

A Simple and Inexpensive Technique to Measure Molecular Diffusion Coefficients

J.M.P.Q. Delgado, M.A. Alves, and J.R.F. Guedes de Carvalho

(Submitted July 12, 2005)

The experiment proposed is simple and inexpensive and provides an accurate method for measurement of the molecular diffusion coefficient, D_m . It is a novel method that has the added advantage of easily providing data at temperatures and pressures that differ significantly from ambient values. The experimental results for naphthalene in air are in excellent agreement with the experimental values of the molecular diffusion coefficient measured by other authors. Experimental measurements of mass transfer in water were also carried out for a range of the relevant parameters. The soluble spheres used in the experiments were made of either benzoic acid or 2-naphthol, and the ranges of temperatures covered were 293-333 and 293-373 K, respectively. Using the mass transfer theory presented in this work, the molecular diffusion coefficient of the two solutes was determined, and good agreement with literature values was found.

1. Introduction

Mass transfer is a topic of central importance in chemical engineering, and molecular diffusion is the basic physical mechanism underlying mass transfer processes, even when convection comes into play. As a result, values of the molecular diffusion coefficient (D_m) are required for mass transfer calculations, and extensive tabulations of this parameter have been prepared in the past.^[1,2] Equations for the prediction of D_m are also available, and, in general, they have reasonable accuracy.^[3] Nevertheless, in many instances it is important to determine D_m values experimentally.

In the simple experiment described here, consideration is given to the process of mass transfer from a volatile solid sphere (a mothball), buried in a packed bed of inert particles (sand or glass "ballotini"), through which air is forced to flow continuously, and also to the similar process of dissolution of slightly soluble spheres buried in a packed beds of inerts through which water flows. These are important model situations for the understanding of such processes as char combustion in fluidized beds^[4] and leaching of ore (or contaminant) from buried rocks (or buried waste).

When these processes are performed with very low fluid velocities, the rates of mass transfer are strongly determined by molecular diffusion, and the experiment may be used to provide an accurate method for the measurement of the

diffusion coefficient. It is an entirely novel method that has the added advantage of easily providing data at temperatures and pressures that differ significantly from ambient values. This is not always easy to achieve with other methods.^[5]

2. Theory

As an introduction to the present analysis, it is useful to consider the simple situation depicted in Fig. 1(a), where the vapor liberated by a buried sphere travels through the interstices of a packed bed of inerts, as a result of molecular diffusion.

2.1 Diffusion Alone

The sphere of slightly volatile solid is assumed to be buried in a packed bed of sand, of "infinite extent," the interstices of the bed being filled with a stagnant gas (e.g., air) that is assumed to be free of solute at a large distance from the sphere (i.e., $C \rightarrow 0$ as $r \rightarrow \infty$). At $r = b$, where the active sphere contacts the gas phase, the molar concentration of solute in the gas is $C^* = P_v/RT$, where P_v is the equilibrium vapor pressure of the solute at the temperature (T) of the experiment.

The concentration gradient will give rise to a process of outward diffusion of solute, but if diffusion is slow, the size of the sphere is taken to be constant, during one experiment; in other words, the assumption of a quasi-steady state is legitimate.

Under that assumption, the rate of diffusion across a spherical surface of radius r , concentric with the solid sphere, will be independent of r . From Fick's law:

$$n = -D'_m(4\pi r^2 \varepsilon) \frac{dC}{dr} \quad (\text{Eq 1})$$

This article is a revised version of the paper printed in the *Proceedings of the First International Conference on Diffusion in Solids and Liquids—DSL-2005*, Aveiro, Portugal, July 6-8, 2005, Andreas Öchsner, José Grácio and Frédéric Barlat, eds., University of Aveiro, 2005.

J.M.P.Q. Delgado, Laboratório de Física das Construções, Departamento de Engenharia Civil; M.A. Alves, CEFT, Departamento de Engenharia Química; and J.R.F. Guedes de Carvalho, LaFSIM, Departamento de Engenharia Química-Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal. Contact e-mail: jdelgado@fe.up.pt.

Section I: Basic and Applied Research

where $D'_m = D_m/\tau$ is the effective diffusion coefficient (τ being the tortuosity factor, accepted to be $\sqrt{2}$ for packed beds of granular materials,^[6] and ε is the bed voidage (assumed constant throughout). Because n is independent of r , integration of Eq 1, between the limits ($r = b, C = C^*$) and ($r \rightarrow \infty, C \rightarrow 0$) gives:

$$n = 4D'_m \varepsilon \pi b (C^* - 0) = 2 \frac{D'_m}{d_1} \varepsilon \pi d_1^2 (C^* - 0) \quad (\text{Eq 2})$$

where $d_1 (=2b)$ is the diameter of the active sphere. Identifying (πd_1^2) as the area of the active sphere helps one

recognize the expression for the mass transfer coefficient as $k = 2\varepsilon D'_m/d_1$. Introduction of the Sherwood number, $Sh' = kd_1/D'_m$, shows that for mass transfer by pure diffusion, around a buried sphere:

$$\frac{Sh'}{\varepsilon} = 2 \quad (\text{Eq 3})$$

an expression similar to the well-known result, $Sh = 2$, for pure diffusion around a sphere in an unbounded fluid.^[6]

2.2 Diffusion with Convection

Figure 1(b) represents again the buried sphere, but it is now exposed to a constant flow of gas, with an average interstitial velocity u_0 . The solute still diffuses away from the surface of the sphere, but the rate of mass transfer is now enhanced because the solute is continuously swept away by the moving fluid. The surfaces of equal concentration are no longer spheres. The analysis of the physical situation is complicated, but it has been worked out in detail.^[7] For the conditions of interest in the present work, the expression:

$$\frac{Sh'}{\varepsilon} = \left[4 + \frac{4}{5} \left(Pe'_p \frac{d_1}{d} \right)^{2/3} + \frac{4}{\pi} \left(Pe'_p \frac{d_1}{d} \right) \right]^{1/2} \quad (\text{Eq 4})$$

has been shown to give accurate values of Sh'/ε , where $Pe'_p = u_0 d/D'_m$ is the Peclet number based on the diameter of the inert particles (d) making up the bed. It may be easily seen that Eq 4 reduces to Eq 3, in the limit of low Pe'_p ($=Pe'_p d_1/d$). As Pe'_p is increased, it is known that Eq 4 becomes inaccurate.^[7] At $Pe'_p \approx 1$, Eq 4 is found to be accurate to within 5%, and therefore this value of Pe'_p should not be exceeded. This is because convective dispersion (rather than molecular diffusion) would then become the relevant mechanism of mass transfer in the packed bed. However, in the case of the experiments described below, conditions are restricted to the range of applicability of Eq 4.

The essence of the experimental method proposed relies on burying a weighed sphere of naphthalene (with initial mass m_0 and diameter d_1) in a packed bed of sand of known porosity (ε) and continuously forcing a metered stream of air (volumetric flow rate, v) through the packed bed (cross-sectional area, A) for a given time interval, Δt . Weighing the sphere at the end of the time interval (mass m_t) gives the rate of sublimation as $(m_0 - m_t)/\Delta t$, and the mass transfer coefficient may be calculated from:

$$k = \frac{m_0 - m_t}{\Delta t M \pi d_1^2 (P_v/RT)} \quad (\text{Eq 5})$$

where M is the molecular weight of naphthalene.

With the interstitial velocity given by $u_0 = v/(A\varepsilon)$, the only unknown in Eq 4 is D'_m . A simple way of solving this equation relies on rearranging it, through multiplication by D'_m , to obtain:

Nomenclature	
A	cross-sectional area of packed bed
b	radius of active sphere
C	solute concentration
C^*	saturation concentration of solute
C_{out}	solute concentration in the outlet stream
d	diameter of inert particles
d_1	diameter of active sphere ($=2b$)
D_m	molecular diffusion coefficient
D'_m	effective molecular diffusion coefficient ($=D_m/\tau$)
k	average mass transfer coefficient
m_0	initial weight of active sphere
m_f	final weight of active sphere
M	molecular weight
n	mass transfer rate
P	pressure in the test column
P_R	pressure in the rotameter
P_v	vapor pressure
Q	volumetric flow rate of water
R	ideal gas constant
r	radial coordinate (distance to the center of the soluble sphere)
t	time
T	absolute temperature
T_R	absolute temperature in the rotameter
u_0	interstitial velocity (far from the active sphere)
v	volumetric flow rate of air in the test column
v_R	volumetric flow rate of air in the rotameter
Greek letters	
ε	bed voidage
τ	tortuosity
Σv	atomic diffusion volumes
Dimensionless groups	
Pe'	Peclet number based on diameter of active sphere ($=u_0 d_1/D'_m$)
Pe'_p	Peclet number based on diameter of inert particles ($=u_0 d/D'_m$)
Sh'	Sherwood number ($=kd_1/D'_m$)
Subscripts	
A, B	component A or B

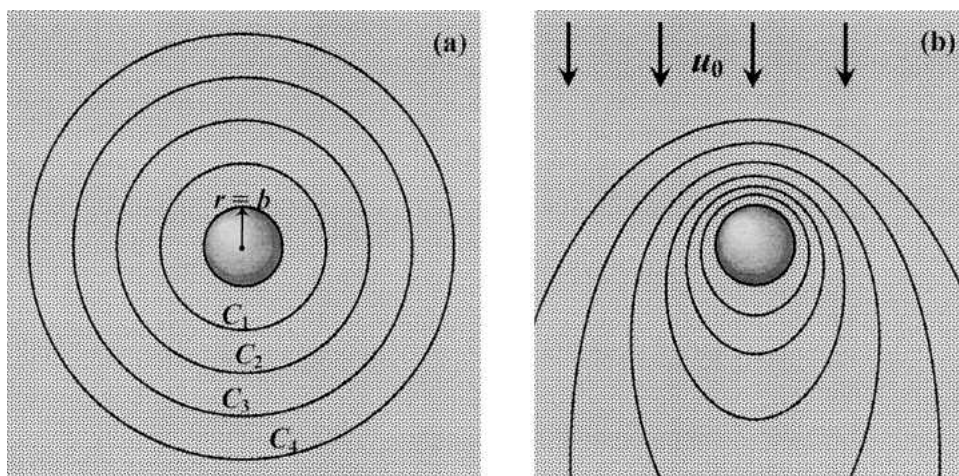


Fig. 1 Sketch of isoconcentration surfaces around active sphere of radius b for (a) pure diffusion and (b) diffusion with convection

$$\frac{kd_1}{\varepsilon} = D'_m \left[4 + \frac{4}{5} \left(\frac{u_0 d_1}{D'_m} \right)^{2/3} + \frac{4}{\pi} \left(\frac{u_0 d_1}{D'_m} \right) \right]^{1/2} \quad (\text{Eq 6})$$

In each experiment, measurement gives k (through Eq 5), d_1 , u_0 , and ε and the value of D'_m ($=D_m/\sqrt{2}$) has to be found, which makes the right side of Eq 6 match the value of the left side.

Several models can be found in the literature for the prediction of diffusion coefficients in binary systems.^[4] Fuller et al.^[8] suggest the use of the following equation:

$$D_m = \frac{\left(\frac{M_A + M_B}{M_A M_B} \right)^{1/2} T^{1.75}}{P[(\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3}]^2} \times 10^{-7} \quad (\text{Eq 7})$$

where P is the absolute pressure (in bar), M_A and M_B are, respectively, the molecular weights of components A and B (in g/mol), and $(\Sigma v)_A$ and $(\Sigma v)_B$ are the values of the atomic diffusion volumes of components A and B, which were tabulated by Reid et al.^[3]

Equation 7 predicts a proportionality between D_m and $T^{1.75}/P$, and this is an important result that may be demonstrated using the experimental technique described in the following section.

3. Experimental Setup

The experimental setup is sketched in Fig. 2. The air supply may determine the maximum pressure at which the experiment can be performed. The tubing and valves connecting the air supply to the low-pressure end of the rig will be standard material for the maximum working pressure intended. The test column, containing the packed bed of sieved sand (or glass ballotini) may be made from a short piece of stainless steel tube (typically with an 80 mm internal diameter and 110 mm long) flanged at both ends. The test column is best kept vertical to avoid settling of the packing to one side, and a downward gas flow will prevent

unwanted fluidization of the bed material. A piece of some sort of gauze will have to be placed over the bottom plate of the test column to prevent the granular material from going into the tubing.

If the rotameter gives the flow rate v_R , at pressure P_R and temperature T_R , the actual gas flow rate in the test column is given as:

$$v = v_R (P_R/P)(T/T_R) \quad (\text{Eq 8})$$

where P is the absolute pressure indicated in the manometer connected to the test column. The vapor pressure is calculated using Uno's correlation.^[9]

In experiments at temperatures differing from ambient, the test column and a significant length of the tubing feeding it have to be kept in a constant temperature bath.

The naphthalene spheres used in the experiments were solidified from the melt in simple molds made of silicone rubber for the purpose. The diameter of each sphere was measured with callipers (along three perpendicular directions, to ensure near sphericity), and it was typically about 20 or 25 mm.

Each sphere was weighed accurately (initial mass, m_0), in an analytical balance, before burying it (with some care, to avoid unwanted erosion) near the middle of the packed bed, which had been previously immersed in the constant temperature bath for a long enough period of time. The top plate of the test column was then bolted in place, and the column was tapped gently a few times, to ensure close packing of the granular material. The test column and associated tubing were then immersed again in the constant temperature bath, and the air supply was then connected to give the intended test pressure and gas flow rate. The air flow rate was kept constant for a time Δt , after which it was interrupted, and the test column was opened, to remove the sphere for weighing (final mass, m_t).

Each experiment lasted between 50 min and 60 h (at $T = 333.2$ and 282.7 K, respectively), the time being chosen to give a measurable loss of weight (typically, 0.05 g), which nevertheless would not correspond to a significant variation in the diameter of the sphere. The time intervals were, however, sufficiently long to reduce inaccuracies

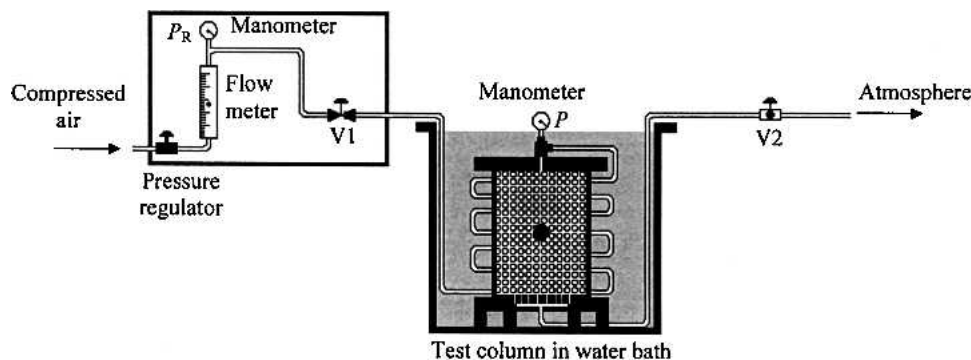


Fig. 2 Experimental setup

caused by evaporation in the stages of sphere introduction and removal from the test column.

The experimental measurements of mass transfer in water were performed on the dissolution of individual spheres of 2-naphthol and benzoic acid, buried in beds of sand through which a metered stream of distilled water (that had been previously deaerated under vacuum) was forced to flow steadily. The experimental technique used with the benzoic acid/water and 2-naphthol/water system is analogous to that described above. But instead of weighing the sphere, the concentration of solute in the outlet stream, C_{out} was measured continuously to give the rate of dissolution. C_{out} was measured by means of a UV-visible spectrophotometer, set at either 226 nm, for benzoic acid, or at 274 nm, for 2-naphthol. When the steady state was reached, the rate of dissolution of the solid could be found directly from $n = QC_{out}$, where Q is the measured volumetric flow rate of water.

The silica sand used in the experiments was initially washed, dried, and sieved. Two packings of sand were used, with average particle diameters of 219 and 322 μm .

4. Results

The experimental results are in excellent agreement with the experimental values of the molecular diffusion coefficient measured by other authors, and repeated measurements of D_m did not differ by more than 10%.^[10-15]

The results obtained with naphthalene in air, at constant temperature, serve to illustrate the inverse proportionality between the molecular diffusion coefficient and the absolute pressure, as shown in Fig. 3.

The influence of temperature is illustrated in Fig. 4 and confirms the proportionality between $D_m P$ and $T^{1.75}$, as predicted by Eq 7. Figure 4 also shows the excellent agreement between the results obtained by the present technique and the experimental values of the diffusion coefficient measured by Caldwell^[10] at 303.2 K and Mack^[11] at 298.2 K (after additional correction in the value of vapor pressure).

Other experiments were performed with water and a sphere (11 and 19 mm internal diameters) of benzoic acid or 2-naphthol, placed in a bed of sand (0.219 and 0.322 mm average diameters, respectively).

Values of D_m were determined in this way, with the benzoic acid/water system, in the interval 293-333 K, and

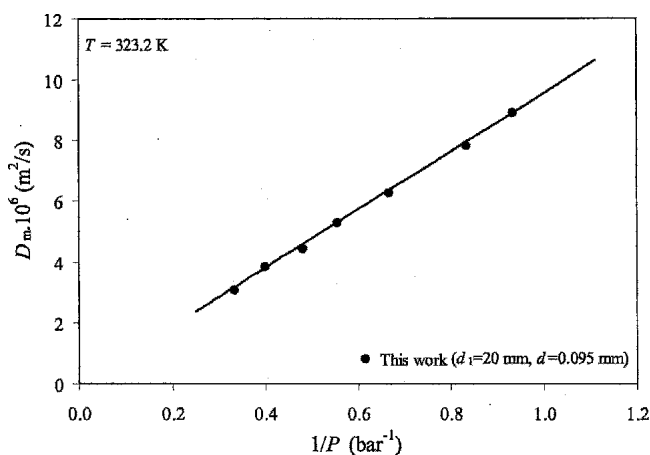


Fig. 3 Influence of pressure on molecular diffusion coefficient (naphthalene in air)

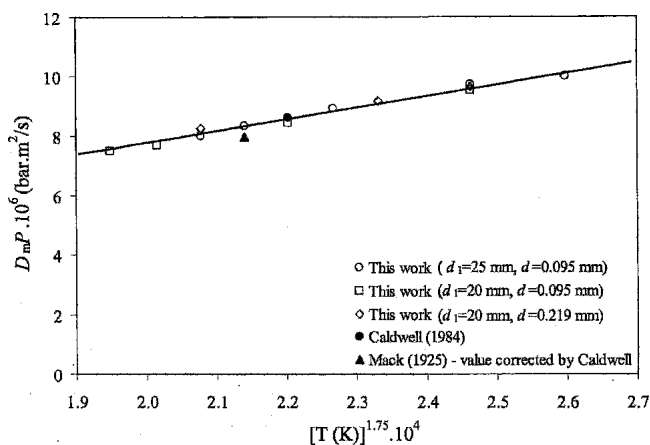


Fig. 4 Influence of temperature and pressure on molecular diffusion coefficient (naphthalene in air)

2-naphthol/water system, in the interval 293-373 K. The interstitial water velocities were in the range of 5.7×10^{-4} to 3.5×10^{-3} mm/s, and the experimental values of D_m are given as a function of temperature in the plots of Figs. 5 and 6.

An aspect to be considered, as a check on the experimental method, is the influence of the diameter of the test

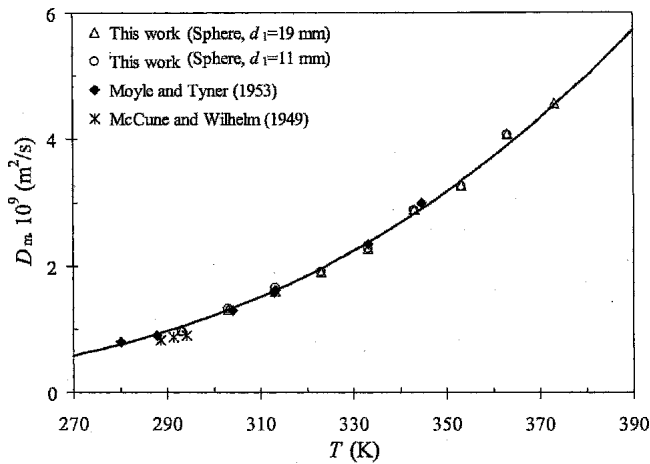


Fig. 5 Variation of D_m with T for 2-naphthol in water

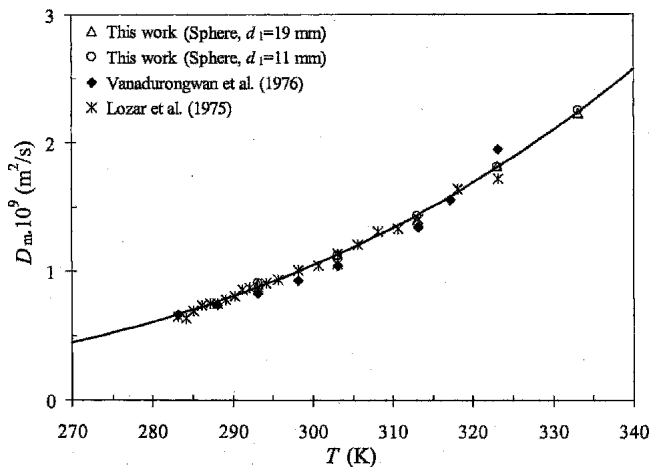


Fig. 6 Variation of D_m with T for benzoic acid in water

sphere on the measured value of D_m . In reality, the two variables are independent, and if our experimental method is valid, values of the diffusion coefficient measured with different diameters of sphere, under otherwise similar conditions, should be equal, within the reproducibility limits. The values of D_m plotted in Fig. 5 and 6, as a function of temperature, are typical, and they illustrate the independence between the measured values of that parameter and the diameter of the soluble spheres used in the experiment.

At the very low values of the Peclet number used, the method presented proves to be accurate for the measurement of molecular diffusion coefficient (D_m) of low-solubility solutes in water. Figures 5 and 6 show a good agreement with the results of other authors, and this is an indication of the accuracy of the proposed method.

Moyle and Tyner^[12] proposed the following equation to represent their data for 2-naphthol in water:

$$D_m(\text{m}^2/\text{s}) = 9.95 \times 10^{-7} \exp\left(-\frac{2012}{T(\text{K})}\right) \quad (\text{Eq 9})$$

and the data are within 8% of this line.

For benzoic acid in water Lozar et al.^[13] proposed:

$$D_m(\text{m}^2/\text{s}) = 2.20 \times 10^{-6} \exp\left(-\frac{2295}{T(\text{K})}\right) \quad (\text{Eq 10})$$

and the data are within 5% of this equation.

5. Conclusions

An inexpensive experimental method for determination of molecular diffusion coefficients is described. The results show that it is possible to obtain good results for the value of the diffusion coefficient with a simple procedure.

The experimental values obtained for the molecular diffusion coefficient of 2-naphthol in water are in good agreement with the values of Moyle and Tyner,^[12] and those for benzoic acid in water are in good agreement with the values proposed by Lozar et al.^[13]

The technique described is simple to use and provides data over a range of temperatures above ambient.

References

1. R.H. Perry and D. Green, *Perry's Chemical Engineer's Handbook*, 6th ed., McGraw-Hill International Editions, New York, 1984
2. National Research Council, *International Critical Tables*, Vol 5, McGraw-Hill International Editions, New York, 1929
3. R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill International Editions, 1988
4. A.M.F.R. Pinto and J.R.F. Guedes de Carvalho, Transverse Dispersion in Granular Beds, Part III: Mass Transfer around Particles Dispersed in Granular Beds of Inerts and the Combustion of Carbon Particles in Beds of Sand, *Trans. IChemE.*, Vol 68, 1990, p 503-509
5. T.R. Marrero and E.A. Mason, Gaseous Diffusion Coefficients, *J. Phys. Chem. Ref. Data*, Vol 1, 1972, p 3-25
6. T.K. Sherwood, R.L. Pigford, and C.R. Wilke, *Mass Transfer*, McGraw-Hill International Editions, Tokyo, 1975
7. J.R.F. Guedes de Carvalho and M.A.M. Alves, Mass Transfer and Dispersion around Active Sphere Buried in a Packed Bed, *AIChE J.*, Vol 45, 1999, p 2495-2502
8. E.N. Fuller, P.D. Schettler, and J.C. Giddings, A New Method for Prediction of Binary Gas-Phase Diffusion Coefficients, *Ind. Eng. Chem.*, Vol 58, 1966, p 19-27
9. S. Uno, "Mass Transfer from Naphthalene Slabs," Ph.D. Thesis, Illinois Institute of Technology, Chicago, 1958
10. L. Caldwell, Diffusion Coefficient of Naphthalene in Air and Hydrogen, *J. Chem. Eng. Data*, Vol 29, 1984, p 60-62
11. E. Mack, Average Cross-Sectional Areas of Molecules by Gaseous Diffusion Methods, *J. Am. Chem. Soc.*, Vol 47 (No. 10), 1925, p 2468-2482
12. M.P. Moyle and M. Tyner, Solubility and Diffusivity of 2-Naphthol in Water, *Ind. Eng. Chem. Res.*, Vol 45, 1953, p 1794-1797
13. J. Lozar, C. Laguerie, and J.P. Couderc, Diffusivité de l'Acide Benzoïque dans l'Eau: Influence de la Temperature, *Can. J. Chem. Eng.*, Vol 53, 1975, p 200-203 (in French)
14. L.K. McCune and R.H. Wilhelm, Mass and Momentum Transfer in Solid-Liquid System, *Ind. Eng. Chem. Res.*, Vol 41, 1949, p 1124-1134
15. V. Vanadurongwan, C. Laguerie, and J.P. Couderc, Diffusivité Moyenne de l'Acide Benzoïque dans l'Eau entre la Dilution Infinie et la Saturation: Influence de la Temperature, *Can. J. Chem. Eng.*, Vol 54, 1976, p 460-463 (in French)