

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI  
Publicat de  
Universitatea Tehnică „Gheorghe Asachi” din Iași  
Volumul 63 (67), Numărul 2, 2017  
Secția  
CHIMIE și INGINERIE CHIMICĂ

## DIFFUSION COEFFICIENTS FROM SORPTION EXPERIMENTAL DATA

BY

IONUȚ OVIDIU FORȚU, RODICA SERETEANU,  
EUGENIA TEODORA IACOB TUDOSE\* and IOAN MĂMĂLIȚĂ

“Gheorghe Asachi” Technical University of Iași,  
Faculty of Chemical Engineering and Environmental Protection

Received: April 25, 2017

Accepted for publication: July 10, 2017

**Abstract.** The diffusion of volatile components through polymers or other materials of different geometry (plane, spherical or cylindrical) is essential for many industrial applications. In order to characterize the mass transport in these processes, an effective diffusion coefficient is needed.

The diffusion coefficients estimation, usually using indirect methods, is based on experimental measurements of volatile components diffusion, retained on sorbents. Hence, the diffusivity is assessed by measuring pressure, sample weight or concentration, externally. These calculations require an appropriate model which describes the processes and the occurring transport phenomena.

In this paper we present estimations of the diffusion coefficients using theoretical and experimental methods. These experimental methods are based on the kinetics of the solvent retention within materials of different shapes.

**Keywords:** cylindrical geometry; diffusion; planar geometry; process; spherical geometry.

---

\*Corresponding author; *e-mail*: etudose@tuiasi.ro

## 1. Introduction

Solute transport through a planar, spherical or cylindrical matrix has a great importance in many processes (polymer films drying, biopolymer devolatilisation, air conditioning, drug release, etc). A lot of adsorbent or catalyst grains, medicine tablets etc. are in spherical or cylindrical form. In many cases, the active component may diffuse in a planar polymeric coating. Spherical and cylindrical carriers such as synthesised silica sol–gel, modified chitosan and hydroxyapatite have been used for drug encapsulation and controlled release (Rong *et al.*, 2007). An effective diffusion coefficient is desired to characterize the mass transport in these processes.

Various techniques for the measurement of diffusion have been developed (Mămăligă *et al.*, 2004; Negoescu and Mămăligă, 2013). For a large number of the indirect methods, the diffusing species, or its concentration profile in the microporous material, is not directly observed; the diffusivity is rather calculated from the external measurement of pressure, concentration, or sample weight. Such computations require suitable models which describe all transport phenomena and possible sorption processes that can occur in the experimental setup. The diffusion coefficients determination is based on uptaken measurements of the volatile component in sorbents. Analysis of the sorption data can be accomplished by various means.

In air conditioning, water vapor adsorption is one of the most important practical applications.

In these studies, methods to determine apparent and effective diffusion coefficients within polymeric films, spherical and cylindrical porous granules, were developed. Diffusion coefficient can be expressed as a function of the normalized adsorption and the length to radius ratio. Its values were determined from individual time and adsorption points. The effective diffusion coefficient of water in a polymeric cylinder was determined by fitting radial diffusion curves to experimental data (Rong *et al.*, 2007; Smith *et al.*, 2004).

In the current paper, some theoretical and experimental methods for diffusion coefficient estimations are presented. The experimental methods are based on the overall kinetics of solvent/gas uptake within polymer films, spherical and cylindrical grains.

## 2. Polymer Film Diffusion

The diffusion of gases and vapors in polymeric films is of particular importance in industry and technology. Some examples are: devolatilization processes, which involve the removal of monomer traces, polymer films and polymer-based adhesives drying, polymeric membranes manufacture.

A diffusion process in a planar sheet can be described by Fick's second law, as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

with the initial and boundary conditions for a  $2l$  film thickness ( $-l$  to  $l$ ) exposed to an infinite quantity of solvent:

$$\begin{aligned} C &= C_0 & \text{at} & \quad 0 < x < l, \quad t = 0 \\ C &= C_1 & \text{at} & \quad x = l, \quad t \geq 0 \\ \frac{\partial C}{\partial x} &= 0 & \text{at} & \quad x = 0, \quad t \geq 0 \end{aligned} \quad (2)$$

where  $C$  is the concentration and  $D$  is the mutual diffusion coefficient. A solution of Eq. (1) with conditions (2) was given by Crank (1975) in the following form:

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right] \cdot \cos\left[\frac{(2n+1)\pi x}{2l}\right] \quad (3)$$

For sorption experiments based on gravimetric techniques, the following equation can be obtained (Crank, 1975):

$$\frac{M_t}{M_{eq}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{l^2}\right] \quad (4)$$

where  $M_t$  is the total amount of solvent diffused into the polymer at time  $t$  and  $M_{eq}$  is the equilibrium corresponding amount. For low values of the diffusion time, Eq. (4) can be set as:

$$\frac{M_t}{M_{eq}} = \frac{2 \cdot D^{1/2}}{l} \sqrt{t} \left\{ \frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nl}{\sqrt{Dt}} \right\} \quad (5)$$

and, in the simplified form:

$$\frac{M_t}{M_{eq}} = \frac{2}{\sqrt{\pi}} \frac{D^{1/2}}{l} \sqrt{t} \quad (6)$$

Following the graphical representation of the  $M_t/M_{eq} - \sqrt{t}$  dependence (Fig. 1), we can determine the diffusion coefficient from the slope at the initial moment  $S$ , according to the equation (Mămăligă *et al.*, 2004):

$$D = \frac{\pi}{4} S^2 \cdot l^2 \quad (7)$$

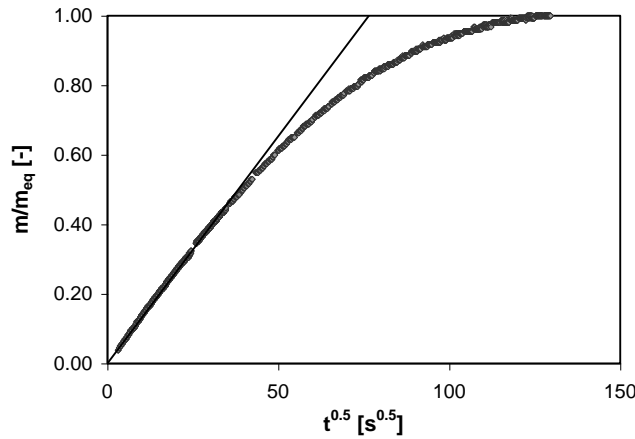


Fig. 1 – Initial slope estimation from kinetic data.

### 3. Diffusion in Spherical Granules

Studies of water vapors adsorption kinetics in porous media offer useful information for air conditioning and gas purification plants design and optimization (Aristov *et al.*, 2006; Simonova *et al.*, 2009). A relatively high number of studies performed on adsorbents such as silica gel or various types of zeolites emphasizes that the adsorption rates are influenced by the water vapor diffusion into adsorbent pores (Kaerger and Rutherford, 1992; Ruthven, 1984). The effective diffusion coefficient,  $D_e$ , includes three different transport mechanisms: molecular, Knudsen and surface diffusion (Kaerger and Ruthven, 1992). To measure the effective diffusion coefficient, several methods were proposed. The solute diffusion into porous spherical particle can be described by the equation given by Ruthven (1984):

$$(1 - \varepsilon) \frac{\partial q}{\partial t} + \varepsilon \frac{\partial C}{\partial t} = \varepsilon D_e \left( \frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (8)$$

where  $D_e$  is the effective diffusion coefficient,  $\varepsilon$  – material porosity,  $q$  – the adsorbate concentration in the solid phase, and  $C$  – the adsorbate concentration in the gaseous phase.

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

$$\frac{\partial q}{\partial t} = K \frac{\partial C}{\partial t} \quad (9)$$

with  $K = K(C_0) = \text{constant}$ . Eq. (8) becomes:

$$(1 - \varepsilon)K \frac{\partial C}{\partial t} + \varepsilon \frac{\partial C}{\partial t} = \varepsilon D_e \left( \frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (10)$$

or:

$$\frac{\partial C}{\partial t} = \frac{\varepsilon D_e}{\varepsilon + (1 - \varepsilon)K} \left( \frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (11)$$

The initial and boundary conditions are as follows:

$$C(R_p, 0) = C_0, \quad q(R_p, 0) = q_0; \quad (12)$$

$$C(R_p, \infty) = C_\infty, \quad q(R_p, \infty) = q_\infty; \quad (13)$$

$$\left. \frac{\partial C}{\partial R} \right|_{R=0} = \left. \frac{\partial q}{\partial R} \right|_{R=0} = 0 \quad (14)$$

where  $R_p$  is the particle radius.

The solution of the Eq. (11) is given by Crank (Crank, 1975):

$$\begin{aligned} \frac{m}{m_\infty} &= \frac{q - q_0}{q_\infty - q_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left( \frac{-n^2 \pi^2 (\varepsilon D_e / (\varepsilon + (1 - \varepsilon)K)) t}{R_p^2} \right) = \\ &= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left( \frac{-n^2 \pi^2 D_{ap} t}{R_p^2} \right) \end{aligned} \quad (15)$$

where:

$$D_{ap} = \varepsilon D_e / (\varepsilon + (1 - \varepsilon)K) \quad (16)$$

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

A simplified equation valid for the beginning of diffusion is given by Ruthven (1984):

$$\frac{m}{m_{\infty}} \approx \frac{2A}{V} \sqrt{\frac{D_{ap} t}{\pi}} = S\sqrt{t} \quad (17)$$

where  $A$  and  $V$  represent, respectively, the particle surface area and volume. In case of spherical particles:  $2A/V = 3/R_p$ . From Eq. (17), one can obtain:

$$S = \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_{ap}}{R_p^2}} \quad (18)$$

which represents the curve slope obtained when graphically representing  $m/m_{\infty}$  as a function of  $t^{0.5}$ . 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 equation:

$$D_{ap} = \frac{\pi}{36} R_p^2 S^2 \quad (19)$$

Using the Eq. (18), the apparent diffusion coefficients for spherical grains of SSB silica gel and two other composite materials, obtained by silica gel impregnation with a hygroscopic salt (MCSS1 and MCSS2), were calculated (Mămăligă *et al.*, 2010). Their values obtained at a temperature of 323 K and at various water vapor pressures are shown in Fig. 2.

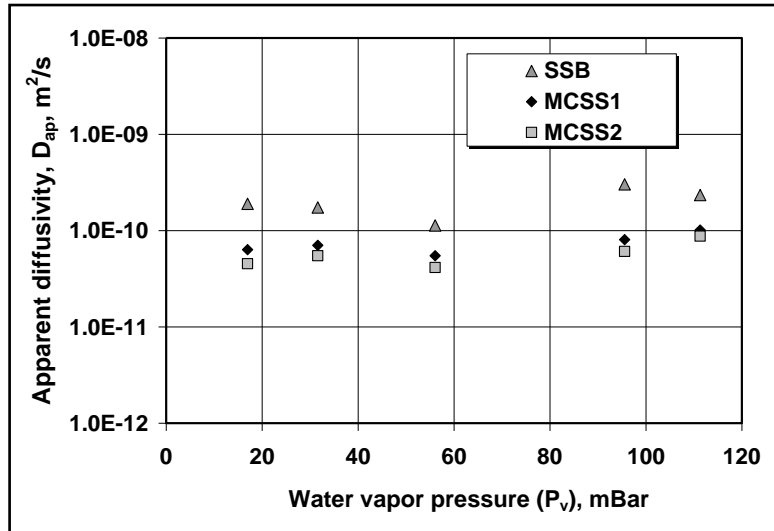


Fig. 2 – Apparent diffusion coefficient for water vapors in SSB and composite materials MCSS1 and MCSS2, at 323 K (Mămăligă *et al.*, 2010).

#### 4. Diffusion in Cylindrical Granules

In Terzyk *et al.* developed (Terzyk and Gauden, 2002; Terzyk *et al.*, 2003), a method to determine diffusion coefficients within cylindrical and spherical carbon granules, was presented. They expressed diffusion coefficient as a function of normalized adsorption for spherical adsorbents. In the present case, the diffusion coefficient was defined for normalized adsorption using both, the cylinder length and radius.

Time dependent adsorption for a finite cylinder, with radius  $R$  and length  $L$ , is given as (Carslaw and Jaeger, 2005; Crank, 1975):

$$\frac{q_t}{q_{\max}} = 1 - \left( \frac{4}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{R^2}\right) \right) \times \left( \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{2m-1} \exp\left(-\frac{\pi^2 (2m-1)^2 Dt}{L^2}\right) \right) \quad (20)$$

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

Eq. (20) is computationally exact but can not be conveniently used in practical numerical valuation.

In order to obtain the expression for adsorption within a finite cylinder we can use the expression for adsorption in an infinite planar sheet and in an infinite cylinder. The equation for a planar infinite sheet of  $L$  thickness is given by (Carslaw and Jaeger, 2005; Crank, 1975):

$$\frac{q_t}{q_{\max}} = 1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{2m-1} \exp\left(-\frac{\pi^2 (2m-1)^2 Dt}{L^2}\right) \quad (21)$$

A solution for a small  $Dt/L^2$  is given by (Rong and Vadgama, 2006):

$$\frac{q_t}{q_{\max}} = 4 \left( \frac{Dt}{\pi L^2} \right)^{0.5} + 8 \left( \frac{Dt}{L^2} \right)^{0.5} \sum_{m=1}^{\infty} (-1)^m \operatorname{ierfc} \left( \frac{mL}{2D^{0.5} t^{0.5}} \right) \quad (22)$$

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

For  $Dt/L^2 < 0.08$ , the second part of Eq. (22) is negligible and it becomes:

$$\frac{q_t}{q_{\max}} = 4 \left( \frac{Dt}{\pi L^2} \right)^{0.5} \quad (23)$$

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

$$f_{i,s} = \frac{a_t}{a_{t,\max}} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{L^2}\right) \quad (24)$$

valid for  $t > 0.05326L^2/D$ ,  $a_t/a_{t,\max} > 0.52$ , and:

$$f_{i,s} = \frac{a_t}{a_{t,\max}} = \frac{4}{L} \left(\frac{Dt}{\pi}\right)^{0.5} \quad (25)$$

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

The diffusion coefficient is calculated from the saturation half time as:

$$D = 0.04908 \frac{L^2}{t_{0.5}} \quad (26)$$

A similar equation at the adsorption in an infinite cylindrical granule is given by:

$$\frac{a_t}{a_{t,\max}} = 1 - 4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{R^2}\right) \quad (27)$$

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

At the adsorption in an infinite cylinder, for small dimensionless time ( $Dt/R^2$ ), the Eq. (27) becomes:

$$\frac{a_t}{a_{t,\max}} = \frac{4}{R} \left(\frac{Dt}{\pi}\right)^{0.5} - \frac{Dt}{R^2} - \frac{(Dt)^{1.5}}{3\pi^{0.5}R^3} \quad (28)$$

For the adsorption in an infinite cylinder, a bipartite expression can be obtained as:

$$f_{i,c} = \frac{a_t}{a_{t,\max}} = 1 - 4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{R^2}\right) \quad (29)$$

valid for  $t > 0.03598L^2/D$ ,  $a_t/a_{t,\max} > 0.3908$ , and:



$$f_{i,c} = \frac{a_t}{a_{t,\max}} = \frac{4}{R} \left( \frac{Dt}{\pi} \right)^{0.5} - \frac{Dt}{R^2} - \frac{(Dt)^{1.5}}{3\pi^{0.5}R^3} \quad (30)$$

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

The diffusion coefficient is calculated from the saturation half time as:

$$D = 0.06306 \frac{R^2}{t_{0.5}} \quad (31)$$

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

$$f_{f,c} = f_{i,s} + f_{i,c} - f_{i,s}f_{i,c} \quad (32)$$

An example of the adsorption kinetics (Iacob Tudose *et al.*, 2015) at 303 K, for the same sample of MCA, at two different water vapor pressure values, successively applied, is presented in Fig. 3.

For the investigated materials, the kinetic curves were obtained at different values of water vapor pressure. From these plots, the half time of diffusion ( $t_{0.5}$ ) was determined and used to calculate the apparent diffusion coefficient (Fig. 4).

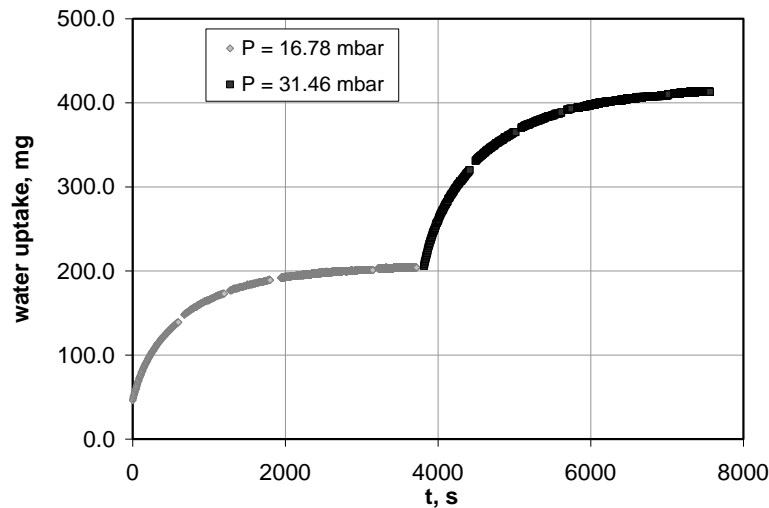


Fig. 3 – Water uptake at 303 K, in cylindrical MCA granules, at two values of water vapor pressure, 16.78 and 31.46 mbar (Iacob Tudose *et al.*, 2015).

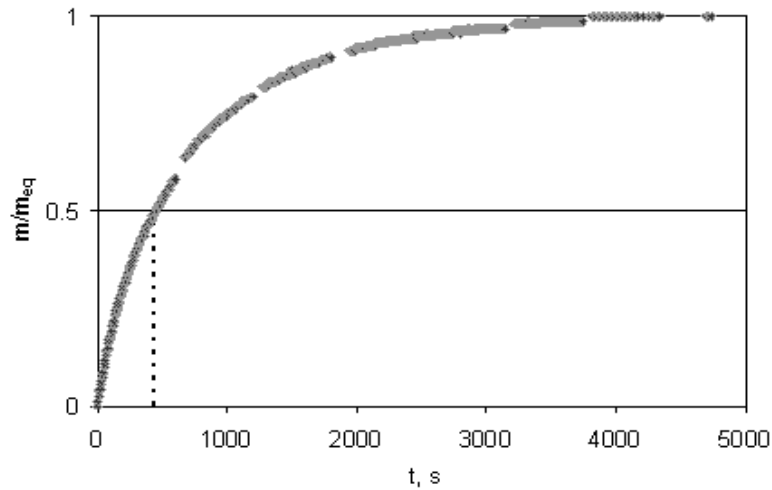


Fig. 4 – Half time of diffusion ( $t_{0,5}$ ) from kinetic data.

Values for an apparent diffusion coefficient, for cylindrical granules of A and MCA, were obtained at a temperature of 323 K and at various pressures of water vapors and are shown in Fig. 5.

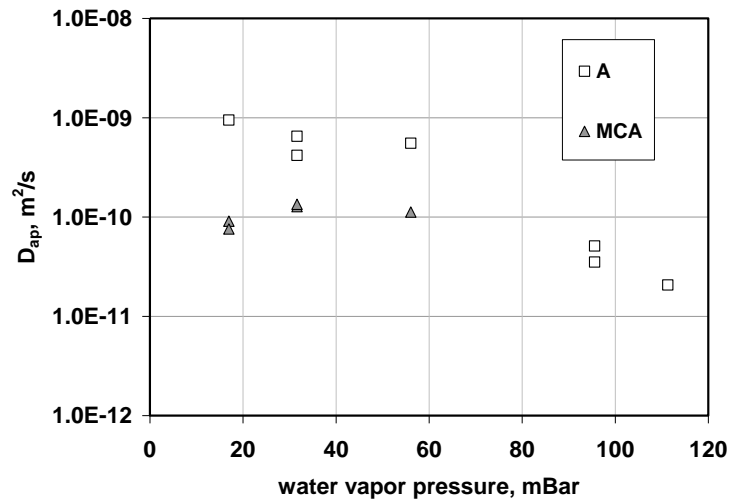


Fig. 5 – Apparent diffusion coefficient of water vapors, in A and MCA samples, at 323 K (Jacob Tudose *et al.*, 2015).

Apparent diffusivity coefficient for grains with an irregular form could be estimated using the diffusion model for spherical grains. Thus, diffusivity in cylindrical particles can be calculated using some equations used for spherical

particles. In the case of cylindrical particles with both length and diameter of 2.5 mm, the form factor differs slightly in comparison to a sphere, with the same diameter. This is a particular case, since the length and the diameter of the cylinder are the same. For L/D ratio larger than 1, some differences can occur. The experimental diffusivities calculated in these ways are presented in Fig. 6.

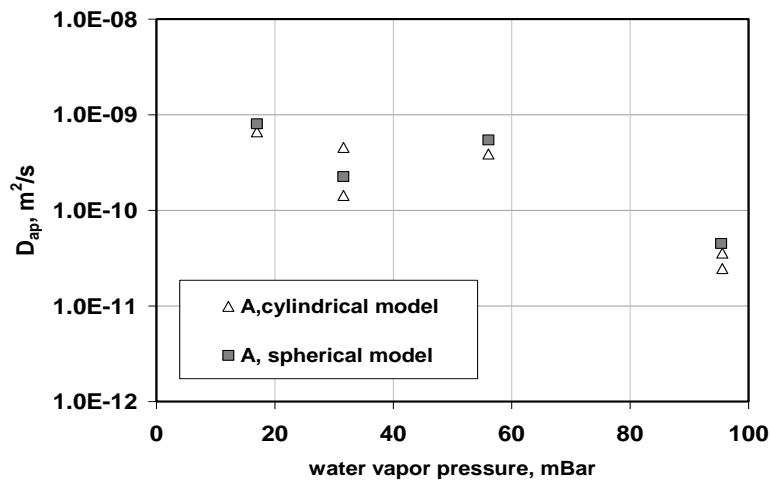


Fig. 6 – Apparent diffusion coefficient estimated using the cylindrical and spherical models.

## 5. Conclusion

In this paper, the theoretical models used to estimate the apparent diffusion coefficient when retaining volatile components or gases onto materials of regular shape (films, spherical and cylindrical) were presented. We have also given some examples based on experimental data which have indicated that one can determine the diffusion coefficient for polymer particles of cylindrical shape with equal length and diameter, using the equations for spherical grains.

## REFERENCES

- Aristov Yu.I., Glaznev I.S., Freni A., Restuccia G., *Kinetics of Water Sorption on SWS-1L (Calcium Chloride Confined to Mesoporous Silica Gel): Influence of Grain Size and Temperature*, *Chemical Engineering Science*, **61**, 5, 1453-1458 (2006).
- Carslaw H.S., Jaeger J.C., *Conduction of Heat in Solids*, Oxford Univ. Press, Oxford, 2005.
- Crank J., *The Mathematics of Diffusion*, 2<sup>nd</sup> Ed., Calderon Press, Oxford, 1975.

- Iacob Tudose E.T., David E., Secula M.S., Mămăligă I., *Adsorption Equilibrium and Effective Diffusivity in Cylindrical Alumina Particles Impregnated with Calcium Chloride*, Environmental Engineering and Management Journal, **14**, 3, 503-508 (2015).
- Kaerger J., Ruthven D.M., *Diffusion in Zeolites and Other Microporous Solids*, Wiley, New York, 1992.
- Mămăligă I., Schabel W., Kind M., *Measurements of Sorption Isotherms and Diffusion Coefficients by Means of a Magnetic Suspension Balance*, Chemical Engineering and Processing: Process Intensification, **43**, 6, 753-763 (2004).
- Mămăligă I., Schabel W., Petrescu S., *Measurements of Effective Diffusivity in Porous Spherical Particles by Means of a Magnetic Suspension Balance*, Revista de Chimie, **61**, 12, 1231-1234 (2010).
- Negoescu C.C., Mămăligă I., *Sorption Kinetics and Thermodynamic Equilibrium of Some Solvents in Polymer Films Using the Pressure Decay Method at Low Pressures*, Materiale Plastice, **50**, 4, 303-306 (2013).
- Rong Z., Terzyk A.P., Gauden P.A., Vadgama P., *Effective Diffusion Coefficient Determination within Cylindrical Granules of Adsorbents Using a Direct Simulation Method*, Journal of Colloid and Interface Science, **313**, 449-453 (2007).
- Rong Z., Vadgama P., *Simple Expressions for Diffusion Coefficient Determination of Adsorption within Spherical and Cylindrical Adsorbents Using Direct Simulation Method*, J. Colloid Interface Sci., **303**, 75-79 (2006).
- Ruthven D.M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- Simonova I.A., Freni I.A., Restuccia G., Aristov Yu. I., *Water Sorption on Composite "Silica Modified by Calcium Nitrate"*, Microporous and Mesoporous Materials, **122**, 1-3, 223-228 (2009).
- Smith R.W., Booth J., Massingham G., Clough A.S., *A Study of Water Diffusion, in Both Radial and Axial Directions, into Biodegradable Monolithic Depots Using Ion Beam Analysis*, Polymer, **45**, 14, 4893-4908 (2004).
- Terzyk A.P., Gauden P.A., *The Simple Procedure of the Calculation of Diffusion Coefficient for Adsorption on Spherical and Cylindrical Adsorbent Particles- Experimental Verification*, J. Colloid Interface Sci., **249**, 256-261 (2002).
- Terzyk A.P., Rychlicki G., Biniak S., Lukaszewicz J.P., *New Correlations Between the Composition of the Surface Layer of Carbon and its Physicochemical Properties Exposed while Paracetamol is Adsorbed at Different Temperatures and pH*, J. Colloid Interface Sci., **257**, 13-30 (2003).

#### DETERMINAREA COEFICIENȚILOR DE DIFUZIUNE DIN DATE EXPERIMENTALE

(Rezumat)

Difuzia componentelor volatile prin materiale de geometrie diferită (plană, sferică sau cilindrică) prezintă o mare importanță pentru aplicațiile industriale. Pentru a

---

caracteriza transportul de masă în aceste procese, este necesară cunoașterea unui coeficient efectiv de difuzie.

Determinarea coeficientului de difuzie în majoritatea metodelor indirecte se bazează pe măsurătorile componentelor volatile reținute de sorbenți. Acest lucru se datorează faptului că specia ce difuzează nu poate fi observată. Prin urmare, difuzivitatea se calculează prin măsurarea externă a presiunii, greutatei probei sau concentrației. Aceste calcule necesită un model adecvat care să descrie procesele și fenomenele de transport de masă care apar.

În aceasta lucrare am prezentat estimări ale coeficienților de difuzie folosind metode teoretice și experimentale. Acestea din urmă se bazează pe retenția unor vapori/gaze în materiale de diferite forme.