We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



2

Diffusion in Polymer Solids and Solutions

Mohammad Karimi
Amirkabir University of Technology, Department of Textile Chemistry
Iran

1. Introduction

The industrial importance of penetrable and/or impenetrable polymer systems is evident when one faces with a huge number of publications considering various aspects of diffusion phenomenon. Strong worldwide interest to realize more details about the fundamental of the process, generalize the governed laws to new findings, and find fast and reliable techniques of measurement, makes motivation to follow in this field of science.

Polymers are penetrable, whilst ceramics, metals, and glasses are generally impenetrable. Diffusion of small molecules through the polymers has significant importance in different scientific and engineering fields such as medicine, textile industry, membrane separations, packaging in food industry, extraction of solvents and of contaminants, and etc. Mass transfer through the polymeric membranes including dense and porous membranes depends on the factors included solubility and diffusivity of the penetrant into the polymer, morphology, fillers, and plasticization. For instance, polymers with high crystallinity usually are less penetrable because the crystallites ordered has fewer holes through which gases may pass (Hedenqvist and Gedde, 1996, Sperling, 2006). Such a story can be applied for impenetrable fillers. In the case of nanocomposites, the penetrants cannot diffuse through the structure directly; they are restricted to take a detour (Neway, 2001, Sridhar, 2006).

In the present chapter the author has goals of updating the theory and methodology of diffusion process on recent advances in the field and of providing a framework from which the aspects of this process can be more clarified. It is the intent that this chapter be useful to scientific and industrial activities.

2. Diffusion process

An enormous number of scientific attempts related to various applications of diffusion equation are presented for describing the transport of penetrant molecules through the polymeric membranes or kinetic of sorption/desorption of penetrant in/from the polymer bulk. The mass transfer in the former systems, after a short time, goes to be steady-state, and in the later systems, in all the time, is doing under unsteady-state situation. The first and the second Fick's laws are the basic formula to model both kinds of systems, respectively (Crank and Park, 1975).

2.1 Fick's laws of diffusion

Diffusion is the process by which penetrant is moved from one part of the system to another as results of random molecular motion. The fundamental concepts of the mass transfer are

comparable with those of heat conduction which was adapted for the first time by Fick to cover quantitative diffusion in an isotropic medium (Crank and Park, 1975). His first law governs the steady-state diffusion circumstance and without convection, as given by Equation 1.

$$J = -D\frac{\partial c}{\partial x} \tag{1}$$

where J is the flux which gives the quantity of penetrant diffusing across unit area of medium per unit time and has units of mol.cm^{-2}.s^{-1}, D the diffusion coefficient, c the concentration, x the distance, and $\partial c/\partial x$ is called the gradiant of the concentration along the axis. If J and c are both expressed in terms of the same unit of quantity, e.g. gram, then D is independent of the unit and has unit of cm^2.s^{-1}. Equation 1 is the starting point of numerous models of diffusion in polymer systems. Simple schematic representation of the concentration profile of the penetrant during the diffusion process between two boundaries is shown in Fig. 1-a. The first law can only be directly applied to diffusion in the steady state, whereas concentration is not varying with time (Comyn, 1985).

Under unsteady state circumstance at which the penetrant accumulates in the certain element of the system, Fick's second law describes the diffusion process as given by Equation 2 (Comyn, 1985, Crank and Park, 1968).

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x}\right] \tag{2}$$

Equation 2 stands for concentration change of penetrant at certain element of the system with respect to the time (t), for one-dimensional diffusion, say in the x-direction.

Diffusion coefficient, D, is available after an appropriate mathematical treatment of kinetic data. A well-known solution was developed by Crank at which it is more suitable to moderate and long time approximation (Crank, 1975). Sorption kinetics is one of the most common experimental techniques to study the diffusion of small molecules in polymers. In this technique, a polymer film of thickness $2l$ is immersed into the infinit bath of penetrant, then concentrations, c_t, at any spot within the film at time t is given by Equation 3 (Comyn, 1985).

$$\frac{c_t}{c_\infty} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right]\times\cos\left[\frac{(2n+1)\pi x}{2l}\right] \tag{3}$$

where c_∞ is the amount of accumulated penetrant at equilibrium, i.e. the saturation equilibrium concentration within the system. $L = 2l$ is the distance between two boundaries layers, x_0 and x_1 (Fig. 1-b).

Integrating Equation 3 yields Equation 4 giving the mass of sorbed penetrant by the film as a function of time t, M_t, and compared with the equilibrium mass, M_∞.

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

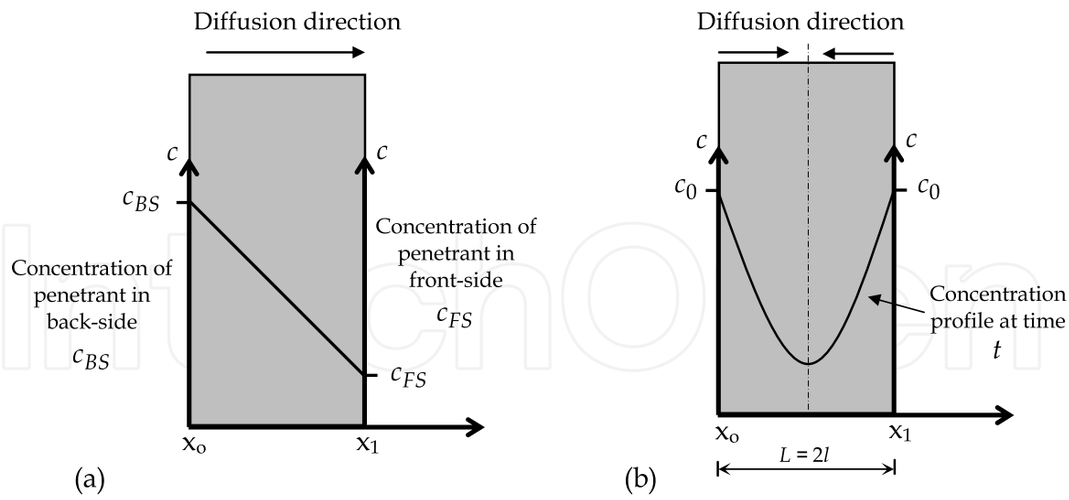


Fig. 1. Concentration profile under (a) steady state and (b) unsteady state condition.

For the processes which takes place at short times, Equation 4 can be written, for a thickness of $L = 2l$, as

$$\frac{M_t}{M_\infty} = \frac{2}{l}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \tag{5}$$

Plotting the M_t / M_∞ as function of $t^{1/2}$, diffusion coefficient can be determine from the linear portion of the curve, as shown in Fig. 2. Using Equation 5 instead of Equation 4, the error is in the range of 0.1% when the ratio of M_t / M_∞ is lower than 0.5 (Vergnaud, 1991).

In the case of long-time diffusion by which there may be limited data at $M_t / M_\infty \leq 0.5$, Equation 4 can be written as follow:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left[\frac{-D\pi^2 t}{4l^2}\right] \tag{6}$$

Equation 6 is usually used in the form of Equation 7, as given following,

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2 t}{4l^2} \tag{7}$$

This estimation also shows similarly negligible error on the order of 0.1% (Vergnaud, 1991). Beyond the diffusion coefficient, the thickness of the film is so much important parameter affected the kinetics of diffusion, as seen in Equation 4. The process of dyeing by which the dye molecules accumulate in the fiber under a non-linear concentration gradient is known as the unsteady-state mass transfer, since the amount of dye in the fiber is continuously increasing. Following, Equation 8, was developed by Hill for describing the diffusion of dye molecules into an infinitely long cylinder or filament of radius r (Crank and Park, 1975, Jones, 1989).

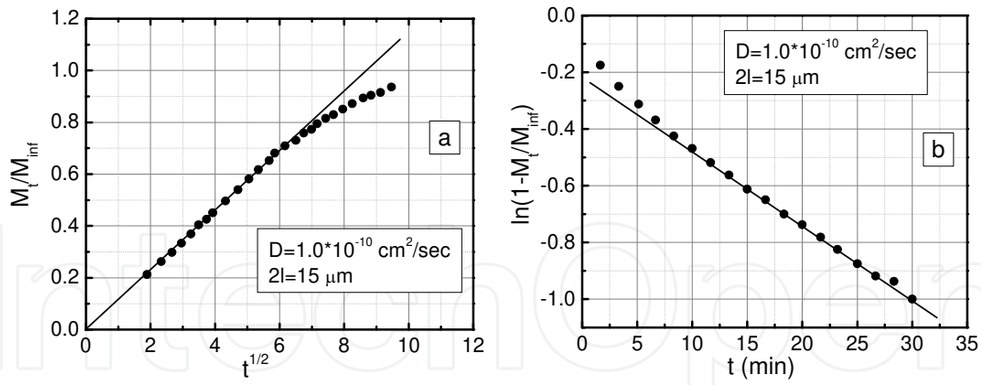


Fig. 2. Kinetics of mass uptake for a typical polymer. (a) M_t / M_∞ as function of $t^{1/2}$, (b) $\ln(1 - M_t / M_\infty)$ as function of t; data were extracted from literature (Fieldson and Barbari, 1993).

$$\frac{C_t}{C_\infty} = 1 - 0.692\left[\exp\left(-5.785Dt / r^2\right)\right] + 0.190\left[\exp\left(-30.5Dt / r^2\right)\right] + 0.0775\left[\exp\left(-74.9Dt / r^2\right)\right] + 0.0415\left[\exp\left(-139Dt / r^2\right)\right] + 0.0258\left[\exp\left(-223Dt / r^2\right)\right] + ...) \quad (8)$$

Variation of C_t / C_∞ for different values of radius of filaments are presented in Fig. 3. As seen in Fig.3, decreasing in radius of filament causes increasing in the rate of saturating.

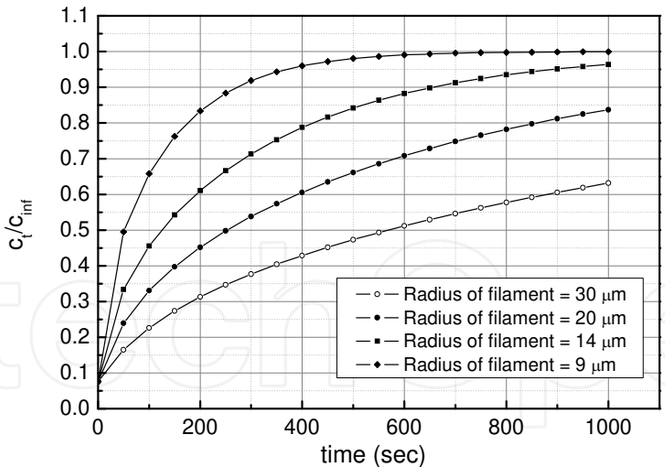


Fig. 3. C_t / C_∞ of dyeing versus t for different radius of fibers.

2.2 Permeability

The permeability coefficient, P, is defined as volume of the penetrant which passses per unit time through unit area of polymer having unit thickness, with a unit pressure diference across the system. The permeabilty depends on solubility coefficient, S, as well as the diffusion coefficient. Equation 9 expresses the permeabilty in terms of solubility and diffusivity, D, (Ashley, 1985).

$$P = D.S \tag{9}$$

Typical units for P are (cm^3 cm)/(s cm^2 Pa) (those units×10^{-10} are defined as the barrer, the standard unit of P adopted by ASTM).
Fundamental of diffusivity was discussed in the previous part and its measurement techniques will be discussed later. Solubility as related to chemical nature of penetrant and polymer, is capacity of a polymer to uptake a penetrant. The preferred SI unit of the solubility coefficient is (cm^3 [273.15; 1.013×10^5 Pa])/(cm^3.Pa).

2.3 Fickian and non-Fickian diffusion

In the earlier parts, steady-state and unsteady-state diffusion of small molecules through the polymer system was developed, with considering the basic assumption of Fickian diffusion. There are, however, the cases where diffusion is non-Fickian. These will be briefly discussed. Considering a simple type of experiment, a piece of polymer film is mounted into the penetrant liquid phase or vapor atmosphere. According to the second Fick's law, the basic equation of mass uptake by polymer film can be given by Equation 10 (Masaro, 1999).

$$\frac{M_t}{M_\infty} = kt^n \tag{10}$$

where the exponent n is called the type of diffusion mechanism, and k is constant which depends on diffusion coefficient and thickness of film.
Fickian diffusion (Case I) is often observed in polymer system when the temperature is well above the glass transition temperature of the polymer (T_g). Therefore it expects that the M_t / M_∞ is proportional to the square-root of time i.e. $n = 0.5$. Other mechanisms has been established for diffusion phenomenon and categorized based on the exponent n, as follow (Sperling, 2006);

$n > 1$	Supercase II
$n = 1$	Case II
$1 > n > \frac{1}{2}$	Anomalous
$\frac{1}{2} > n$	Pseudo-Fickian

The Case II diffusion is the second most important mechanism of diffusion for the polymer. This is a process of moving boundaries and a linear sorption kinetics, which is opposed to Fickian. A sharp penetration front is observed by which it advances with a constant rate. More detailed features of the process, as induction period and front acceleration in the latter stage, have been documented in the literatures (Windle, 1985).
An exponent between 1 and 0.5 signifies anomalous diffusion. Case II and Anomalous diffusion are usually observed for polymer whose glass transition temperature is higher than the experimental temperature. The main difference between these two diffusion modes concerns the solvent diffusion rate (Alfrey, 1966, as cited in Masaro, 1999).

2.4 Deborah number

A solid phase is generally considered as a glass or amorphous if it is noncrystalline and exhibits a second-order transition frequently referred to the glass transition (T_g) (Gibbs and Dimarzio, 1958), which is the transition between a glassy, highly viscous brittle structure,

and rubbery, less viscous and more mobile structure, states. The rubbery state ($T > T_g$), represents a liquid-like structure with high segmental motion resulting an increase of free volume with temperature. When the penetrant diffuses into the polymer, the plasticization occurs resulting a decrease of the T_g (Sperling, 2006) and increase of free volume of the mixture (Wang, 2000).

Since the mobility of polymer chain depends on temperature, it greatly decreases below and increases above the glass transition temperature. On the other hand, sorption and transport of penetrant into the polymer can change the mobility of the segments because of T_g depression. Consequently, the relaxation time of polymer decreases with increasing temperature or concentration of penetrant. The overall sorption process reflects all relaxation motions of the polymer which occur on a time scale comparable to or greater than the time scale of the concurrent diffusion process. Indeed, a Deborah number can be defined as the ratio of the relaxation time to the diffusion time. Originally introduced by Vrentas et al. (Vrentas, 1975), it is given by Equation 11.

$$D_e = \frac{\tau_e}{t} \tag{11}$$

where t is the characteristic time of diffusion process being observed and τ_e is the characteristic time of polymer. The Deborah number (D_e) is a useful scaling parameter for describing the markedly different behavior frequently being observed in diffusion process. For the experiments where that number is much less than unity ($D_e \ll 1$), relaxation is fast, penetrants are diffusing in where conformational changes in the polymer structure take place very quickly. Thus the diffusion mechanism will be Fickian. When the number is near unity, ($D_e \cong 1$), intermediate behavior is observed and can be called of 'coupled' diffusion-relaxation or just 'anomalous' (Rogers, 1985). If $D_e \gg 1$, the diffusing molecules are moving into a medium which approximately behaves as an elastic material. This is typical case of diffusion of small molecules into the glassy polymer. When the penetrantes diffuse into the polymer matrix until the concentration reaches an equilibrium value, a sharp diffusion front is formed that starts to move into the polymer matrix, where the glass transition of mixture drops down the experimental temperature. This process is the 'induction period' and represents the beginning of case II mechanism (Lasky, 1988).

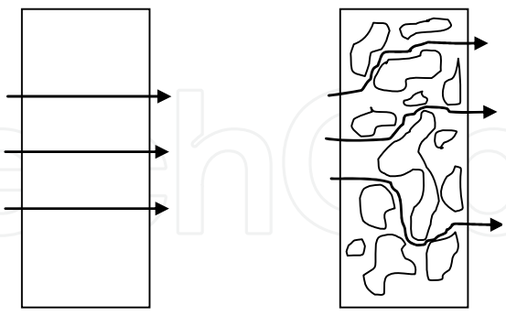
2.5 Geometrical impedance factor

Diffusing penetrant through the polymer is greatly affected by the presence of impenetrable micro- and or nano-pieces which are located into the structure. Crystallites and micro and nano fillers are impenetrable and behave as barrier in advancing penetrant, causing to form a tortuosity in diffusion path, see Fig. 4. Considering the geometrical aspect of diffusion process, Michael et al. (Michaels and Parker, 1959, Michaels and Bixler, 1961, cited in Moisan, 1985, Hadgett, 2000, Mattozzi, 2007) proposed the following relationship between the overall diffusivity (D) and the diffusivity of the amorphous component (D_a).

$$D = \frac{D_a}{\tau\beta} \tag{12}$$

where β is an 'immobilization' factor and τ is a 'geometrical impedance' factor. β is almost equal to 1 for helium, that is a diffuser having very low atomic radius. It has been

recognized that τ increases very rapidly with increasing concentration of impenetrable pieces, and that the two factors increase much more rapidly in large molecules than in small ones (Moisan, 1985).



(a) (b)

Fig. 4. Schematic demonstration of path through the structure; (a) homogeneous medium, (b) heterogeneous medium.

Filled polymer with nano-particles has lower diffusion coefficient than unfilled one. Poly(methyl methacrylate) (PMMA), for instance, is a glassy polymer, showing a non-Fickain diffusion for water with $D = 3.35 \times 10^{-8}\ cm^2.s^{-1}$. The diffusion coefficient of water is reduced to $D_e = 3.15 \times 10^{-9}\ cm^2.s^{-1}$ when the polymer is filled by silicate nanolayers of Cloisite 15A (Eyvazkhani and Karimi, 2009). Geometerical dimension, size distribution and amount of fillers as well as its level of dispersion into the polymer matrix are important factors controlling the rate of mass transfer through the filled polymer, especially nanocomposites.

As cleared, diffusing penetrants through a homogeneous polymer structure are advancing in a straight line, while they meander along the path, passing through the heterogeneous polymer structure such as nanocomposite. Polymer nanocomposites (PNCs) form by dispersing a few weight percent of nanometer-sized fillers, in form of tubular, spherical, and layer. Compared to neat polymer, PNCs have tendency to reduce the diffusion coefficient of penetrant through the increase in path length that is encountered by a diffusing molecule because of the presence of a huge number of barrier particles during the mass transfer. The largest possible ratio of the diffusivity of a molecule through the neat polymer (D) to that of the same molecule through the filled polymer (D_e) was formulated by several researchers whose equations were recently looked over by Sridhar and co-workers (Sridhar, 2006).

Block copolymers as well as polyblends are other interesting materials; have attracted the attention of a great number of scientists because of designable structure on a nanometer scale. These polymers have a multiphase structure, assembling at various textures. Sorption and transport in both have been approached along the lines discussed above. Tecoflex-EG72D (TFX), a kind of polyurethane, has potential to employ in medical application. Two-phase structure of this copolymer causes the path of penetrating into the TFX to be detour, not to be straight line. Generally, such materials have two different transition temperatures regarding to the phases, making them to be temperature sensitive incorporated with water vapor permeability. Fig. 5 shows the amount of water passing through the TFX membrane

as a function of time at different temperatures in steady state condition (Hajiagha and Karimi, 2010). Noticeably, an acceleration in permeability is observed above 40 °C concerning to glass transition temperature of soft phase. Controlling the microstructure of these multi-phase systems allows tuning the amount of permeability. Strong worldwide interest in using temperature sensitive materials shows these materials have potential to employ in textile industry, medicine, and environmental fields. For instance, combining these materials with ordinary fabrics provides variable breathability in response to various temperatures (Ding, 2006).

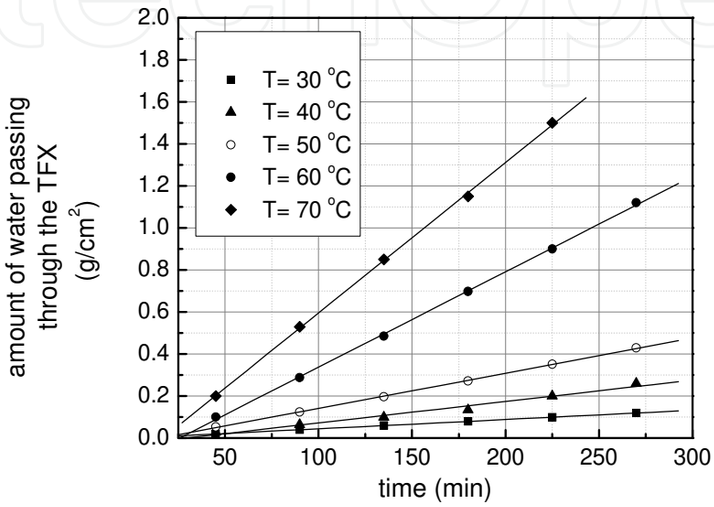


Fig. 5. Diffusion through the TFX film under steady-state conditions.

3. Thermodynamic of penetrant/polymer mixture

Thermodynamically describing the penetrant/polymer mixture is based on mobility of polymer chain during the diffusion process. Diffusion of penetrant into the polymer yeilds plasticization, resulting in significant depression of glass transition temperature. Indeed, a glassy polymer isothermally changes into a rubbery state only by diffusion of penetrant. Using classical thermodynamic theory, the glass transition temperature of the solvent and polymer mixture can be described by the following expression, which was derived by Couchman and Karasz (Couchman and Karasz, 1978).

$$T_{gm} = \frac{x_1 \Delta C_{p1} T_{g1} + x_3 \Delta C_{p3} T_{g3}}{x_1 \Delta C_{p1} + x_3 \Delta C_{p3}} \tag{13}$$

where T_{gm} and T_{gi} are the glass transition temperatures of the mixture and the pure component i, respectively. ΔC_{pi} is the incremental change in heat capacity at T_{gi}, and $x_i = n_i / (n_1 + n_3)$ represents the mole fraction defined on the basis of the repeat unit of the polymer. Most values of solvent glass transition have been published from free volume theory (Hong, 1995).

A solid phase of polymer is ordinarily designated as a glass if it is non-crystalline and if it exhibits at a certain higher temperature a second-order transition, often referred to as the

glass transition (Gibbs and Dimarzio, 1958). It was found that the specific volume of those polymers diminishes linearly with the temperature until the glass transition temperature T_g is achieved. Below this temperature the reduction continues but at a smaller rate. The difference between the volume observed at absolute zero temperature and the volume measured at transition temperature was considered as space, which, in the amorphous solid, is available for oscillations (Dimarzio, 1996). For the following model derivation, we assume that the state of the investigated polymer at the beginning is a glass. In this state the polymer chains are fixed on their location at least in comparison with the typical time constants of individual jump events of diffusing water molecules from one hole of the free volume to another. On the other hand, according to the free volume theory characterizing the excluded volume of a glassy polymer system, there is "free" space between atoms of the polymer chain, which can be occupied by small penetrant molecules. However, due to their size and shape, these penetrants can only "see" a subset of the total free volume, termed as the "accessible free volume". In this way accessible free volume depends on both, polymer and penetrant, whereas the total free volume depends only on the polymer. The situation is illustrated schematically in Fig. 6 on a lattice where it is assumed that the polymer chain consists of segments, which have the same volume as a penetrant particle.

This accessible free volume consists of the empty lattice sites and the sites occupied by the penetrant. For a corresponding lattice model, the primary statistical mechanical problem is to determine the number of combinatorial configurations available for the system (Sanchez and Lacombe, 1978, Prausnitz and Lichtenthaler, 1999). From the assumption of the glassy state, it follows that there is only one conformation for the polymer chain. This situation is different to the case of a polymer solution. Furthermore it is assumed for the thermodynamic model that also during the diffusion of penetrants through the polymer bulk, the conformation of the polymer chains does not change and remains as before (One should have in mind that diffusion is in reality only possible by rearrangement of polymer segments, i.e. by the opening of temporary diffusion channels. Therefore the zero-entropy is describing the extreme case of a completely stiff, i.e. ultra-glassy polymer, in which strictly speaking no diffusion could occur.). Therefore the number of possible conformations, for polymer chain, does not vary and is equal to one $(\Omega = 1)$. It results that the entropy change during the penetration is zero, $S_{polymer} = k\ln(\Omega) = 0$. Thus, if the situation is glassy, the Gibbs free energy of mixing (penetrant/polymer), ΔG_m, is given by Karimi and co-workers (Karimi, 2007),

$$\Delta G_m = \Delta H_m - T\Delta S_m = RT\left[\chi_{12}^{*} n_1\phi_2 + n_1\ln(\frac{\phi_1}{\phi_{FV}}) + n_0\ln(\frac{\phi_0}{\phi_{FV}})\right] \tag{14}$$

where ϕ_{FV} is fractional free volume of pure polymer, ϕ_o volume fraction of holes, R the gas constant, T the absolute temperature, and n_1 and n_o are the number of moles of penetrant and holes respectively.

The GP model (Equation 14) represents, according to the definition, the thermodynamic state of a penetrant/polymer system where the polymer chains are completely inflexible and this stiffness will not be influenced by the sorption of the penetrant. In general such a condition will be only fulfilled if the quantity of penetrant in the polymer matrix is very small. Mainly hydrophobic polymers are candidates, which will meet these requirements

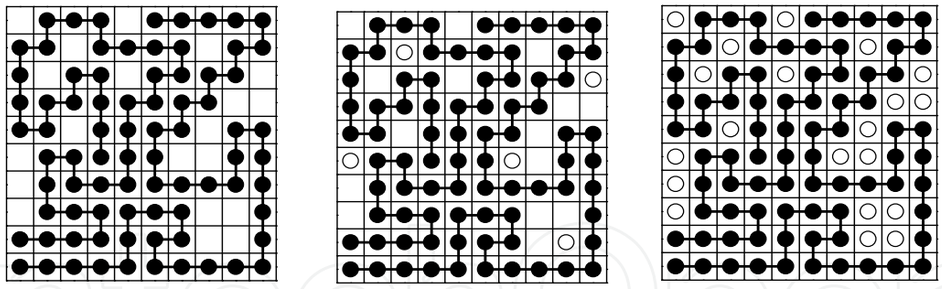


Fig. 6. Segments of a polymer molecule located in the lattice and penetrant molecules distributed within, schematically.

completely. However it cannot be expected that the GP model can also describe nonsolvent/polymer systems for hydrophilic membrane polymers. Therefore in order to extent the GP-model, it is assumed in the following that the status of the wetted polymer sample can be considered as a superposition of a glassy state and a rubber-like state (as well-described by Flory and Huggins, 1953), in general. We consider the polymer sample partly as a glass and partly (through the interaction with penetrant) as a rubber. The ratio of glassy and rubbery contributions will be assumed to be depending on the stiffness of the dry polymer sample (characterized e.g., by the glass temperature) and the quantity of sorbed penetrant. The glass temperature T_{gm} of a penetrant/polymer mixture can be estimated by Equation 13. Thus, the Gibbs free energy is given as follow (Karimi, 2007)

$$\frac{\Delta G_m}{RT} = \frac{\Delta H_m}{RT} - \frac{T\Delta S_m}{RT} = \chi_{12}^{*} n_1 \phi + \beta\left[n_1 \ln(\phi_1) + n_2 \ln(\phi_2)\right] + (1-\beta)\left[n_1 \ln(\frac{\phi_1}{\phi_{FV}}) + n_0 \ln(\frac{\phi_0}{\phi_{FV}})\right] \tag{15}$$

β is difinned according to $\beta = (T_{gm} - T_{g2}) / (T - T_{g2})$.

Actually, β represents a measure for the relative amount of "rubber-like regions" in the polymer at the temperature T of interest in the sorbed state. Per definition the β values vary between 0 and 1 for a completely glass-like and a completely rubber-like state, respectively, if both states are present. However β-values higher than 1 can be indicating a completely rubber-like state, well-describing by Flory-Huggins theory (Flory, 1956).

$$\frac{\Delta G_M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} n_1 \phi_2 \tag{16}$$

In Equation 16, the first two terms is the combinatorial entropy computed by considering the possible arrangement of only polymer chains on the lattice.

With assumption of rubbery state, swelling of polymer by which the penetrant diffuses into the polymer more than free volume and the junction point is constant; Flory-Rehner equation (Flory, 1950, as cited in Prabhakar, 2005) is applicable.

$$\ln a_1 = \ln(1-\phi_2) + \phi_2 + \chi \phi_2^{\,2} + \frac{V_1 \rho_2}{\bar{M}_c}(\phi_2^{1/3} - \frac{1}{2}\phi_2) \tag{17}$$

where a_1 is penetrant activity and ϕ_2 volume fraction of polymer.

4. Measurement of diffusion

4.1 FTIR-ATR spectroscopy

Measuring the diffusion of small molecules in polymers using Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy, is a promising technique which allows one to study liquid diffusion in thin polymer films in situ. This technique has increasingly been used to study sorption kinetics in polymers and has proven to be very accurate and reliable. Fig 7 shows schematic of the ATR diffusion experiment. In practice, the sample is cast onto one side of the ATR prism (optically dense crystal) and then the diffusing penetrants are poured on it. Various materials such as PTFE are used to seal the cell.

According to the principle of ATR technique (Urban, 1996), when a sample as rarer medium is brought in contact with totally reflecting surface of the ATR crystal (as a propagating medium), the evanescent wave will be attenuated in regions of the infrared spectrum where the sample absorbs energy. The electric field strength, E, of the evanescent wave decays exponentially with distance from interface, as shown in Fig 7. The distance, which is on the order of micrometers, makes ATR generally insensitive to sample thickness, allowing for dynamic measurement in a layer with certain thickness. The penetration depth of the IR beam in sample can be calculated by Equation 18.

$$dp = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}} \tag{18}$$

where depth of penetration of evanescent wave is shown by dp, λ is the wavelength of the infrared radiation, n_1 and n_2 are the refractive indices of flat crystals and polymer solutions respectively and θ is the angle of incidence beam. By increasing the refractive index of the ATR crystal, the depth of penetration will decrease (i.e changing from ZnSe to Ge, with refractive indices equal to 2.4 and 4, respectively). This will decrease the effective path length and therefore decrease the absorbance intensity of the spectrum. High index crystals are needed when analyzing high index materials. The refractive index of some ATR crystal is listed in Table 1.

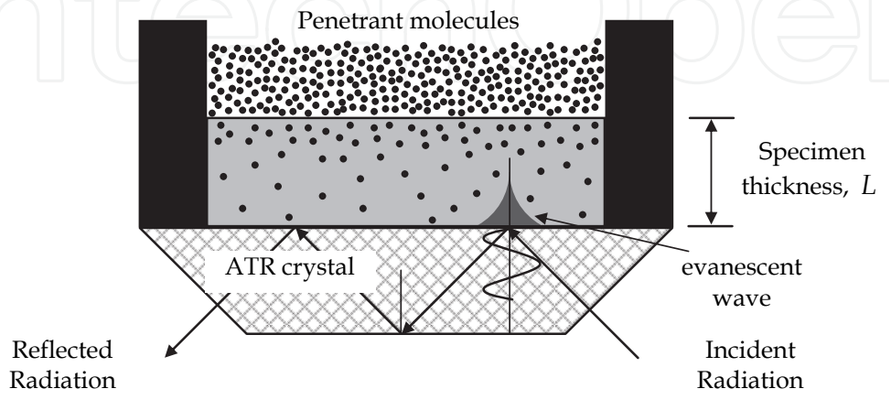


Fig. 7. Schematic representation of the ATR equipment for diffusion experiment.

ATR prism	Refractive index
ZnSe	2.4
Ge	4
ZnS	2.2
AMTIR	2.5
Si	3.4

Table 1. Refractive index of some ATR prism

As the goal of IR spectroscopic application is to determine the chemical functional group contained in a particular material, thus it is possible to measure the dynamic change of components containing such functional groups where they make a mixture. Considering water molecules as penetrant into the kind of polymer, the characteristic peak of water in region between 3800 cm^{-1} and 2750 cm^{-1} should be increase as results of increasing the concentration of water into the bottom layer of polymer, in contact with ATR prism. A representative sample of the spectra recorded is shown in Fig 8. This is a dynamic measurement of diffusing water into the PMMA uniformly thin film contacted on the ATR crystal.

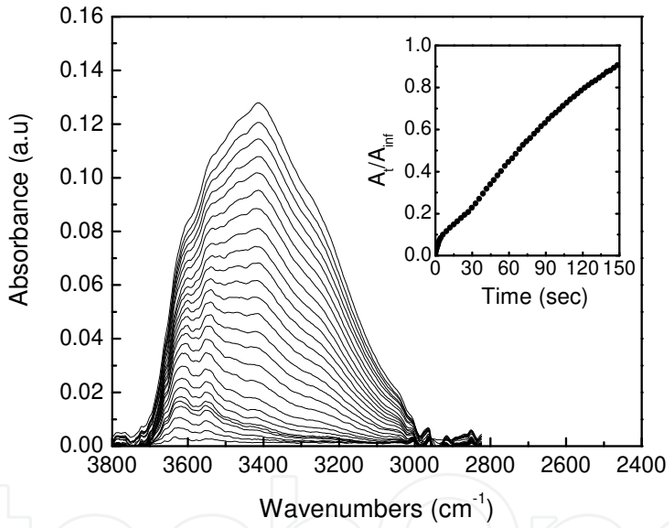


Fig. 8. Sequence of time-evolved spectra from PMMA sample treated at 25 ^{o}C.

To quantify the water concentration the simplest quantitative technique i.e. Beer-Lambert law, can be applied. Beer's law states that not only is peak intensity related to sample concentration, but the relationship is linear as shown in the following equation.

$$A = abc \tag{19}$$

where a is absorptivity of the component at the measured frequency, b pathlenght of the component, and c is the concentration of the component. Quantity of absorptivity, a, is determined based on certain calibration models. Various calibration models are available for quantifying unknown concentration of components. These models are simple Beer's law, classical least squares (CLS), stepwise multiple linear regression (SMLR), partial least squares (PLS), and principal component regression (PCR).

As a result, the Fickian concentration profile can be developed by Equation 20 (Fieldson, Barbari, 1993).

$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1-\exp(-2\gamma l)]} \times \left[\frac{\exp\left(\frac{-D\pi^2 t}{4l^2}\right)\left(\frac{\pi}{2l}\exp(-2\gamma l) + (2\gamma)\right)}{\left(\frac{\pi^2}{4l^2} + 4\gamma^2\right)} \right] \tag{20}$$

where $\gamma = 1/dp$.

In Equation 20, it is assumed that the value of γ is constant. This is not entirly correct because it depends on the polymer refractive index, which can vary as the concentration of penetrant increases. Equation 20 could be simplified if following condition could be found in the experiment (Fieldson, Barbari, 1993):

$$4\gamma^2 \gg \frac{\pi^2}{4l^2} \quad \text{and} \quad 1 \gg \exp(-2\gamma l) \tag{21}$$

therefore

$$\ln(1 - \frac{A_t}{A_\infty}) = \ln(\frac{4}{\pi}) - \frac{D\pi^2}{4l^2}t \tag{22}$$

With Equation 22, the logarithm of the absorbance data is plotted as a function of time, and then the diffusion coefficient, D, is given by the slope of a linear least square regression. This is completely similar to the use of Equation 7 to determine the diffusion coefficient in gravimetric sorption experiments at long time. This technique has been increasingly employed in recent years (Fieldson and Barbari, 1993, Sammon, 2000, Yi and Pellegrino, 2002, Hua, 2004, Pereira, 2005, Doppers, 2006).

4.2 Other techniques of measuring

Beside with FTIR-ATR technique, a great variety of methods are available for measuring diffusion coefficients of penetrant into the polymeric systems. Gravimetric techniques that directly follow mass changes with time are frequently used for investigating the sorption kinetics (Chandra and Koros, 2009, Karimi, 2005, Cotugno, 2005). This is more applicable for gases and vapors which are almost condensable. The polymer thin film is hung on calibrated magnetic suspension balance; both are placed in a chamber maintained at the certain temperature. Sorption kinetics are obtained by recording the sample weight as function of time after introduction of the vapor into the chamber.

If non-condensable gases such as carbon dioxide, nitrogen, and methane are given to monitor sorption kinetics, pressure decay techniques are often employed (Liu and Tomasko, 2007). The polymer sample is loaded into the vessel conditioned at certain temperature. Then, penetrating gas is introduced to the vessel at a preset pressure. As the gas sorption proceeded, the detected system pressure gradually decreased from the initial reading. The saturation state reaches when no fluctuation in the pressure is observed.

'Wet cup' is the other most applicable technique to measure the diffusion coefficient as well as permeability of the polymer, not to measure sorption kinetics (Hubbell, 1975, Hu, 2007).

Based on the water cup method, referring to ASTM E96-00 standard, the vapor passing through the polymer film measured as function of time. That is, an open cup containing water sealed with the specimen membrane, and the assembly is placed in a test chamber at the certain temperature, with a constant relative humidity of 50%, and the water lost isrecorded after certain period of time

5. Mass transfer across the interface between polymer solution and nonsolvent bath

Polymer solutions are important for a variety of purposes, especially, for manufacturing fibers and membranes. Generally, solidification of polymer in shape of interest takes place by solvent evaporation from nonsolvent diffusion into the polymer solution. During the process, polymer solution is undergoing a change in the concentration of components. A schematic representation of mass transfer through the interface between polymer solution and nonsolvent bath is depicted in Fig. 9. During the quench period, solvent-nonsolvent exchange is doing with time and eventually polymer precipitation takes place. The ratio of solvent-nonsolvent exchange, predicting mass transfer paths on the thermodynamic phase diagram, is an important factor to control the ultimate structure of product (Karimi and Kish, 2009).

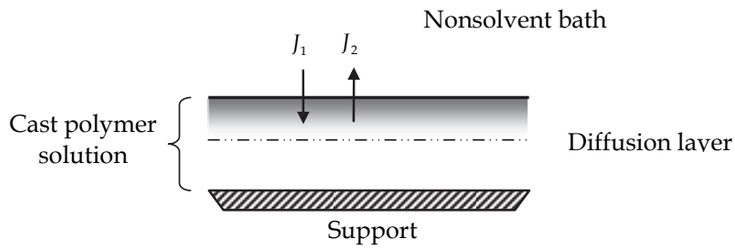


Fig. 9. Schematic presentation of mass transfer through the interface between polymer solution and nonsolvent bath.

Such a mass transfer process requires a consideration based on the thermodynamics of irreversible processes which indicates that the fundamental driving forces for diffusion through the interface of multiphase system are the gradients of the chemical potential of each of the system components. Here, considering polymer solution and nonsolvent bath as two-phase system, the amount of molecules passing through the interface could be described by Fick's law if the intrinsic mobility (M) of each component could be known. The flux (J) due to pure diffusion is:

$$J = -(\frac{\mathrm{M}\phi}{N})(\frac{\partial \mu}{\partial x}) \tag{23}$$

where N is Avogadro's number and μ is chemical potential (partial molar free energy). Replacing $\mu = RT\ln a$ in to the Equation 23 then,

$$J = -RT\frac{\mathrm{M}\phi}{N}(\frac{\partial \ln a}{\partial x}) \tag{24}$$

where a is the activity, R the gas constant, and T is the absolute temperature. Mobility coefficient some times are called self-diffusion coefficient (D^*), presenting the motion and diffusion of molecules without presence of concentration gradient and/or any driving force for mass transfer, given by $D^* = \mathrm{M}RT / N$. Then

$$J = -D^* \phi (\frac{\partial \ln a}{\partial x}) \tag{25}$$

Since it is difficult to measure the self-diffusion coefficient, a thermodynamic diffusion (D_T) is introduce to use in theories regarding the concentration and temperature dependence of diffusion, as given by

$$D_T = D(\frac{\partial \ln c_1}{\partial \ln a_1}) \tag{26}$$

According to Equation 25 to determine the mass transfer of solvent and or nonsolvent across the interface, it should be given their chemical potentials. Flory-Huggins (FH) model is well-established to use for describing the free energy of the polymer solution, as given in Equation 26. It should be noted that the FH model can be extended for multi-component system if more than one mobile component exists for mass transfer; more details for Gibbs free energy of multi-components system are documented in literatures (Karimi, 2005, Boom, 1994)

5.1 Mass transfer paths

Polymer membrane which is obtained by the so-called nonsolvent-induced phase separation (NIPS) (Fig. 9), has a structure determined by two distinct factors: (1) the phase separation phenomena (thermodynamics and kinetics) in the ternary system, and (2) the ratio and the rate of diffusive solvent-nonsolvent exchange during the immersion (Karimi, 2009, Wijmans, 1984). The exchange of the solvent and the nonsolvent across the interface initiates the phase separation of the polymer solution in two phases; one with a high polymer concentration (polymer-rich phase), and the other with a low polymer concentration (polymer-lean phase). The morphology of the membranes, the most favorable feature, is strongly related to the composition of the casting film prior and during the immersion precipitation. The compositional change during the phase separation has been frequently discussed theoretically (Tsay and McHugh, 1987), but the experimental results for the composition of the homogeneous polymer solution prior to precipitation of polymer are scarce (Zeman and Fraser, 1994, Lin, 2002). In particular, composition changes of all components prior to the demixing stage are necessary. In order to find out the change of composition during the phase inversion process it needs to determine the rate of solvent outflow (J_1) and nonsolvent inflow (J_2) through the diffusion layer. By this measurement the calculation of the changes in polymer content becomes possible.

As stated earlier, the flux for mobile components involved in the NIPS process can be described by Equation 27

$$J_i = -(RT)^{-1} D_i(\phi) \phi_i (\frac{\partial \mu_i}{\partial x}) \tag{27}$$

where J_i is the volume flux of component i. Here the self-diffusion coefficient (D_i) is considered as concentration-dependence.
To determine the mass transfer path for the polymer solution immersed into the nonsolvent bath the ratio of mass flaxes of nonsolvent to which of solvent should be plotted. Therefore we have

$$\frac{J_1}{J_2} = \sigma = \frac{\phi_1}{\phi_2} . \frac{d\mu_1}{d\mu_2} \tag{28}$$

The assumption made here is that the ratio of $D_1(\phi_1,\phi_2) / D_2(\phi_1,\phi_2)$ is constant and unity. If the differentials of the chemicals potential are expressed as functions of the volume fractions, one finds

$$\frac{d\phi_1}{d\phi_2} = \frac{\phi_1 \left(\partial\mu_1/\partial\phi_2\right)_{T,P,\phi_1} - k\phi_2 \left(\partial\mu_2/\partial\phi_2\right)_{T,P,\phi_1}}{k\phi_2 \left(\partial\mu_2/\partial\phi_1\right)_{T,P,\phi_2} - \phi_1 \left(\partial\mu_1/\partial\phi_1\right)_{T,P,\phi_2}} \tag{29}$$

This first order differential equation yields the relation between ϕ_1 and ϕ_2 in the diffusion layer as a function of the ratio $\sigma = J_1 / J_2$ and one of the boundary conditions.
With the aid of the Flory-Huggins expressions for the chemical potentials together with Equation 29, Cohen and co-workers (Cohen, 1979) calculated, for the first time, the composition paths within the ternary phase diagram and discussed them in relation to the formation of membranes. Equation 29 has been derived using the steady-state condition.
When a solution of a polymer in a solvent is immersed in a bath of a nonsolvent, there are, depending on the preparation condition, various possible outcomes as the solvent release from polymer solution and is replaced to a greater or lesser extent by nonsolvent (i.e. $d\phi_1 / d\phi_2 = ?$) (Karimi, 2009, Stropnik, 2000): *Region I,* as demonstrated in Fig. 10, the total polymer concentration decreases along the route. The change of composition in this region is a one-phase dilution of polymer solution without solidification. *Region II,* the routes intersect the binodal curve and enter the two-phase region. In this region there are two outcomes that depend on the location of the routes with respect to the route assigned by

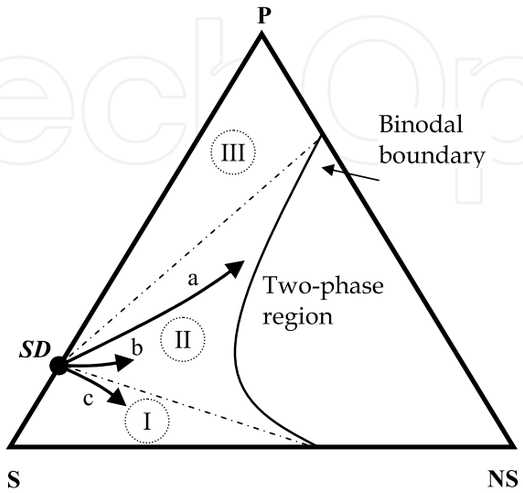


Fig. 10. Mass transfer paths in a triangle phase diagram.

$d\phi_1 / d\phi_2 = 1$, i.e. the path parallel to S~NS line. When $d\phi_1 / d\phi_2 > 1$, polymer content decreases along the route; Solidification of the system is possible as a result of phase transition, but loose heterogeneous structures result. In contrast, when $d\phi_1 / d\phi_2 < 1$, polymer concentration increases and solidification results from the increase of polymer content as well as from possible phase transitions. *Region III,* yields the most dense and homogeneous structures as located outside the two-phase region.

5.2 Measurement of mass transfer paths

Diffusion in polymer solution has been studied for decades using several techniques such as gravimetry (Hu, 1996), membrane permeation (Smith, 1988), fluorescence (Winsudel, 1996), and dynamic light scattering (Asten, 1996), Raman spectroscopy (Kim, 2000, Tsai and Torkelso, 1990), and recently ATR-FTIR (Karimi, 2009, Lin, 2002).

Through the FTIR spectroscopy a spot near the interface of a thin layer of casting solution has been examined. There are two problems with this method. One is the difficulty of introducing the nonsolvent (especially water) into the liquid cell by a syringe due to the capillary action of water. The other is the saturation of coagulation bath with solvent due to limitation of circulation in the nonsolvent bath. It seems that the investigations of the phase demixing processes by such arrangements limits the information about the compositional change prior the phase demixing step.

FTIR-ATR as a promising toll is recently used (Karimi and Kish, 2009) to measure the compositional path during the mass transfer of immersed polymer solution. A special arrangement to determine the concentration of components in the diffusion layers under quench condition prior to the phase separation and the concentration of all components in front of the coagulation boundary was introduced. This technique allows a simultaneous determination of solvent outflow and water inflow during the immersion time. Determination of the composition of all components becomes possible by using the calibration curves.

To measure the concentration of each component, polymer solution was cast directly on surface of the flat crystal (typically ZnSe, a 45o ATR prism), similar arrangement as shown in Fig. 7. The flat crystal is equipped with a bottomless liquid cell. The penetrant is

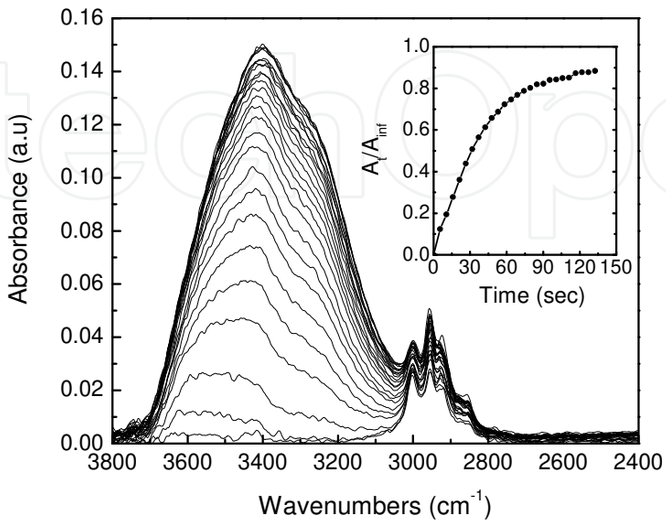


Fig. 11. Intensity (H2O/AC/PMMA system).

transferred into the cell, and simultaneously the recording of the spectrum is started. Fig 11 shows a series of recording spectra at wave number ranging from 2400 to 3800 cm^{-1} for the water/acetone/PMMA system.

Having the FTIR-ATR spectrum measured and the system calibrated, the composition of polymer solution at the layer close to ATR prism could be accurately determined if the method described in part 4.1 could be properly chosen. In the case of polymer solution, generally, simple Beer's law deosn't result correctly. Other methods are normally evaluated with standard solutions to choose the proper one. Advantage of these methods is found to be satisfactory for solving complex analytical problems where the component peaks overlap. The principle component regression (PCR) is succefully used by Karimi (Karimi and Kish, 2009) to resolve the bands in overlapped regions for water/acetone/PMMA and water/DMF/PMMA systems. Since there exists overlapped characteristic peaks the spectra, simple Beer's law deos not predict reliable results.

5.3 Composition path and structure formation

Undoubtedly, the rate of compositional change as well as the ratio of mass transfer of components across the interface of polymer solution are affecting factors controlling the ultimate structure, however, it should not be neglected that the thermodynamics is also the other affecting factor. Mass transfer paths can be derived from the model calculations defined in two different ways: The composition path can represent the composition range in the polymer solution between the support and the interface at a given time. The composition path can also be defined as the composition of a certain well defined element in the solution as a function of time. Some researchers have attempted to make relation between mass transfer and ultimate structure of polymer system. Many of them have referred to the rate of solvent and nonsolvent exchange, postulating instantaneous and delay demixing. This classification was clarified many observations about membrane morphologies. But there are several reports in the literatures that they didn't approve this postulation.

Direct measuring the time dependence of concentration of system components (for instance ϕ_1, ϕ_2, and ϕ_3) during the immersion precipitation process can clarify some obscure aspects of the structure formation. When the polymer solution comes to contact with nonsolvent bath, the solvent release may become higher than the nonsolvent penetration (i.e $d\phi_2 / d\phi_1 > 1$) that leads to an increase in polymer content of the dope and the solvent moves to mix with water in the water bath. The development of structure of this system will differ from which the solvent release is lower than the nonsolvent penetration (i.e $d\phi_2 / d\phi_1 < 1$). Different morphologies for PMMA membrane followed by different ratio of solvent and water exchange, $d\phi_2 / d\phi_1$, have been reported by Karimi (Karimi and Kish, 2009). Fig 12 shows such morphologies for PMMA membrane in which they developed from H_2O/DMF/PMMA and H_2O/AC/PMMA systems.

However the determination of mass transfer is very applicable to make clear some aspects of membrane morphologies, but there is a limitation regarding to the rate of data capturing. Some interesting morphologies were observed during the fast mass transfer in membrane-forming system. For example, Azari and et al. (Azari, 2010) have reported a structure transition when the thickness of cast polymer solution is changed. Fig 13 shows different structures of poly(acrylo nitrile) membrane preparing by same system (H_2O/DMF/PAN).

The authors believe that mass transfer during the process can describe the morphology development if it can be possible to measure.

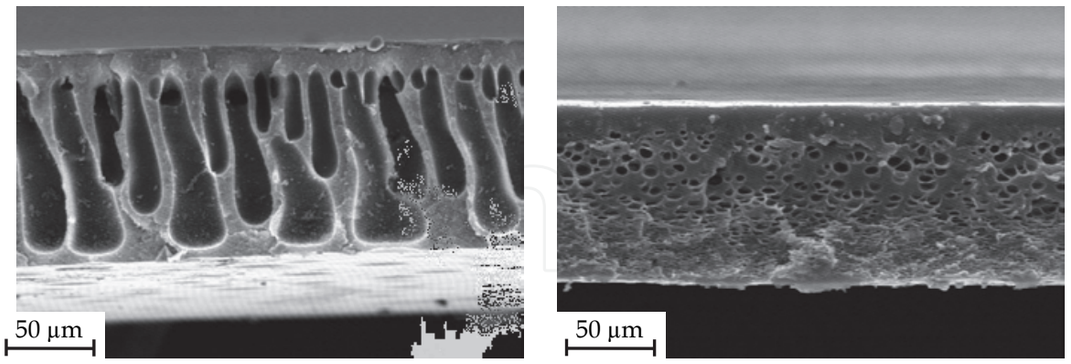


Fig. 12. SEM micrographs of PMMA membrane formed from different solvents; (a) Acetone, (b) N-dimethylformamide.

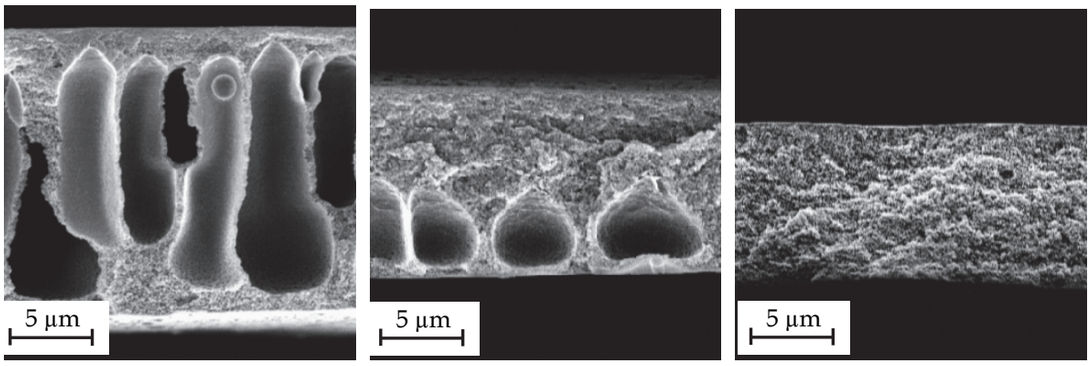


Fig. 13. Effect of membrane thickness on PAN membrane structure (dope, PAN/DMF: PAN 20 wt %: casting temperature 25 ^{o}C: coagulant, water).

6. Conclusion

Diffusion is an important process in polymeric membranes and fibers and it is clear that mass transfer through the polymeric medium is doing by diffusion. Analyzing the diffusion which is basically formulated by Fick's laws, lead to the following conclusions

1. Various mechanisms are considered for diffusion, which it is determined by time scale of polymer chain mobility
2. The rate of permeability can be controlled by loading impenetrable nano-fillers into the structure
3. Driving force for mass transfer across the interface of multiphase systems is chemical potential-base

As well described in this chapter, measuring the diffusion of small molecules in polymers using Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy, is a promising technique which allows one to study liquid diffusion in thin polymer films in situ. This technique can be successfully employed for quantifying the compositional path during the mass transfer of immersed polymer solution, in which it is strongly involved to the structure development.

7. Acknowledgment

Helpful discussions with Prof. S. H. Amirshahi of Amirkabir University of Technology and Dr. N. Taheri of Tehran University are gratefully acknowledged.

8. List of symbols

A	absorption
a	activity
a	absorptivity
b	pathlenght of the component
c	concentration
ΔC	incremental change in heat capacity at T_g
D	diffusion coefficient
D^*	self-diffusion coefficient
D_T	thermodynamic diffusion
D_e	Deborah number
dp	depth of penetration
G	Gibbs free energy
H	Enthalpy
l	film thickness
M	intrinsic mobility
M	mass uptake
N	Avogadro's number
n	number of mole
P	permeability coefficient
R	gas constant
r	radius of filament
S	diffusivity coefficient
S	Entropy
T_g	glass transition
T	temperature
t	film thickness
x	mole fraction
J	flux
τ_e	characteristic time of polymer
β	immobilization factor
τ	geometrical impedance factor
ϕ_{FV}	fractional free volume
ϕ	volume fraction
χ	interaction parameter
ρ	density
υ	molar volume

λ wavelength
μ chemical potential

9. References

Ashley, R. J. (1985). Permeability and Plastics Packaging, In: *Polymer Permeability,* J. Comyn, 269-308, Elsevier Applied Science, ISBN 0-85334-322-5, Northern Ireland.

Azari, S.; Karimi, M. & Kish, M. H. (2010). Structural Properties of the Poly(acrylonitrile) Membrane Prepared with Different Thicknesses. *Industrial & Engineering Chemistry Research,* Vol.49, No. 5, (March 2005), pp. 2442-2448, ISSN 0888-5885

Boom, R. M.; Boomgaard, R. M. & Smolder, C. A. (1994). Equilibrium Thermodynamics of a Quaternary Membrane-Forming System with Two Polymers. I. Calculations. *Macromolecules,* Vol.27, No. 8, (April 1994), pp. 2034-2040, ISSN 0024-9297

Chandra, P. & Koros, W. J. (2009). Sorption and Transport of Methanol in Poly(ethylene terphthalate). *Polymer*, Vol. 50, No. 1, (January 2009), pp. 236-244, ISSN 0032-3861

Cohen, C.; Tanny, G. B. & Prager, S. (1979). Diffusion-Controlled Formation of Porous Structures in Ternary Polymer Systems. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 17, No. 3, (March 1979), pp. 477-489, ISSN 0887-6266.

Comyn J. (1985). Introduction to Polymer Permeability and the Mathematics of Diffusion, In: *Polymer Permeability,* J. Comyn, 1-10, Elsevier Applied Science, ISBN 0-85334-322-5, Northern Ireland.

Cotugno, S., Maio, E. D., Mensitieri, G., Iannace, S., Roberts, G. W., Carbonell, R. G. & Hopfenberg, H. B. (2005). Characterization of Microcellular Biodegradable Polymeric Foams Produced from Supercritical Carbon Dioxide Solutions. *Industrial & Engineering Chemistry Research,* Vol.44, No. 6, (March 2005), pp. 1795-1803, ISSN 0888-5885

Couchman, P. R. & Karasz, F. E. (1978). A classical thermodynamic discussion of the effect of composition on glass-transition temperature. *Macromolecules,* Vol.11, No. 1, (January 1978), pp. 117-119, ISSN 0024-9297

Crank, J. & Park, G. S. (1968). *Diffusion in Polymer* (First Edition), Academic Press, ISBN 0-12-197050-7, USA

Crank, J. (1975). *The Mathematics of Diffusion* (Second Edition), Claredon Press, ISBN 0-19-853344-6, England

Dimarzio, E. A., Castellano, C., & Yang, A. (1996). Glass temperature depression of polymers by use of mixed solvents: A colligative property. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 34, No. 3 , (February 1996), pp. 535-543, ISSN 0887-6266

Doppers, L. M., Sammon, C., Breen, C. & Yarwood, J (2006). FTIR-ATR Studies of the Sorption of Acetone/Water Mixtures in Poly(vinyl alcohol). *Polymer*, Vol. 47, No. 8, (April 2006), pp. 2714-2722, ISSN 0032-3861

Eyvazkhani, A. & Karimi M. (2009). Influence of Silica Nanolayers on the Water Diffusion through PMMA/Layered Silicate Nanocomposites. *Proceedings of the International Conference on Textile Engineering,* Rasht, Iran, October 27-29, 2009.

Fieldson, G. T. & Barbari, T. A. (1993). The Use of FTi.r.-a.t.r Spectroscopy to Characterize Penetrant Diffusion in Polymers. *Polymer*, Vol. 34, No. 6, (March 1993), pp. 1146-1153, ISSN 0032-3861

Flory, P. J. (1953). *Principle of Polymer Chemistry*, Cornell University Press, ISBN 0-8014-0134-8, USA

Gibbs, J. H. & DiMarzio, E. A. (1958). Nature of the Glass Transition and the Glassy State. *The Journal of Chemical Physics*, Vol. 28, No. 3 , (March 1958), pp. 373-383, ISSN 0021-9606

Hadgett, P. M., Goldbeck-Wood, G., Windle, A. H. (2000). Lattice Modelling of Penetrant Diffusion Through Heterogeneous Polymers. *Polymer*, Vol. 41 No. 16 , (Julay 2000), pp. 6151-6160, ISSN 0032-3861

Hajiagha, S., Karimi, M. & Ahmadzadeh, R. (2010). Use Different Solvents for Preparation of Temperature-Sensitive Polyurethane Membrane for Smart Textile, *Proceedings of the International Conference on Intelligent Textiles,* ISBN 978-89-92265-14-0, pp. 125-126, Seoul, Korea, June 17-18, 2010.

Hedenqvist, M. & Gedde, U. W. (1996). Diffusion of Small Molecule Penetrants in Semicrystalline Polymers. *Progress in Polymer Science,* Vol. 21, No. 2, (February 1996), pp. 299-333, ISSN 0079-6700

Hong, S. U. (1995). Prediction of Polymer/Solvent Diffusion Behavior Using Free-Volume Theory. *Industrial & Engineering Chemistry Research,* Vol.34, No. 7, (Julay 1995), pp. 2536-2544, ISSN 0888-5885

Hu, D. C. G. & Chou, K. J. N. (1996). Kinetics of Water Swelling and Development of Porous Structure in Ionic Poly(Acrylonitrile-Acrylamide-Acrylic Acid) Hydrogels. *Polymer,* Vol.37, No. 6, (February 1996), pp. 1019-1025, ISSN 0032-3861

Hu, J. (2007). *Shape Memory Polymers and Textiles* (First Edition), Woodhead Publishing, 978-1-84569-047-2, England

Hua, H. Rivard, T. & Dube, M. A. (2004). Off-line Monitoring of Styrene/Butyl Acrylate Copolymerizations in Toluene Using ATR-FTIR Spectroscopy. *Polymer*, Vol. 45, No. 2, (January 2004), pp. 345-354, ISSN 0032-3861

Hubbell, W. H., Brandt, H. & Munir, Z. A. (1975). Transient and Steady-State Water Vapor Permeation Through Polymer Films. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 13, No 3. , (March 1975), pp. 493-507, ISSN 0887-6266

Jones, F. (1989). Diffusion and Rate of Dyeing, In: *The Theory of Coloration of Textiles*, A. Johnson, pp. 373-427, Society of Dyers and Colourists, ISBN 0-901956-48-1, ?

Karimi M., Heuchel, M., Albrecht, W. & Hofmann, D. (2007). A Lattice-Fluid Model for the Determination of the Water/Polymer Interaction Parameter from Water Uptake Measurements. *Journal of Membrane Science*, Vol. 292, No. 1-2 , (April 2007), pp. 80-91, ISSN 0376-7388

Karimi M.; Albrecht, W.; Heuchel, M.; Kish M. H.; Frahn, J.; Weigel, Th.; Hofmann, D.; Modaress, H. & Lendlein, A. (2005). Determination of Water/Polymer Interaction Parameter for Membrane-Forming Systems by Sorption Measurements and Fitting Techniques. *Journal of Membrane Science*, Vol. 265, No 1-2, (November 2005), pp. 1-12, ISSN 0376-7388

Karimi, M. & Kish, M. H. (2009). Poly(methyl methacrylate) Membrane: Dynamic Measurement of Concentrations During Water-Induced Phase Separation. *Macromolecular Symposia,* Vol. 279, No. 6, (May 2009), pp. 210-220, ISSN 1521-3900

Kim, H. J.; Fouda, A. E. & Jonasson, K. (2000). In Situ Study on Kinetic Behavior during Asymmetric Membrane Formation via Phase Inversion Process Using Raman

Spectroscopy. *Journal of Applied Polymer Science*, Vol. 75, No. 1, (January 2000), pp.135-141 , ISSN 0021-8995

Lasky, R. C., Kramer, E. J., Hui, C. Y. (1988). The Initial Stages of Case II Diffusion at Low Penetrant Activities. *Polymer*, Vol. 29, No. 4 , (April 1988), pp. 673-679, ISSN 0032-3861

Lin, Y.; Wang, D. M. & Lai, J. Y. (2002). Nonsolvent induced gelation and its effect on membrane morphology. *Macromolecules,* Vol.35, No. 17, (August 2002), pp. 6697-6706, ISSN 0024-9297

Liu, D. & Tomasko, D. L. (2007).Carbon Dioxide Sorption and Dilation of Poly(lactide-co-glycolide). *Journal of Supercritical Fluids*, Vol. 39, No. 3, (January 2007), pp. 416-425, ISSN 0896-8446

Massaro, L. & Zhu, X. X. P (1999). Physical Models of Diffusion for Polymer Solutions, Gels and Solids. *Progress in Polymer Science,* Vol. 24, No. 5, (August 1999), pp. 731-775, ISSN 0079-6700

Mattozzi, A., Hedenqvist, M. S., Gedde, U. W. (2007). Diffusivity of n-hexane in Poly(ethylene-stat-octene)s Assessed by Molecular Dynamics Simulation. *Polymer*, Vol. 48, No. 17 , (August 2007), pp. 5174-5180, ISSN 0032-3861

Moisan, J. Y. (1985). Effects of Oxygen Permeation and Stabiliser Migration on Polymer Degradation, In: *Polymer Permeability,* J. Comyn, (Ed.), 11-73, Elsevier Applied Science, ISBN 0-85334-322-5, Northern Ireland.

Neway, B., Hedenqvist, M. S., Mathot, V. B. F. & Gedde, U. W. (2001). Free Volume and Transport Properties of Heterogeneous Poly(ethylene-co-octene)s. *Polymer*, Vol. 42, No. 12 , (June 2001), pp. 5307-5319, ISSN 0032-3861

Pereira, A. M., Lopes, M. C., Timmer, J. M. K. & Keurentjes, J. T. F. (2005). Solvent Sorption Measurements in Polymeric Membranes with ATR-IR Spectroscopy. *Journal of Membrane Science*, Vol. 260, No. 1-2, (September 2005), pp. 174-180, ISSN 0376-7388

Prabhakar, R. S.; Merkel, T. C.; Freeman, B. D.; Imizu T. and Higuchi, A. (2005). Sorption and Transport Properties of Propane and Perfluoropropane in Poly(dimethylsiloxane) and Poly(1-trimethylsilyl-1-propyne). *Macromolecules,* Vol.38, No. 5, (March 2005), pp. 1899-1910, ISSN 0024-9297

Prausnitz, J. M. & Lichtenthaler, E. G. A. (1999). *Molecular Thermodynamics of Fluid-Phase Equilibria*, (Tired Edition), Ptrntice Hall, ISBN ,

Rogers, C. B. (1985). Permeation of Gases and Vapours in Polymer, In: *Polymer Permeability,* J. Comyn, 11-73, Elsevier Applied Science, ISBN 0-85334-322-5, Northern Ireland.

Sammon, C., Yarwood, J. & Everall, N. (2000). A FTIR-ATR Study of Liquid Diffusion Processes in PET Films: Comparison of Water with Simple Alcohols. *Polymer*, Vol. 41 No. 7, (March 2000), pp. 2521-2534, ISSN 0032-3861

Smith, B. A. H. & Sefton, M. V. (1988). Permeability of Heparin-Polyvinyl alcohol Hydrogel to Thrombin and Antithrombin III. *Journal Biomedical Materials Research,* Vol.22, No. 8, (August 1988), pp. 673-685, ISSN 1549-3296

Sperling, L. H. (2006). *Introduction to Physical Polymer Science* (Fourth Edition), Wiley-Interscience, 13987-0-471-70606-9, USA

Sridhar, L. N., Gupta, R. K. & Bhardwaj, M. (2006). Barrier Properties of Polymer Nanocomposites. *Industrial & Engineering Chemistry Research*, Vol. 45, No. 25, (December 1996), pp. 8282-8289, ISSN 0888-5885

Stropnik, C.; Musil, V. & Brumen, M. (2000). Polymeric Membrane Formation by Wet-Phase Separation; Turbidity and Shrinkage Phenomena as Evidence for the Elementary Processes. *Polymer*, Vol. 41, No. 26, (December 2000), pp. 9227-9237, ISSN 0032-3861

Sunchez, I. C. & Lacombe, R. H. (1978). Statistical Thermodynamics of Polymer Solution. *Macromolecules*, Vol. 11, No. 6, (November 1978), pp. 1145-1156 , ISSN 0024-9297

Tsai F. J. & Torkelson, J. M. (1990). The Roles of Phase Separation Mechanism and Coarsening in the Formation of Poly(methyl methacrylate) Asymmetric Membranes. *Macromolecules*, Vol.23, No. 3, (February 1990), pp. 775-784, ISSN 0024-9297

Tsay, C. S. & McHugh A. J. (1990). Mass transfer modeling of asyinmetric membrane formation by phase inversion. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 28, No. 8, (July 1990), pp. 1327-1365, ISSN 0887-6266

Urban, M. W. (1996). *Attenuated Total Reflectance Spectroscopy of Polymers: Theory and Practice*, American Chemical Society, ISBN 13: 9780841233458, USA

Van Asten, A. C. ; Kok, W. T. ; Tilssen, R. & Roppe, H. (1996). Characterization of Thermal Diffusion of Polystyrene in Binary Mixtures of THF/Dioxane and THF/Cyclohexane. *Journal of Polymer Science: Part B: Polymer Physics,* Vol.34, No. 2, (January 1996), pp. 283-295, ISSN 0887-6266

Vergnaud, J. M. (1991). *Liquid Transport Processes in Polymeric Materials: Modeling and Industrial Applications*, Prentice Hall, 0-13-538315-3, USA

Vrentas, J. S., Jarzebski, C. M., & Duda, J. L. (1975). A Deborah number for diffusion in polymer-solvent systems. *AIchE Journal,* Vol. 21, No. 5, (September 1975), pp. 894-901, ISSN 0001-1541

Wang, B. G., Yamaguchi, T. & Nakao, S. I. (2000). Solvent Diffusion in Amorphous Glassy Polymers. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 38, No. 2 , (January 2000), pp. 346-356, ISSN 0887-6266

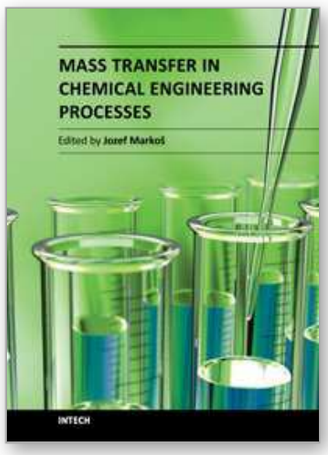
Wijmans, J. G.; Altena F. W. & Smolders C. A. (1984). Diffusion during the Immersion Precipitation Process. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 22, No. 3, (March 1984), pp. 519-524, ISSN 0887-6266

Windle, A. H. (1985). Case II Sorption, In: *Polymer Permeability,* J. Comyn, 75-118, Elsevier Applied Science, ISBN 0-85334-322-5, Northern Ireland.

Wisnudel, M. B. & Torkelson, J. M. (1996). Small-Molecule Probe Diffusion in Polymer Solution: Studies by Taylor Dispersion and Phosphorescence Quenching. *Macromolecules,* Vol.29, No. 19, (September 1996), pp. 6193-6207, ISSN 0024-9297

Yi, X., & Pellegrino, J. (2002).Diffusion Measurements with Fourier Transform Infrared Attenuated Total Reflectance Spectroscopy: Water Diffusion in Polypropylene. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 40, No. 10, (May 2002), pp. 980-991, ISSN 0887-6266

Zeman L. & Fraser T. (1994). Formation of air-cast cellulose acetate membranes. Part II. Kinetics of demixing and macrovoid growth. *Journal of Membrane Science*, Vol. 87, No. 3, (March 1994), pp. 267-279, ISSN 0376-7388



Mass Transfer in Chemical Engineering Processes

Edited by Dr. Jozef MarkoÅ¡

ISBN 978-953-307-619-5
Hard cover, 306 pages
Publisher InTech
Published online 04, November, 2011
Published in print edition November, 2011

This book offers several solutions or approaches in solving mass transfer problems for different practical chemical engineering applications: measurements of the diffusion coefficients, estimation of the mass transfer coefficients, mass transfer limitation in separation processes like drying, extractions, absorption, membrane processes, mass transfer in the microbial fuel cell design, and problems of the mass transfer coupled with the heterogeneous combustion. I believe this book can provide its readers with interesting ideas and inspirations or direct solutions of their particular problems.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Mohammad Karimi (2011). Diffusion in Polymer Solids and Solutions, Mass Transfer in Chemical Engineering Processes, Dr. Jozef MarkoÅ¡ (Ed.), ISBN: 978-953-307-619-5, InTech, Available from: http://www.intechopen.com/books/mass-transfer-in-chemical-engineering-processes/diffusion-in-polymer-solids-and-solutions

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the Creative Commons Attribution 3.0 License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen