [10]. The same coatings were taken into consideration in this study for the estimation of their effective diffusion coefficients by using the EMT equation.

2.4. Determination of the values of parameters in the EMT equation

In the first part of the calculations carried out, the ambient pressure was taken to be equal to 1 atm, in accordance with the operating conditions of the TGA experiments performed previously, while the temperature was assumed to be equal to 300 K. The variations of the effective diffusion coefficient values of the coatings with temperature and pressure were also investigated.

As a first approach, a value of 1 was used for k in the EMT model. Since a flow system was utilized in determining the experimental diffusivities and also since the coatings had open structures, there seems to be no significant restriction concerning the amount of water vapor in air and, thus, the partitioning of water vapor in the zeolite and void regions mainly depends on the relative ease of mass transport within the zeolite and desorption occurring from the zeolite at the zeolite–void interfaces. It is known that the mass transport in porous adsorbents is generally controlled by diffusion within the pore network, rather than the kinetics of sorption at the surface [18]. Thus, the adsorbate is not expected to encounter any special difficulty in using the void regions in the zeolite coatings, rationalizing the use of 1 for the k value in the EMT model. Additionally, in order to show the changes that may occur in the effective diffusivities when closed void regions are significant in the coatings and/or a flow system is not used, a relationship was obtained from the literature to determine the ratio of the concentration of water in the zeolite and water vapor [19]. Accordingly, for coatings with closed void regions, a k value of 260 was estimated by assuming a concentration of 0.28 g water/g zeolite 4A at 25 °C [20]. The k value is expected to change only slightly in the operational range used to estimate the diffusivity values in the TGA method. It may be observed from the ideal gas law and the adsorption isotherm of zeolite 4A for water that as the temperature is increased, the concentration of water in the vapor phase and in the zeolite decrease by rather similar amounts.

The void fractions of the zeolite coatings were determined from the information on the equivalent and the actual measured average coating thicknesses. The equivalent coating thicknesses had been reported previously [10]. The actual coating thicknesses of the same coatings, on the other hand, were measured in this study by using a micrometer. Due

to the inhomogeneous texture of the coatings, the measured thickness values generally vary to some extent. A proper number of measurements were carried out to determine the actual average thicknesses, in order to minimize the errors. In other words, at least 16 measurements were carried out and new measurements were performed till the difference between the last two estimates for the average thickness decreased below 1%.

3. Results and discussion

Examples of the inhomogeneous sponge-like zeolite 4A coatings prepared by the substrate heating method may be seen in Fig. 1(a and b). Fig. 1(a and b) shows the SEM pictures of the coating grown after 72 h of synthesis followed by the additional treatment mentioned before. In the figures, the side views close to the outer layers of the coatings are given at different magnifications.

The equivalent thicknesses of the zeolite 4A coatings and the corresponding void fractions determined by the help of the actual coating thicknesses are depicted in Fig. 2. It may be observed from the figure that the highest void fraction of the coatings obtained by using the synthesis conditions investigated in this study was equal to about 0.25. Coatings with different void fractions were obtained by using different synthesis conditions. For the thicker coatings prepared at longer synthesis times and/or by using an additional treatment, the void fraction increased. This may indicate that the EMT equation, which requires a random distribution of the phases and hence a homogeneous effective medium, may remain insufficient in some cases to predict the effective diffusion coefficients of the zeolite coatings prepared by the substrate heating method. However, it is also observed that the rate of the increase in porosity with increasing thickness slowed down to a large extent for the relatively higher thicknesses. It seems that initially the zeolite coating was relatively more dense. In this study, the effects that may originate from the presence of relatively denser regions of the zeolite coating forming initially were neglected in the estimation of the effective diffusion coefficient values.

3.1. Estimation of effective diffusivity by EMT

The EMT equation, represented by Eq. (1), was employed to estimate the effective diffusion coefficient of water in the zeolite 4A coatings prepared by the substrate heating method. k values of 1 and 260 were used in the EMT equation. The variations of the effective diffusivity with respect to the void fraction and equivalent thickness of the coatings are shown in Figs. 3 and 4, respectively. The effective diffusion coefficient values of water in zeolite 4A coatings estimated by the experimental TGA method [10] are also given in the figures for comparison. The TGA method had also been used to determine the diffusivity of water in a consolidated powder zeolite 4A sample with negligible void

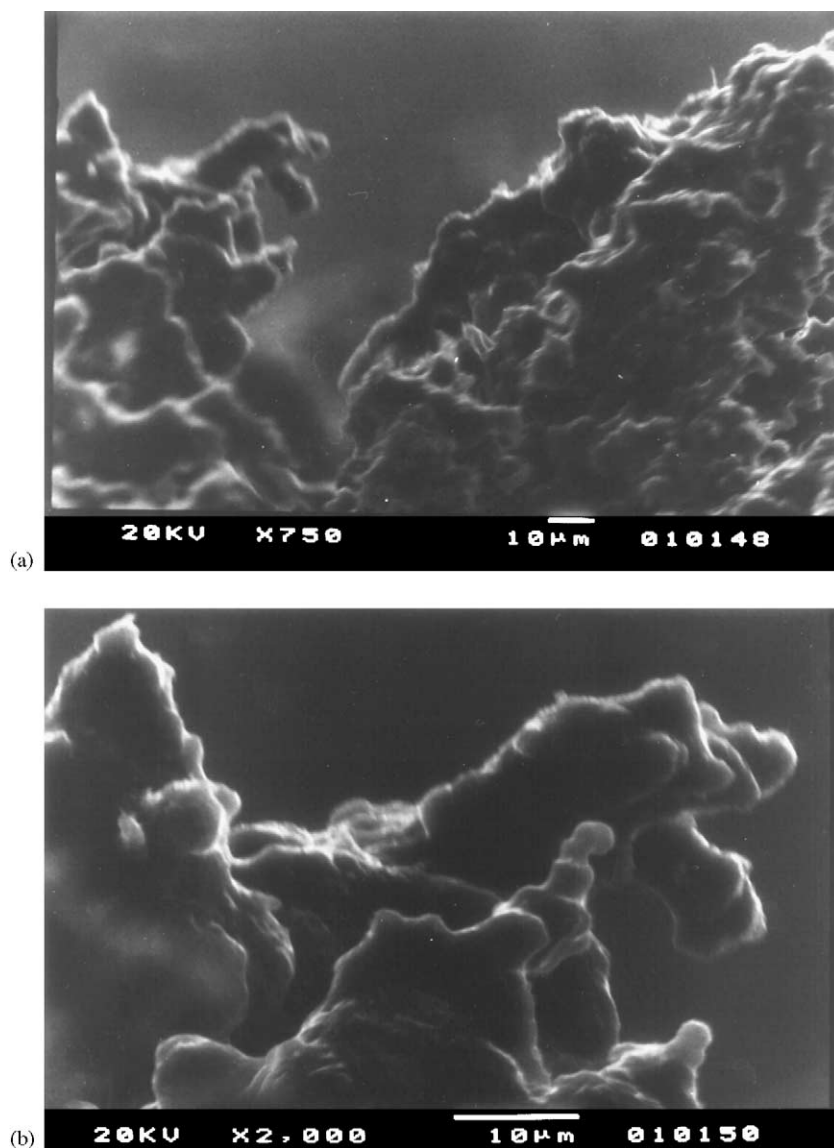


Fig. 1. SEM pictures of the inhomogeneous coatings grown after 72 h of synthesis followed by an additional treatment.

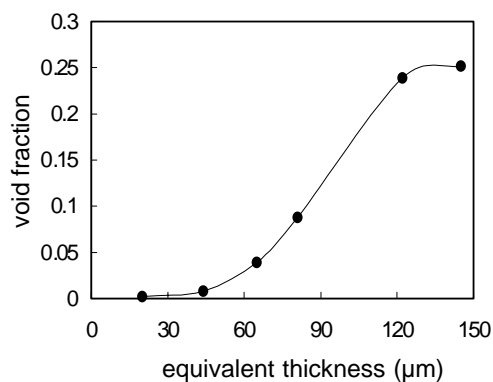


Fig. 2. The relationship between the equivalent thicknesses of the zeolite 4A coatings and their void fractions.

fraction [10]. The result obtained had been compared to that measured by PFG NMR [16]. Both values are shown in Figs. 3 and 4. The diffusion coefficients correspond to the same temperature (300 K) and pressure (1 atm) values for all the cases investigated. As shown in the figures, the magnitudes of the diffusivities determined by the TGA method for the consolidated sample—as well as for the coatings of very low void fractions—are quite comparable with that obtained from the well-known PFG NMR method.

It may be observed from the figures that the effective diffusivity of water in the zeolite coatings estimated from the EMT equation increased with the increasing void fraction and equivalent thickness of the coatings. The EMT estimates fitted experimental data quite well, especially when k was taken to be equal to 1. As mentioned before, the zeolite coatings prepared by the substrate heating method are quite open in nature, thus, a k value of 1 seems to be

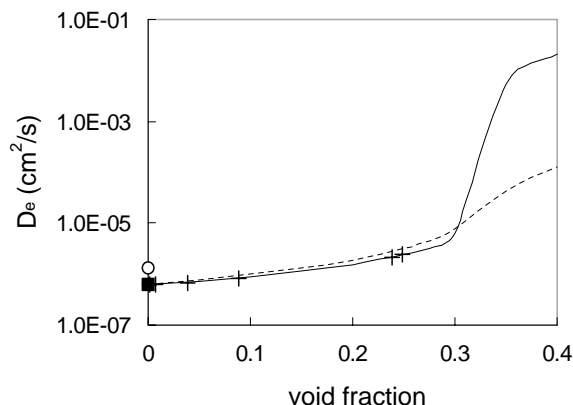


Fig. 3. The variation of the effective diffusivity of water in zeolite 4A coatings with respect to the void fraction in the coatings when k in the EMT equation is equal to (—) 1 and (---) 260. (+) represents the experimental effective diffusivities obtained for the same coatings by using the TGA method [10]. (■) and (○) denote the intracrystalline diffusivity of water in zeolite 4A, as measured by TGA [10] and PFG NMR [16] methods, respectively.

reasonable for the system investigated. The good agreement existing between the diffusivities determined by the experimental method and the EMT equation tended to disappear only slightly as the value of k was increased from 1 to 260. Further calculations were performed to determine the k value at which the diffusivity values estimated from the EMT model exhibit the smallest amount of deviation from those obtained by the TGA measurements. As a result, it was established that the minimum amount of deviation ($\approx 3.8\%$) is obtained at a k value very close to unity, that is, at 1.2. In case k is taken to be equal to 1, the amount of deviation increases only slightly and attains a value of about 4.4%.

The sudden increase in the diffusivity values estimated by EMT at a void fraction of about 1/3, as shown in Fig. 3, is also in accordance with the previous experimental findings. This probably indicates that the percolation limit is at-

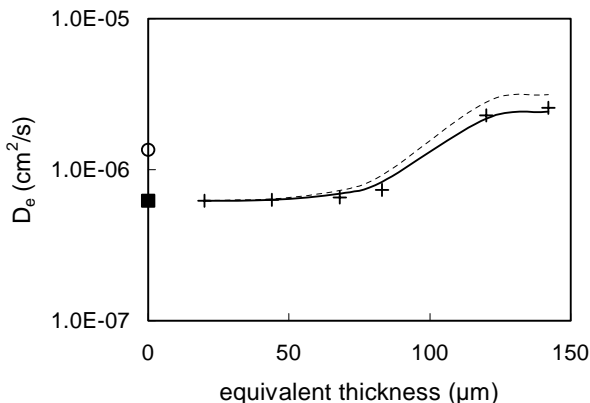


Fig. 4. The variation of the effective diffusion coefficient of water in zeolite 4A coatings with respect to the equivalent thickness of the coatings. Legend as in Fig. 3.

tained at a void fraction of about 1/3. It is known that the connectivity of a structure disappears above the percolation limit, thus, the preparation of continuous zeolite coatings with void fractions higher than 1/3 does not seem possible. As mentioned before, the highest void fractions of the coatings prepared by using the substrate heating method at the synthesis conditions investigated up to now remained at about 0.25. It should be noted that, below the percolation limit, which depicts the coating thickness range of actual practical significance, the differences between the EMT diffusivity estimates obtained by using k values of 1 and 260 were quite moderate. The difference became significant only above the percolation threshold, where using a k value of 1 resulted in quite higher diffusivities. This may be rationalized by considering that at a k value of 1, which represents a uniform partitioning of the diffusing species in the material, the disconnected state of the coatings resulted in the removal of the limitations imposed by the zeolite diffusivity on the effective diffusion coefficient which was observed when the zeolite pathways in the coatings were connected.

As mentioned before, it may be possible that initially the zeolite coatings prepared by the substrate heating method are relatively more compact and homogeneous. Hence, the distribution of the voids in the coatings may not be truly random. However, the good agreement between the diffusivities obtained experimentally and by using the EMT equation, which assumes a random distribution of the different phases in a multiphase material, indicates that the assumption made in this study, neglecting the effects originating from the presence of relatively denser regions in the zeolite coatings, is reasonable.

3.2. Estimation of effective diffusivity by different models

Theoretical models other than EMT seem to be insufficient to explain the variation of the effective diffusivity of water in open zeolite A coatings with the increasing void fraction of the coatings. The arrangements of the different phases in a composite material implied by the series and parallel models do not seem possible to represent open zeolite coatings. The diffusivities predicted by the geometrical mean and Maxwell models [11] do not seem to fit experimental data, either, especially, at the relatively high void fractions. For the zeolite coating having a void fraction of about 0.25, for example, the geometrical mean model estimates a diffusivity of about six folds higher than the experimentally determined value while the Maxwell model predicts a value of about two folds lower. Actually, at the relatively high void fractions, the latter model predicts a very small amount of increase in the diffusivity compared to the intracrystalline diffusion coefficient of water in zeolite 4A. These observations indicate the superiority of the EMT model over other models available in the literature. The good prediction in the relatively thick and more open zeolite coatings by this model is especially significant.

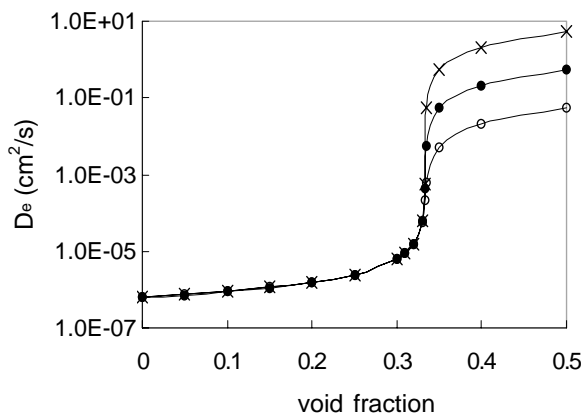


Fig. 5. The variation of the effective diffusion coefficient of water in zeolite 4A coatings, as estimated by EMT, with respect to the void fractions of the coatings when the pressure is equal to: (×) 0.01 atm; (●) 0.1 atm; (○) 1 atm.

3.3. Effects of pressure and temperature on effective diffusivity as estimated by EMT

The variations of the effective diffusion coefficient of water in zeolite 4A coatings, as estimated by the EMT equation, with respect to the void fractions of the coatings were also investigated for different pressure and temperature values. The possible variations in the intracrystalline diffusivity of water in zeolite 4A with changes in concentration were neglected. Fig. 5 represents the case where the pressure was varied. In this case, the k and temperature values were kept constant at 1 and 300 K, respectively. It may be observed that lowering the pressure leads to an increase in the effective diffusion coefficients only above a void fraction of about 1/3, in other words, above the percolation threshold. Below the percolation threshold, on the other hand, no significant change is observed. Thus, taking into consideration the fact that stable coatings cannot be prepared with void volumes above the percolation limit, it may be deduced that the employment of zeolite 4A coatings in different pressure environments, such as under sub-atmospheric pressures, will not lead to any significant change in the mass transfer characteristics of the coatings. The variation of the effective diffusion coefficient of water in the zeolite 4A coatings prepared by using the substrate heating method with respect to the void fraction is depicted in Fig. 6 for different temperatures. In this case, the k and pressure values were kept constant at 1 and 1 atm, respectively. It may be observed from the figure that the effective diffusivities increase at higher temperatures, for void fractions both below and above the percolation threshold. Below the percolation limit, the effective diffusivity increases by factors of about 3 and 1.8 as the temperature is increased from 200 to 300 K and from 300 to 400 K, respectively. Magnitudes of the effective diffusivities of the coatings for void fractions below the percolation threshold are mainly determined by

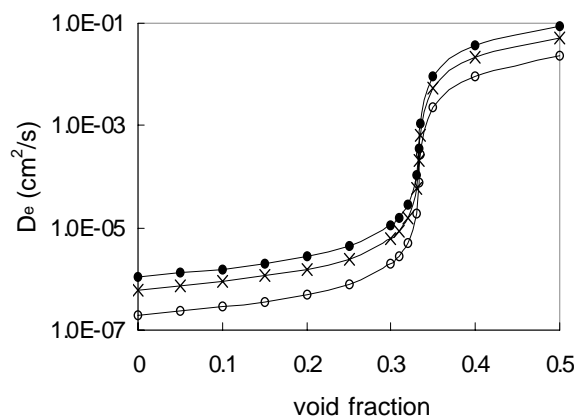


Fig. 6. The variation of the effective diffusion coefficient of water in zeolite 4A coatings, as estimated by EMT, with respect to the void fractions of the coatings when the temperature is equal to: (○) 200 K; (×) 300 K; (●) 400 K.

the intracrystalline diffusion coefficient of water in zeolite 4A. Thus, in this region, the increase observed in the effective diffusion coefficient with temperature is mainly related to the temperature dependency of the intracrystalline diffusivity.

4. Conclusions

The effective diffusion coefficients of water in the inhomogeneous open zeolite 4A coatings prepared by the substrate heating method were estimated by using the EMT equation, which assumes a random distribution of the different phases constituting a multiphase material. The estimated diffusivities increased with the void fractions of the coatings and were in good agreement with those determined experimentally in a previous study by using the TGA method, especially when k was taken to be equal to 1. This signifies an equal partitioning of water vapor in the zeolite and void regions. The good agreement existing between the diffusivities determined by the experimental method and the EMT equation tended to disappear slightly as the value of k was increased from 1 to 260. It may be concluded that the effective medium theory is a reliable method to be used in the determination of the effective diffusion coefficient values of the inhomogeneous open zeolite 4A coatings whenever the void volumes of the coatings are known, or vice versa.

Lowering the ambient pressure in the estimations carried out by using the EMT equation resulted in higher effective diffusion coefficients above a void fraction of about 1/3, which seems to represent the percolation threshold for the zeolite coatings. Below the percolation threshold, no significant change was observed. The effective diffusivities increased at higher ambient temperatures, for void fractions both below and above the percolation threshold.

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