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## ADSORPTION EQUILIBRIUM AND EFFECTIVE DIFFUSIVITY IN CYLINDRICAL ALUMINA PARTICLES IMPREGNATED WITH CALCIUM CHLORIDE

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### Abstract

Adsorption equilibrium and effective diffusion coefficients of water vapor, in cylindrical particles of activated alumina (A) and activated alumina impregnated with calcium chloride (MCA), are experimentally determined. The experiments were conducted at 303 K and 323 K using cylindrical particles with 2.5 mm in both length and diameter. Diffusion coefficients were determined from the kinetics of water sorption. The measurements were conducted in a constant pressure unit based on a magnetic suspension balance (Rubotherm) under isothermal conditions. The sorption capacity depends on temperature and it was found to be higher by 25 % for the MCA material compared with the A material. The water diffusion coefficient depends itself on the adsorption equilibrium taking into account the local slope of the water sorption isotherm. The effective diffusivity of water is almost 2 times lower in impregnated than in non-impregnated alumina. The obtained diffusion data could be used to model the dynamic adsorption.

*Key words:* adsorption equilibrium, composite alumina - calcium chloride, effective diffusion coefficient

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### 1. Introduction

Adsorption processes are encountered at a wide scale in industry for gas separation and purification, for humidity control, for environmental protection etc. To calculate and design the adsorption apparatus, equilibrium and diffusion data are needed. In literature, several experimental methods to determine the equilibrium and diffusion coefficients in porous materials are presented (Figueiredo and Matos Freitas, 2013; Igwe et al., 2013; Luis et al., 2014; Mamaliga et al., 2009; Mamaliga et al., 2010; Simonova et al., 2009; Terzyk and Gauden, 2002; Witek-Krowiak, 2013). Studies of adsorption kinetics of water vapors in porous materials offer information to design and operate air conditioning and gas purification plants (Aristov et al., 2006; Simonova et al., 2009; Solomon et al., 2013). Porous alumina

particles are obtained by dehydration of alumina hydrates (commonly  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), in controlled temperature conditions, up to approximately 6 percent moisture content. The surface has stronger polarity than silica gel and has both acid and basic characteristics, reflecting the amphoteric nature of aluminum. At room temperature, the affinity of activated alumina for water is comparable to the affinity of silica gel, but the adsorption capacity is lower. At elevated temperatures, activated alumina has a higher adsorption capacity than silica gel. Thus, activate alumina is used as drying agent for water vapor and is also employed for removal of polar gases from hydrocarbon streams.

Analytical solutions to Fick's second law of diffusion for the kinetics of adsorption in planar sheet, spherical and cylindrical adsorbents, are well known, but the numerical applications are limited

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because the solutions are given as infinite series. In various studies (Terzyk and Gauden, 2002; Terzyk et al., 2003) a method to determine diffusion coefficient within cylindrical and spherical carbon granules was developed. They expressed diffusion coefficient as a function of normalized adsorption for spherical adsorbents. For cylindrical adsorbents, the diffusion coefficient was defined in normalized adsorption using both the cylinder length and radius. In this paper, we give a practical approach to adsorption kinetics for cylindrical adsorbents.

Time dependent adsorption for a finite cylinder with radius  $R$  and length  $L$  is given as (Carslaw and Jaeger, 2005; Crank, 1979) (Eq. 1):

$$\frac{q_t}{q_{max}} = 1 - \left( \frac{4}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{R^2}\right) \right) \times \left( \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{2m-1} \exp\left(-\frac{\pi^2 (2m-1)^2 Dt}{L^2}\right) \right) \quad (1)$$

where  $q_t$  and  $q_{max}$  are the quantities retained at time  $t$  and, respectively, at saturation,  $D$  is the effective diffusion coefficient and  $\alpha_n$  are roots of the zero-order Bessel function:  $J_0(\alpha_n)=0$ .

Eq. (1) is computationally exact, but cannot be conveniently used in practical numerical valuation.

The expression for adsorption within a finite cylinder could be obtained using the expressions for adsorption within an infinite cylinder and an infinite planar sheet. An expression for adsorption within an infinite planar sheet of  $L$  thickness is given as (Carslaw and Jaeger, 2005; Crank, 1979) (Eq. 2):

$$\frac{q_t}{q_{max}} = 1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{2m-1} \exp\left(-\frac{\pi^2 (2m-1)^2 Dt}{L^2}\right) \quad (2)$$

A solution for small  $Dt/L^2$  can be obtained in the form of (Carslaw and Jaeger, 2005; Crank, 1979) (Eq. 3):

$$\frac{q_t}{q_{max}} = 4 \left( \frac{Dt}{\pi L^2} \right)^{0.5} + 8 \left( \frac{Dt}{L^2} \right)^{0.5} \sum_{m=1}^{\infty} (-1)^m ierfc\left( \frac{mL}{2D^{0.5}t^{0.5}} \right) \quad (3)$$

where  $ierfc(y)$  is the integral of the error function  $erfc(y)$ , and,  $ierfc(y) = \exp(-y^2)/\pi^{0.5} - y \operatorname{erfc}(y)$ .

For  $Dt/L^2 < 0.08$ , the second part of Eq. (3) is negligible, so the equation becomes (Eq. 4):

$$\frac{q_t}{q_{max}} = 4 \left( \frac{Dt}{\pi L^2} \right)^{0.5} \quad (4)$$

For adsorption in an infinite planar sheet, Rong and Vadgama (Rong and Vadgama, 2006) derived the Eq. (5):

$$f_{i,s} = \frac{a_t}{a_{t,max}} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{L^2}\right) \quad (5)$$

valid for  $t > 0.05326L^2 / D$ ,  $a_t / a_{t,max} > 0.52$ , and (Eq. 6):

$$f_{i,s} = \frac{a_t}{a_{t,max}} = \frac{4}{L} \left( \frac{Dt}{\pi} \right)^{0.5} \quad (6)$$

for  $t < 0.05326L^2 / D$ ,  $a_t / a_{t,max} < 0.52$ .

The diffusion coefficient is calculated from the half time of saturation as (Eq. 7):

$$D = 0.04908 \frac{L^2}{t_{0.5}} \quad (7)$$

A similar equation at the adsorption in an infinite cylindrical granule is given as (Eq. 8):

$$\frac{a_t}{a_{t,max}} = 1 - 4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{R^2}\right) \quad (8)$$

where:  $R$  is the granule radius and  $\alpha_n$  are roots of the zero order Bessel function:  $J_0(\alpha_n)=0$ .

At the adsorption in an infinite cylinder, for small dimensionless time ( $Dt/R^2$ ), Eq. (8) becomes Eq. (9):

$$\frac{a_t}{a_{t,max}} = \frac{4}{R} \left( \frac{Dt}{\pi} \right)^{0.5} - \frac{Dt}{R^2} - \frac{(Dt)^{1.5}}{3\pi^{0.5}R^3} \quad (9)$$

For the adsorption in an infinite cylinder, a bipartite expression can be obtained (Eq. 10):

$$f_{i,c} = \frac{a_t}{a_{t,max}} = 1 - 4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{R^2}\right) \quad (10)$$

valid for  $t > 0.03598L^2 / D$ ,  $a_t / a_{t,max} > 0.3908$ , and (Eq. 11):

$$f_{i,c} = \frac{a_t}{a_{t,max}} = \frac{4}{R} \left( \frac{Dt}{\pi} \right)^{0.5} - \frac{Dt}{R^2} - \frac{(Dt)^{1.5}}{3\pi^{0.5}R^3} \quad (11)$$

for  $t < 0.03598L^2 / D$ ,  $a_t / a_{t,max} < 0.3908$

The diffusion coefficient is calculated from the half time of saturation as (Eq.12):

$$D = 0.06306 \frac{R^2}{t_{0.5}} \quad (12)$$

The equation for adsorption within a finite cylinder is (Rong and Vadgama, 2006) (Eq. 13):

$$f_{f,c} = f_{i,s} + f_{i,c} - f_{i,s}f_{i,c} \quad (13)$$

For our particular cylindrical granule, with radius  $R=1.25 \text{ mm}$  and length  $L= 2.5 \text{ mm}$ , Eq. (13) is a function of the product  $D \times t$  and, the apparent diffusion coefficient,  $D$ , can be estimated from the half adsorption time as (Eq. 14):

$$D_{ap} = \frac{4.6 \cdot 10^{-8}}{t_{0.5}}, m^2 / s \quad (14)$$

Further, the effective diffusion coefficient can be calculated using the equation (Aristov et al., 2006) (Eq. 15):

$$D_e = D_{ap} \frac{\varepsilon + (1 - \varepsilon)K}{\varepsilon}, m^2 / s \quad (15)$$

where:  $\varepsilon$  is the material porosity and  $K$  is the local slope of the adsorption isotherm.

In this paper, we present an experimental study on water vapor equilibrium and diffusion in alumina (A) and composite material (MCA) cylindrical particles.

## 2. Experimental part

### 2.1. Materials

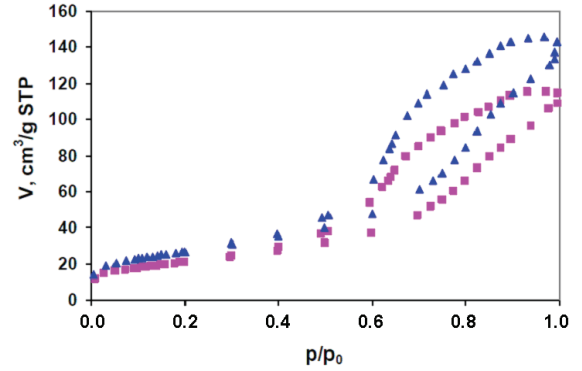
Two different materials were used in our experiments, namely: activated alumina (A) and activated alumina impregnated with a calcium chloride solution (MCA) (Table 1). The materials consist of cylindrical granules of 2.5 mm diameter and length. The porous matrix was dried in an oven for 4 hours, at 160°C, and left afterwards to cool down in a dessicator, at room temperature.

The composite material was obtained by impregnating alumina with a calcium chloride solution of 15% mass, at 25 °C, in a stirring vessel, at a rotation of 300 rpm. After 2 hours of impregnation, each sample of porous material was separated from the salt solution by vacuum filtration, at room temperature. The retained granules were again dried for 4 hours in an oven, at 160°C, and left to cool down in a dessicator, at room temperature. The resulting  $\text{CaCl}_2$  impregnated alumina (MCA) had a salt content of 7.92%. The nitrogen adsorption-desorption isotherms obtained for A and MCA materials correspond, according to the IUPAC classification, to the Type IV isotherm with hysteresis.

**Table 1.** Characteristics of the materials used in the experimental study on water vapor equilibrium and diffusion

Materials	Total specific surface ( $m^2/g$ )	Total porosity (%)	Pore diameter (nm)
A	96.275	64.133	5.390
MCA	43.339	37.153	5.517

One can observe that in the pressure range when the adsorption monolayer is formed, the two curves presented in Fig. 1 have an identical behavior, of Type II isotherm. An enhanced adsorption is registered at higher vapor pressures, fact corresponding to the capillary condensation in mesopores.



**Fig. 1.** Sorption isotherms for  $\text{N}_2$  in cylindrical granules of A and MCA materials

### 2.2. Experimental set up

In order to obtain the experimental equilibrium data and diffusion coefficients a magnetic suspension balance system (Rubotherm, Germany, accuracy  $\pm 0.1 \text{ mg}$ ) was used. This allows the measurement of the material mass variation in time. The scheme of the experimental set-up was presented in previous works (Mamaliga, 2004; Mamaliga et al., 2004; Mamaliga et al., 2010). The investigated material was situated on a support suspended by the hook of magnetic coupling. Mass was measured using a balance (Sartorius:  $210 \text{ g} \pm 0.1 \text{ mg}$ ). Adsorption experiments were carried out at constant temperature and different pressure values in an adsorption cell. Pressure in the adsorption cell was controlled by means of the evaporating water and was measured with a pressure sensor.

The amount of solvent absorbed is very small, thus the buoyancy forces at different pressures are important and were taken into account (Mamaliga et al., 2010).

### 2.3. Experimental protocol

To determine the diffusion coefficient, experiments were led as follows:

1. The porous material was placed into the adsorption cell and dried under vacuum (pressure lower than 0.5 mbar) until a constant mass is obtained. The temperature in sorption cell is maintained at a certain value by means a thermostat.

2. Temperature in the water evaporator is adjusted and maintained to a prescribed value.

3. Water vapors will be kept in contact with the porous material until adsorption equilibrium is

reached. The mass variation of adsorbent material is recorded in time.

4. In order to start a new experiment, parameters such as the evaporator temperature or water vapor pressure would be adjusted. Each experiment gives a point on the equilibrium isotherm.

### 3. Results and discussion

An example of adsorption kinetics at 303 K, for the same sample of MCA, at two different water vapor pressure values, successively applied is given in Fig. 2. For the investigated materials, kinetic curves were obtained at different values of water vapor pressure. From these plots was determined the half time of diffusion ( $t_{0.5}$ ), used to calculate the apparent diffusion coefficient. Using Eq. (14), apparent diffusion coefficient for cylindrical granules of A and MCA was calculated. Values obtained at a temperature of 323 K and at various pressures of water vapors are shown in Fig. 3.

Equilibrium isotherms, expressed in two different ways, for the investigated materials at an adsorption temperature of 323 K, are presented in Fig. 4. The slopes of adsorption isotherms, K, are determined from Fig. 4b. The amount of water uptake and the slope K of MCA is significantly higher (20-25 %) than for activated alumina (A). The local slope K is presented in Table 2.

With these values and taking into account material porosities (Table 1), the effective diffusion coefficients were calculated based on Eq. (15). The MCA values at a temperature of 323 K, in comparison with those obtained for diffusion in activated alumina (A), are shown in Fig. 5. At low vapor pressure, the effective diffusion coefficients are almost constant and for alumina decrease slightly from values of vapor pressure in the range 60-120 mbar.

Analyzing data shown in Fig. 5, it can be seen that the water vapor effective diffusion coefficient values in activated alumina (A) are higher than in composite materials. The presence of calcium chloride modifies the porous structure of alumina and the pore distribution. The effective diffusion coefficients in the composite material are almost 60 % lower than those obtained in non-impregnated alumina. The difference between the values of effective diffusion coefficients could be attributed to the unequal contributions of the three transport mechanisms (bulk, Knudsen and surface diffusion) occurring in the materials.

For the MCA material, an average effective diffusion coefficient has been determined to have a value of  $8.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ . For activated alumina, the effective diffusion coefficient values were lower at higher vapor pressures. This could be due to the sorption mechanism changes and occurrence of phenomena such as capillary vapor condensation. Thus, the obtained values are closer to the liquid diffusion coefficients. The temperature influence on

the sorption isotherms for the MCA material is presented in Fig. 6 (a, b).

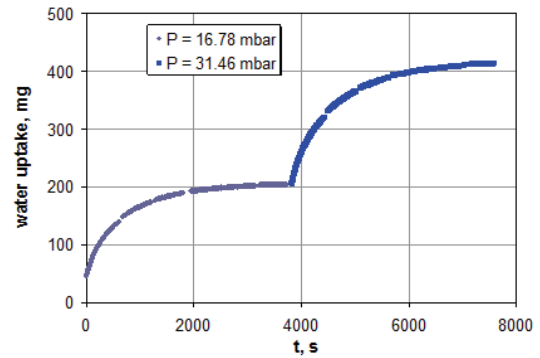


Fig. 2. Water uptake at 303 K in cylindrical MCA granules (diameter and length of 2.5 mm) at two values of water vapor pressure, 16.78 and 31.46 mbar

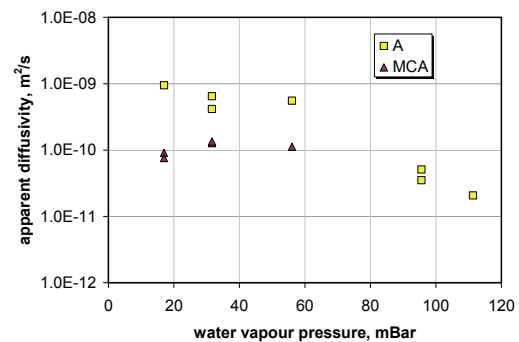


Fig. 3. Apparent diffusion coefficient of water vapors in A and MCA at 323 K

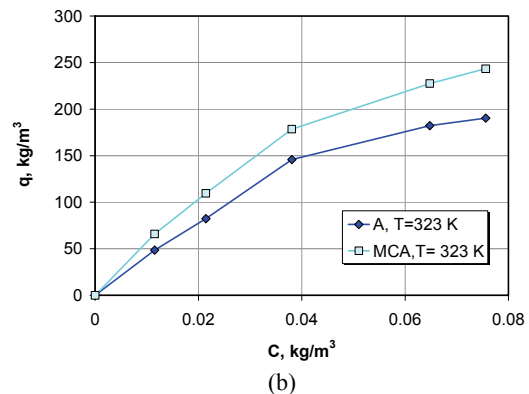
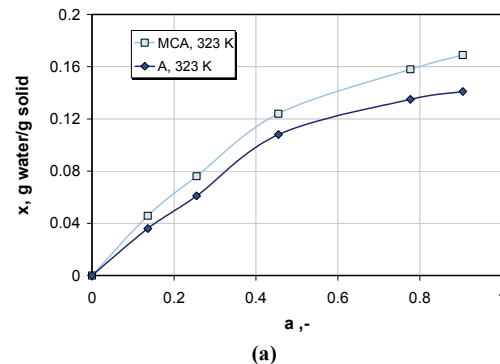
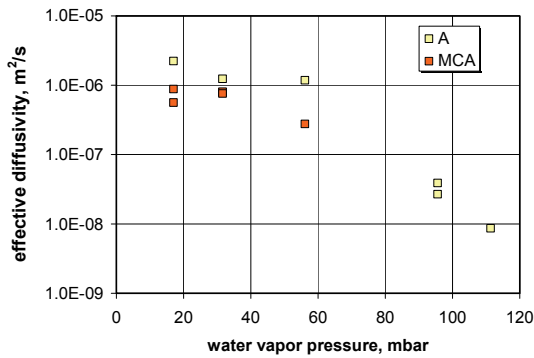


Fig. 4. Sorption isotherm for A and MCA materials at 323 K

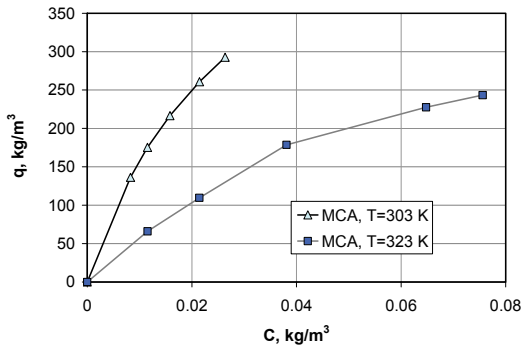
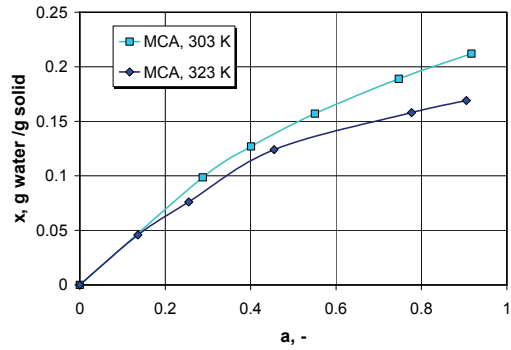
The diffusion data obtained at water vapor adsorption on MCA granules at a temperature of 303 K are presented in Table 3. It includes, also, the local slopes determined from Fig. 6b. In Fig. 7 the temperature influence on the effective diffusion coefficients for the MCA material is presented.

**Table 2.** Sorption Equilibrium (slope K) at 323 K

Water vapor pressure, mbar	A Local slope, K	MCA Local slope, K	Water activity, -
16.97	4216.7	5722.2	0.138
31.57	3403.6	4400.1	0.257
56.07	3813.1	4145.2	0.456
95.37	1365.6	1834.3	0.777
111.32	747.7	1462.2	0.905



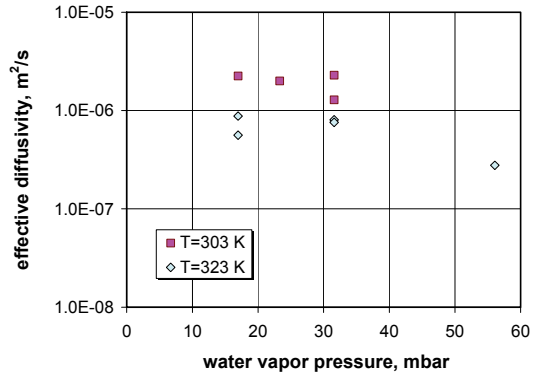
**Fig. 5.** Effective diffusion coefficients of water vapors in A and MCA at 323 K



**Fig. 6.** Sorption isotherms for the MCA material at 303 K and 323 K

**Table 3.** Diffusion data for MCA at a sorption temperature of 303 K

Water vapor pressure, mbar	Apparent diffusivity, m²/s	Local slope, K	Effective diffusivity, m²/s
16.97	8.177E-11	16450	2.2421E-06
23.29	7.272E-11	12028	1.99397E-06
31.6	8.345E-11	9637	2.28786E-06
31.6	4.694E-11	9637	1.28692E-06



**Fig. 7.** Effective diffusion coefficients of water vapors in MCA at two temperatures

Analyzing data shown in Fig. 7, it can be seen that the water vapor effective diffusion coefficient values in the MCA material at 303 K are higher than values at 323 K. This could be explained based on an increase in vapor viscosity with temperature.

**4. Conclusions**

Effective diffusion coefficients of water vapors in cylindrical granules of activated alumina (A) and activated alumina impregnated with calcium chloride (MCA) were determined.

Experiments were performed at 303 K and 323 K granules having the same diameter and length (2.5 mm). The experiments were conducted at constant vapor pressure by means of a technique based on a magnetic suspension balance (Rubotherm, Germany). The apparent diffusion coefficient was determined from half time of diffusion. The effective diffusion coefficients depend on the apparent diffusion coefficients, the local slopes of the sorption isotherms and the material porosities.

For the impregnated alumina, the effective diffusion coefficients are almost 60 % lower than for non – impregnated activated alumina. The temperature has a certain influence on the vapor diffusion coefficients.

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