

Characterization of Water Vapour Diffusion into Spherical Silica Gel Particles

IOAN MAMALIGA^{1*}, WILHELM SCHABEL², STELIAN PETRESCU¹

¹ Technical University of Iasi, Department of Chemical Engineering, 71 Mangeron Blv., 700050, Iasi, Romania

² Institute of Thermal Process Engineering- Thin Film Technology, Karlsruhe Institute of Technology (KIT), D-76131, Karlsruhe, Germany

Effective diffusion coefficients of water vapour in pure and calcium chloride and lithium bromide impregnated silica gel particles have been experimentally determined. The experiments were carried out at 323 K using spherical particles with 3.57 mm in diameter. Diffusion coefficients were determined from experimental registration of water sorption kinetics. The measurements were performed in a constant pressure unit based on a magnetic suspension balance (Rubotherm) under isothermal conditions. The apparent water diffusivity depends itself on the adsorption equilibrium taking into account the local slope of the water sorption isotherm. The effective diffusivity of water is almost three times lower in impregnated silica gel than in non-impregnated silica gel.

Keywords: diffusions coefficients, composite silica gel - calcium chloride, lithium bromide

Adsorption processes are widely employed at industrial scale for gas separation and purification. In literature are presented several experimental determination methods for diffusion coefficients in porous materials [5]. Studies of adsorption kinetics of water vapors in porous media offer useful information for designing and optimizing of air conditioning and gas purification plants [1,6]. A relatively high number of studies performed by using silica gel or various types of zeolites as adsorbents emphasize that adsorption rates are influenced by the diffusion of water vapors into adsorbent pores [3,5]. The effective diffusion coefficient, D_e , includes three different transport mechanisms: molecular, Knudsen and surface diffusion [3]. For measuring the effective diffusion coefficient, several methods were proposed [5].

Diffusion of a penetrant into porous spherical particle can be described by the equation [5]:

$$(1-\varepsilon)\frac{\partial q}{\partial t} + \varepsilon\frac{\partial C}{\partial t} = \varepsilon D_e \left(\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (1)$$

where:

D_e is the effective diffusion coefficient;

ε - material porosity;

q - adsorbate concentration in solid phase;

C - adsorbate concentration in gas phase.

If the concentration variation is low, equilibrium relationship can be considered linear:

$$\frac{\partial q}{\partial t} = K \frac{\partial C}{\partial t} \quad (2)$$

with $K = K(C_0) = \text{constant}$. Equation (1) becomes:

$$(1-\varepsilon)K \frac{\partial C}{\partial t} + \varepsilon \frac{\partial C}{\partial t} = \varepsilon D_e \left(\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (3)$$

or:

$$\frac{\partial C}{\partial t} = \frac{\varepsilon D_e}{\varepsilon + (1-\varepsilon)K} \left(\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (4)$$

Initial and limiting conditions are as follows:

$$C(R_p, 0) = C_0, \quad q(R_p, 0) = q_0;$$

$$C(R_p, \infty) = C_\infty, \quad q(R_p, \infty) = q_\infty;$$

$$\left. \frac{\partial C}{\partial R} \right|_{R=0} = \left. \frac{\partial q}{\partial R} \right|_{R=0} = 0,$$

where R_p is the particle radius.

The solution of equation (4) is given by [2]:

$$\begin{aligned} \frac{m}{m_\infty} = \frac{q - q_0}{q_\infty - q_0} &= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2 \pi^2 (\varepsilon D_e / (\varepsilon + (1-\varepsilon)K)) t}{R_p^2}\right) = \\ &= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2 \pi^2 D_{ap} t}{R_p^2}\right) \end{aligned} \quad (5)$$

where:

$$D_{ap} = \varepsilon D_e / (\varepsilon + (1-\varepsilon)K) \quad (6)$$

q is the quantity adsorbed at time t , and K is the slope of adsorption isotherm.

A simplified equation valid for the beginning of diffusion is given by [5]:

$$\frac{m}{m_\infty} \approx \frac{2A}{V} \sqrt{\frac{D_{ap} t}{\pi}} = S \sqrt{t} \quad (7)$$

where A and V represent particle surface area and volume respectively. In case of spherical particles:

$$2A/V = 3/R_p.$$

From equation (7) it can be obtained:

$$S = \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_{ap}}{R_p^2}} \quad (8)$$

which represent the curve slope obtained by representing graphically m/m_∞ as a function of $t^{0.5}$.

* e-mail: imamalig@ch.tuiasi.ro; Tel.: 0040 749 036662

Table 1
PROPERTIES OF USED MATERIALS

Characteristics	Material composite		
	Silica gel		
	(SSB)	MCSS1 Silica gel with CaCl ₂	MCSS2 Silica gel with LiBr
Pore volume, cm ³ /g	0.381	0.362	0.372
Pore mean diameter, nm	2.39	2.21	2.17
BET specific area, m ² /g	664.9	645.1	642.3
Hygroscopic salt concentration, weight %	-	5.57 % CaCl ₂	7.1 % LiBr
Bulk density, kg/m ³	798.7	841.6	864.1

If the particle radius and curve slope (S) at the initial time are known, the apparent diffusion coefficient, D_{ap} , can be calculated with the relationship:

$$D_{ap} = \frac{\pi}{36} R_p^2 S^2 \quad (9)$$

Further, the effective diffusion coefficient can be calculated with the relationship:

$$D_e = D_{ap} \frac{\varepsilon + (1-\varepsilon)K}{\varepsilon} \quad (10)$$

where ε is the material porosity and K is the slope of adsorption isotherm.

The characterization of water vapour diffusion in spherical grains of silica gel and two composite materials (MCSS1, MCSS2), obtained by impregnating silica gel with calcium chloride (MCSS1) and lithium bromide (MCSS2) respectively, are the paper aim. Diffusion coefficients of water vapours in spherical grains were determined using kinetic adsorption-desorption curves. Experiments were carried out at temperatures of 323 K. In order to measure the quantity of water adsorbed on the porous material, it was employed a gravimetric technique based on a magnetic suspension balance (Rubotherm, Germany).

Experimental part

Materials used in experiments

Spherical silica gel grains having a diameter of 3.57 mm and spherical grains of composite materials having the same diameter were used in the experimental investigations of water vapour adsorption. Composite

materials were obtained by impregnating silica gel in aqueous solution of calcium chloride and respectively aqueous solution of lithium bromide. Experiments were performed at temperatures 323 K. Different properties of the employed materials are shown in table 1.

Experimental set-up

In order to perform the experimental determination of diffusion coefficients it was employed an installation provided with a magnetic balance (Rubotherm, Germany), which determines the material mass with an accuracy of ± 0.1 mg [4, 7].

The experimental set-up is presented in figure 1. The main components of the installation are represented by adsorption cell (1), magnetic suspension coupling (2), analytic balance (3), evaporator (4) and a data acquisition system (9). The temperature in evaporator and adsorption cell was measured and adjusted with an accuracy of ± 0.1 K, while the absolute pressure in evaporator and adsorption cell was measured using pressure transducers having an accuracy of 0.1 %. The adsorption cell consists in a stainless steel recipient having a diameter of 35 mm and a height of 110 mm. Temperature in the sorption cell is maintained at a constant value by means of thermostat (5).

The porous material was placed on a plane support suspended by the hook of magnetic coupling. The temperature in evaporator was maintained by means of cryostat (7) with an accuracy of ± 0.1 K. Mass was measured using balance (3) (Sartorius: 210 g \pm 0.1 mg). Adsorption experiments were carried out at constant temperature and various values of pressure in the adsorption cell. Pressure in adsorption cell was controlled by means of evaporator temperature and measured with a pressure sensor. Due to the mass of adsorbed solvent is very low (milligrams order), the buoyancy forces of the porous material and support at different pressures (densities) are important and thus they were taken into account.

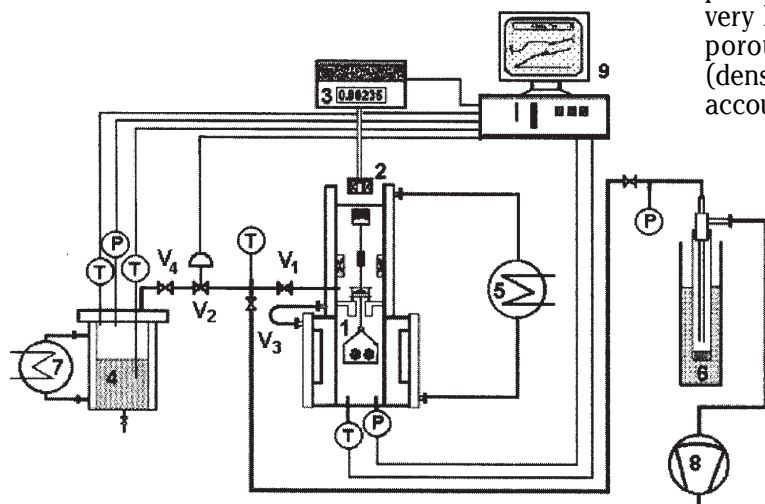


Fig. 1- Experiment set-up scheme: 1 – adsorption cell, 2 – magnetic suspension balance, 3 – analytic balance, 4 – evaporator, 5 – thermostat, 6 – cooling trap, 7 – cryostat, 8 – vacuum pump, 9 – data acquisition system, V_1 - V_4 – valves

The relationship (11) was used for mass of water vapours adsorbed [4]:

$$M = M_n(T, P_n) - M_{n-1,eq}(T, P_{n-1}) + \rho_g(T, P_n - P_{n-1})[V_s + V_m] \quad (11)$$

where:

M_n and M_{n-1} are the values read on the balance at pressure P_n and P_{n-1} (pressure corresponding to a prior experiment) respectively;

ρ - the gas density (g cm^{-3});

V_s and V_m - support and material volume, respectively, cm^3 .

Experimental protocol

To determine diffusion coefficient, experiments were lead as follows.

The porous material is placed into the adsorption cell and dried under vacuum (pressure lower than 0.5 mbar) till constant mass. By means of thermostat (5) a certain temperature is maintained in the adsorption cell. Evaporator (4) is emptied by means of vacuum pump (8) and cooling trap (6).

Distilled water is introduced in evaporator (4) and temperature is adjusted and maintained to a certain value by means of cryostat (7).

Valves V_1 and V_4 between evaporator and adsorption cell are opened, and when the established operating parameters are reached, valve V_2 is automatically opened. Thus, water vapors make contact to the porous material taking place their adsorption until equilibrium is reached. The mass variation of adsorbent material is recorded in time. After equilibrium is reached, temperature and pressure in adsorption cell are maintained constant.

In order to start another experiment, step 3 is repeated with new adjusted parameters.

Diffusion coefficients can be determined using the adsorption kinetic curves.

Results and discussion

Figure 2 shows time evolution for sample MCSS2 mass, at temperature of 323 K and three different temperatures in evaporator (288 K, 298 K and 308 K). Some dependences m/m_{eq} (in case of adsorption experiments) as a function of

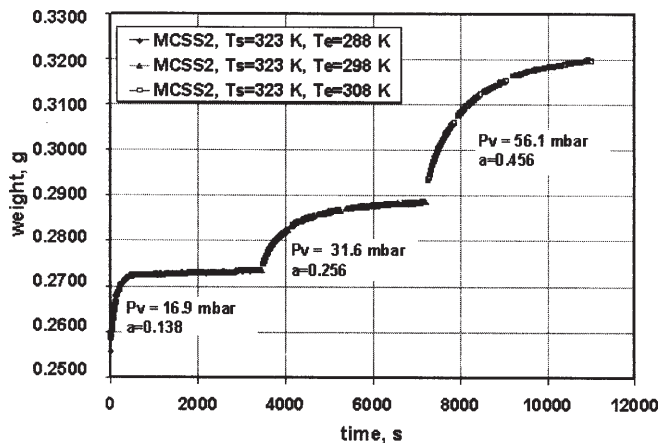


Fig.2. Sample mass variation during adsorption at different water activity

square root of diffusion time for the investigated materials are presented in figure 3. For the investigated materials, kinetic curves were obtained at different values of relative humidity. From these plots was determined slope S used to calculate the apparent diffusion coefficient.

Using relationship (8), apparent diffusion coefficient for spherical grains of SSB silica gel and MCSS1 and MCSS2 composite materials was calculated. Values obtained at temperature of 323 K and at various pressures of water vapors are shown in figure 4.

Equilibrium isotherms of the investigated materials at an adsorption temperature of 323 K are presented in figure 5. From figure 5 the slopes of adsorption isotherms K are determined. The amount of water uptake and the slope K of MCSS1 and MCSS2 is significantly higher (8, 15.5 %) than of pure silica gel. MCSS2 has the highest water uptake values. E.g. at a water vapor pressure of 111.3 mbar (relative humidity 0.905) the water uptake is 287 kg/m^3 . The slope K is presented in table 2.

With this values and taking into account material porosities (Table 1), effective diffusion coefficients can be calculated based on relationship (10). Their value of MCSS1 and MCSS2 at temperature of 323 K, in comparison with those obtained for diffusion in silica gel, are shown in figure 6. As can be seen, effective diffusion coefficients are

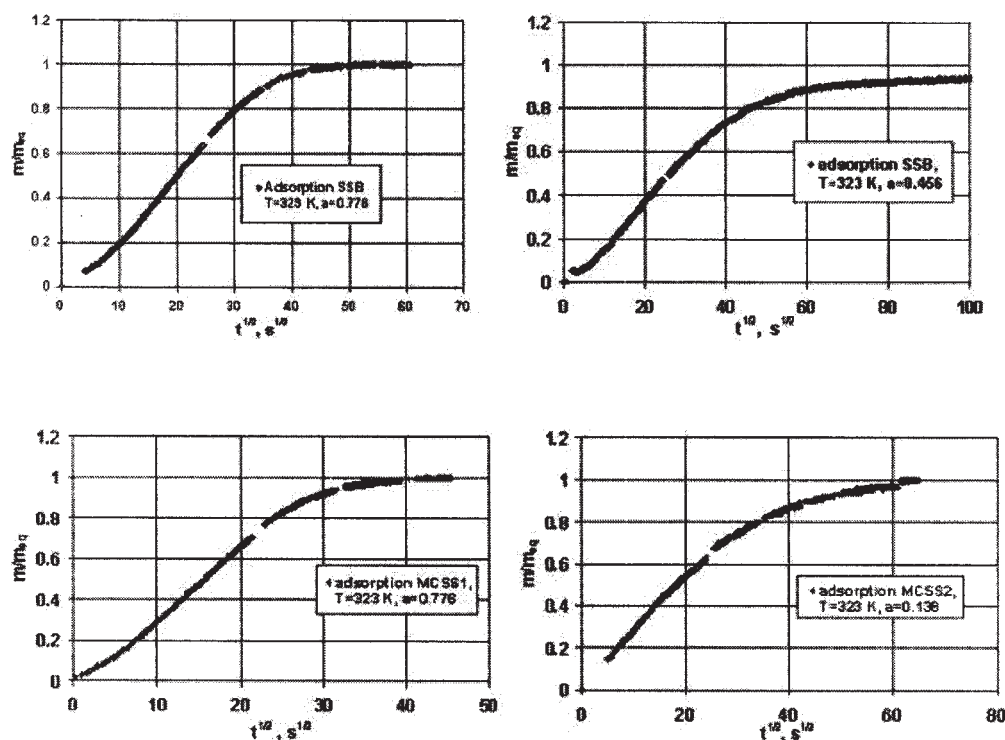


Fig. 3 - Adsorption (m/m_{eq}) curves as a function of the square root of time

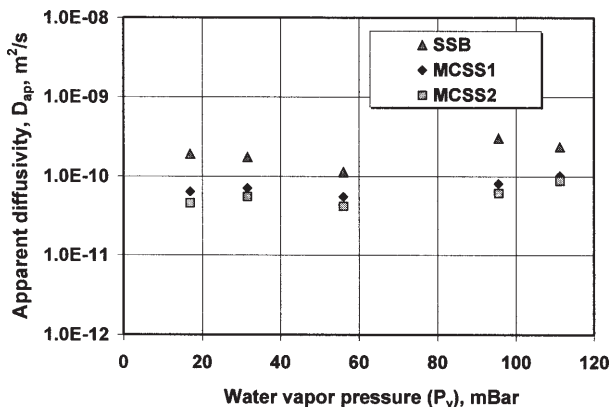


Fig. 4. Apparent diffusion coefficient of water vapours in SSB and composite materials MCSS1 and MCSS2 at 323

Table 2
SORPTION EQUILIBRIUM (SLOPE K)

Water vapor pressure, mbar	SSB Slope, K	MCSS1 Slope, K	MCSS2 Slope, K
16.97	3430	3707	4853
31.57	3450	3710	3960
56.08	3435	3715	3965
95.57	3430	3700	3970
111.32	2540	2680	2688

almost independent on the value of vapour pressure, and the values obtained for the two composite materials differ slightly. For MCSS1 composite material, an average effective diffusion coefficient has been determined with a value of $3.45 \cdot 10^{-7} \text{ m}^2/\text{s}$, and for MCSS2, $2.56 \cdot 10^{-7} \text{ m}^2/\text{s}$. Both values are lower than those obtained for silica gel non-impregnated ($5.46 \cdot 10^{-7} \text{ m}^2/\text{s}$). The maximum error does not exceed 20 percent.

Values of diffusion coefficients in spherical particles of silica gel impregnated with calcium chloride are close of those obtained by the researchers who have studied the influence of particle diameters and temperature over the values of effective diffusion coefficients in similar materials [1]. They emphasized that both particle magnitude and temperature present insignificant influences over the values of effective diffusion coefficient, and that effective diffusion coefficient is $(0.24 \pm 0.12) \cdot 10^{-6} \text{ m}^2/\text{s}$ in the temperature range of 306-343 K. Values of effective diffusion coefficients in silica gel impregnated with lithium bromide obtained in the present work are of $(0.256 \pm 0.05) \cdot 10^{-6} \text{ m}^2/\text{s}$, while those obtained for silica gel impregnated with calcium chloride are $(0.3450.07) \cdot 10^{-6} \text{ m}^2/\text{s}$ and are in good agreement with those reported by [1]. We can emphasize that our experimental technique is suitable for diffusivity measurements in porous materials.

Analyzing data shown in figure 6 it was noted that the values of effective diffusion coefficients of water vapors in silica gel are higher than in composite materials obtained by impregnating silica gel with calcium chloride or lithium bromide. The presence of calcium chloride or lithium bromide modifies the porous structure of silica gel and pore distribution. Effective diffusion coefficients in composite material are almost two times lower than those of non-impregnated silica gel. The difference between the values of effective diffusion coefficient could be due to the unequal contributions of the three transport mechanisms (bulk, Knudsen and surface diffusion).

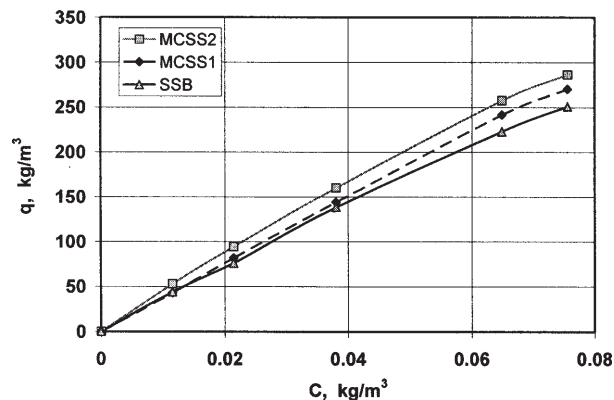


Fig. 5. Equilibrium isotherms for used materials at 323 K (q denotes the water adsorbed in porous material and C is the water content in gas phase).

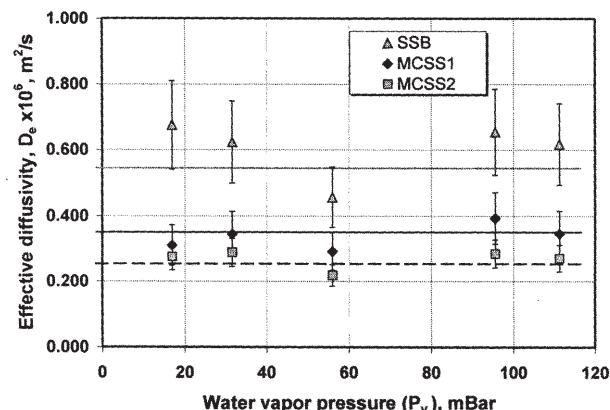


Fig. 6 - Effective diffusion coefficients of water vapours in composite materials MCSS1 and MCSS2 at 323 K

Conclusions

Effective diffusion coefficients of water vapors in spherical particles of silica gel and silica gel impregnated with calcium chloride and lithium bromide were determined. Experiments were performed at 323 K using spherical particles having a diameter of 3.57 mm. Measurements were carried out at constant pressures using a gravimetric technique based on a magnetic balance (Rubotherm, Germany). The obtained results emphasize values of effective diffusion coefficient two times lower in impregnated silica gel than non-impregnated silica gel. Values of effective diffusion coefficient are in good agreement with those reported in literature [1].

Acknowledgements: The authors gratefully acknowledge the financial support of CNCSIS Romania (Grant PN II-IDEI, COD 608, Nr. 63/01.10.2007). Karlsruhe Institute of Technology, Institute of Thermal Process Engineering is also thanked for collaboration and technical support.

References

- ARISTOV, YU. I., GLAZNEV, I. S., FRENI, A., RESTUCCIA, G., Chem. Eng. Sci., **61**, 2006, p. 1453
- CRANK, J., The Mathematics of Diffusion, 2nd Ed., Calderon Press, Oxford, 1975
- KAERGER, J., RUTHVEN, D. M., Diffusion in Zeolites and Other Microporous Solids, Wiley, New York, 1992
- MAMALIGA, I., SCHABEL, W., KIND, M., Chem. Eng. Proc., **43**, 2004, p. 753
- RUTHVEN, D. M., Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984
- SIMONOVA, I. A., FRENI, I. A., RESTUCCIA, A., ARISTOV, G., YU. I., Microporous and Mesoporous Materials, **122**, 2009, p. 223
- MAMALIGA, I., Mat. Plast., **41**, no. 3, 2004, p. 180

Manuscript received: 7.05.2010