

## **DIFFUSION PROCESSES IN ORGANIC PROTECTIVE COATINGS**

**P.C. Thapliyal and Astha Dhawan**

Organic Building Materials Division  
Central Building Research Institute, Roorkee-247667.

### **ABSTRACT**

Towards the end of the twentieth century, great attention has been focused on the field of diffusion, sorption and permeation because these basic phenomenon play a vital role in several important areas of engineering and industry including protective coatings such as paints and varnishes. Diffusion studies are of considerable importance especially when we came across problems like designing a barrier material. In order to design highly efficient and economically viable barrier materials and membranes, the elucidation of the relationship between transport properties and molecular structure of polymer is necessary. The research in this field is going on to establish mechanism and laws, relating solubility and diffusion in polymeric membranes, to their molecular properties, the nature of penetrates and polymer morphology.

In this paper an attempt is made to explain the importance of the basic mathematical concepts in routine R&D work of organic building materials with specific reference to the selected areas of protective coatings. The whole idea is to introduce the synergy between chemistry of coatings with the fundamentals of mathematics and brief description of the ongoing challenges involved.

### **INTRODUCTION**

Better improved economics and technology have resulted in continuous demand for new products. The advantages consist of reduced capital cost, lower energy consumption and lower installation costs. Various membrane separation techniques and pervaporation have become very important. Hence, the aim of research in this area nowadays is to establish mechanisms and new laws, relating solubility and diffusion in organic protective coatings, to their molecular properties, the nature of the penetrants and the polymer morphology. To limit the scope of discussion, we will concentrate on diffusion processes only.

Diffusion is the spontaneous net movement of particles from an area of high concentration to an area of low concentration through a semi-permeable membrane. For example, diffusing molecules will move randomly between areas of high and low concentration but because there are more molecules in the high concentration region, more molecules will leave the high concentration region than the low concentration one. Therefore, there will be a net movement of molecules from high to low concentration. Initially, a concentration gradient leaves a smooth decrease in concentration from high to low which will form between the two regions.

As time progresses, the gradient will grow increasingly shallow until the concentrations are equalized.

Diffusion is a spontaneous process and is simply the statistical outcome of random motion. Diffusion increases entropy, decreasing Gibbs free energy, and therefore is thermodynamically favorable. Diffusion operates within the boundaries of the second law of thermodynamics because it demonstrates nature's tendency to wind down, as evidenced by increasing entropy. The diffusion equation provides a mathematical description of diffusion. This equation is derived from Fick's law, which states that the net movement of diffusing substance per unit area of section is proportional to the concentration gradient (how steeply the concentration changes in space), and is toward lower concentration [1].

## TYPES OF DIFFUSION

The spreading of any quantity that can be described by the diffusion equation or a random walk model (e.g. concentration, heat, momentum) can be called diffusion. Some of the most important examples are listed below.

- Atomic diffusion
- Brownian motion
- Effusion of a gas through small holes
- Electron diffusion
- Facilitated diffusion
- Gaseous diffusion
- Heat flow
- Ito diffusion
- Knudsen diffusion
- Momentum diffusion
- Osmosis
- Photon diffusion
- Reverse diffusion
- Surface diffusion

## DIFFUSION ACROSS POLYMERIC FILMS

The diffusion of small molecules through a polymer membrane occurs due to random molecular motion of individual molecules [1]. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between the two phases. Here onwards we will discuss diffusion processes only. The diffusion process slowly tries to equalize the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane. This process can be described in terms of Fick's first law of diffusion, according to which the flux  $J$ , in the direction of flow is proportional to the concentration gradient ( $\partial c/\partial x$ ) as

$$J = -D (\partial c/\partial x) \quad (1)$$

Here  $D$  is the diffusion coefficient. Eq. (1) is applicable to the diffusion in the steady state. On the other hand, Fick's second law describes the nonsteady state for the diffusion process, which is given by the rate of change of the penetrant concentration ( $\partial c/\partial t$ ) at a plane within the membrane, i.e.

$$(\partial c/\partial t) = D (\partial^2 c/\partial x^2) \quad (2)$$

This is an ideal case in which the membrane is isotropic and the diffusion coefficient is independent of distance, time and concentration. Depending upon the boundary conditions, many solutions are available for Eq. (2).

$D$  is dependent on concentration because strong polymer-penetrant interaction occurs with many organic penetrant molecules. Therefore Eq. (2) becomes,

$$(\partial c/\partial x) = \partial D(c) (\partial c/\partial x) / \partial x \quad (3)$$

Analytically this cannot be solved easily and hence another form of Eq. (3) is commonly used.

$$(\partial c/\partial x) = D(c) (\partial^2 c/\partial x^2) + (\partial D(c)/\partial c) (\partial c/\partial x)^2 \quad (4)$$

In general, experiments are conducted over relatively small intervals of  $c$  and the term  $(\partial D(c)/\partial c)$  is negligible compared to  $D(c)$ . Then we get a mean or integral diffusion coefficient  $(\partial D(c)/\partial c)$  over a concentration range  $c_1$  to  $c_2$ , as given by

$$(\partial D(c)/\partial c) = \frac{1}{c_2 - c_1} \int_{c_1}^{c_2} D(c) dc \quad (5)$$

where  $c_1$  and  $c_2$  are the concentration of penetrant at low and high concentration sides of the film, respectively. In the steady state, diffusion flow is constant and the diffusion coefficient independent of concentration. Then Eq. (1) may be integrated to give

$$J = D (c_1 - c_2)/h \quad (6)$$

where  $h$  is the membrane thickness. The penetrant distribution between the penetrant and polymer phase is described by Nernst distribution law.

$$c = KC \quad (7)$$

where  $c$  is the sorbed concentration,  $C$ , the ambient penetration concentration in contact with the polymer surface and  $K$  depends on temperature and  $c$ . In the case of diffusion of gases and vapours, pressure  $p$  is used instead of surface concentration.

According to Henry law

$$c = Sp \quad (8)$$

where  $S$  is solubility coefficient. The combination of Eq. (6) & (8) gives the well known permeation equation

$$J = DS (p_1 - p_2)/h \quad (9)$$

where  $p_1$  and  $p_2$  are the ambient pressures on two sides of a film of thickness  $h$ . The product  $DS$  is called the permeability coefficient  $P$ , so that

$$P = DS \quad (10)$$

In terms of permeability, the flux Eq. (9) can be written as

$$J = P (p_1 - p_2)/h \quad (11)$$

## FACTORS AFFECTING DIFFUSION PROCESSES

1. Nature of the polymer
2. Nature of crosslink
3. Effect of plasticizers
4. Nature of the penetrant
5. Fillers
6. Temperature

Among these factors, temperature effect is well established mathematically. The variation of diffusivity, solubility and permeability coefficients with temperature is best described by the following Arrhenius relations [1].

$$D = D_0(e^{-E_D/RT}) \quad (12)$$

$$S = S_0(e^{-\Delta H_s/RT}) \quad (13)$$

$$P = P_0(e^{-E_p/RT}) \quad (14)$$

where  $E_D$  and  $E_p$  are the activation energies of diffusion and permeation respectively,  $\Delta H_s$  is the heat of solution of the penetrant in the polymer and  $D_0$ ,  $S_0$  and  $P_0$  are the pre-exponential factors. Both  $E_p$  and  $E_D$  are related as follows

$$E_p = E_D + \Delta H_s \quad (15)$$

The enthalpy of sorption  $\Delta H$  can be calculated using Van't Hoff relation

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (16)$$

Here  $K_s$  is the thermodynamic sorption constant and  $\Delta S$  the entropy of sorption. Deviations from the above relations exist i.e. a break between two straight lines in the Arrhenius plot is

observed and the calculated activation energy values are greater above  $T_g$  than below it as in case of diffusion, solubility and permeation of hydrogen, helium, argon and neon through PVA [2].

## DIFFUSION PROCESSES IN DIFFERENT POLYMERIC SYSTEMS

A proper understanding of the diffusion mechanism will provide direct information on the R&D of an appropriate membrane and coating. There are two approaches to describe mass transport in diffusion

1. Solution – diffusion Model
2. Pore flow Model

In general, the solubility and diffusivity are concentration dependent in first model while in second model it is assumed that there are bundles of straight cylindrical pores on the membrane surface. Distinguishing feature of the pore flow model is that it assumes a liquid-vapour phase boundary inside the membrane [1].

Diffusion in rubbery polymers, glassy polymers and polymer blends has been studied by various researchers from time to time [1-5]. Among polymeric organic coating systems and membranes following diffusion processes are of vital importance:

1. Vapour permeation
2. Gas permeation

In vapour permeation, diffusion of a condensable vapour through a dense coating membrane consecutive to an activity gradient takes place. This process offers a unique feature of studying the diffusion process of a single permeant through a dense coating membrane under various upstream activities. Such characteristics can be obtained by liquid permeation, where the modification of the upstream activity of a component can only be achieved by adding another compound to the mixture [2].

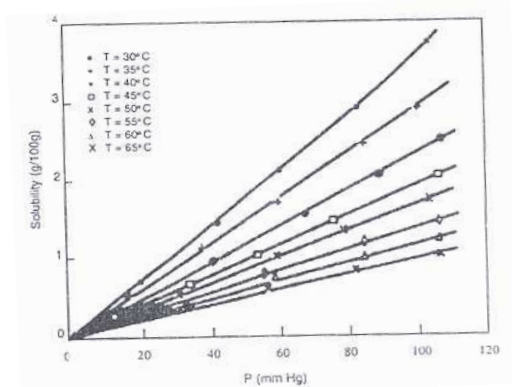
$$D = 1/6 \lim_{t \rightarrow \infty} d(r(t) - r(0))^2 / dt \quad (17)$$

The activity of both components is modified in this case in compliance with the Gibbs - Duhem relation, Eq. 18, which complicates diffusion analysis.

$$SdT - Vdp + \sum N_i d\mu_i = 0 \quad (18)$$

where  $S$  is entropy and  $\mu$  is chemical potential.

On the contrary coupling phenomenon are not to be considered with pure vapour permeation results. Further more the calculation of upstream solvent activity demands the use of somewhat vapour liquid equilibrium methods. In the case of pure solvent vapour permeation, upstream activity can be easily calculated, provided upstream pressure is precisely monitored. This method offers direct practical conclusions for the understanding and rational designs of volatile organic components (VOC) vapour recovery from contaminated air streams. This technique also offers significant opportunities for energy saving and solvent release, compared to classical VOC control processes such as incineration, oxidation or active carbon absorption [6].



**Fig.1: A typical adsorption isotherm for n-hexane-PP systems.**

Absorption data of hydrocarbon vapours in PE and PP films using Flory-Huggins, Michael-Hausslein and Flory-Rehner theories have been studied extensively (Eq. 19-21). Prediction of penetrant activity values through these theories fit quite well with experimental results, with deviation of 4-11%. As can be seen in fig. 1, the solubility depends on temperature and almost linearly on pressure [7].

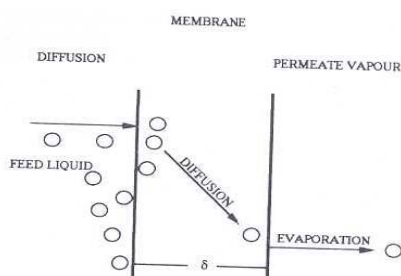
$$\ln a_{1el} = \frac{\left[ \frac{M_1 \rho_2}{\rho_1} \frac{\Delta H_M}{R} \left( \frac{1}{T} - \frac{1}{T_M} \right) - (\phi_1 - \chi \phi_1^2) \right]}{\left[ \frac{3}{2f\phi_2} - 1 \right]} \quad (19)$$

$$\chi = \frac{(\ln a_{1inc} + \ln a_{1fv})}{\phi_1^2} \quad (20)$$

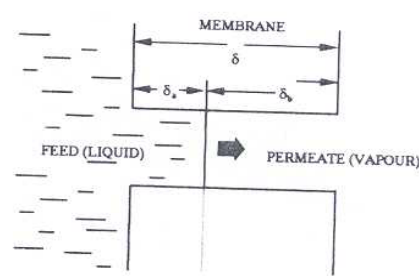
$$\ln a_{1el} = \left( \frac{\rho_a M_1}{\rho_1 M_c} \right) \phi_2^{1/3} \quad (21)$$

where  $\Delta H_M$  is polymer melting change of enthalpy,  $T$  is absolute temperature,  $\Phi$  is the volume measured fraction,  $\chi$  is Flory parameter,  $f$  is fraction of elastic effective chains in amorphous region,  $\rho$  is density and  $M$  is molecular weight.

Gas diffusion through polymeric coatings is an area of growing interest as materials with unique diffusion properties continue to find use in new, specialized applications ranging from extended life tennis ball to natural gas separation systems. The ability to relate polymer molecular structure to gas diffusion properties is crucial in any attempt to rationally design materials for specific permeability applications such as gas barriers. In literature, the availability of experimental permeability data is limited mostly to common / commercial polymers and the information demonstrated that gas diffusion rates of polymer may vary by many orders of magnitude [3-5]. A variety of techniques have been used to measure gas permeation through polymer membranes. The most common method utilizes Dow permeation cell wherein the film is sealed in the cell. The down stream side of the cell is evacuated and the test gas is passed upstream at a given pressure to reach equilibrium with the film while maintaining vacuum on the downstream side. The coating film must be dry as the method does not differentiate between the test gas permeating the polymer sample and water vapour. Traditionally the behaviour of the gas separation membrane was dominated by diffusion of absorbed molecules. The gas flux was driven by the concentration gradient of absorbed molecules in polymer matrix. This leads to simple model which known as solution diffusion model (Fig. 2). The permeating species interact with the polymer matrix and selectively dissolves in it, resulting in diffusive mass transport along a chemical potential gradient. Besides solution diffusion model, there are viscous flow, Knudson flow and molecular sieving for explaining gas transport through porous membranes (Fig. 3).



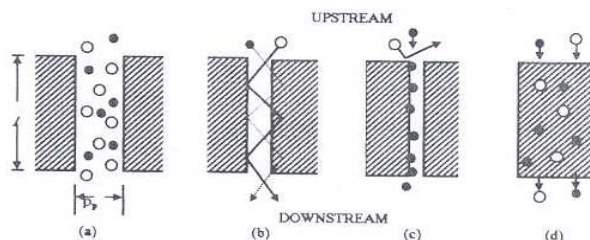
**Fig. 2: Solution diffusion model.**



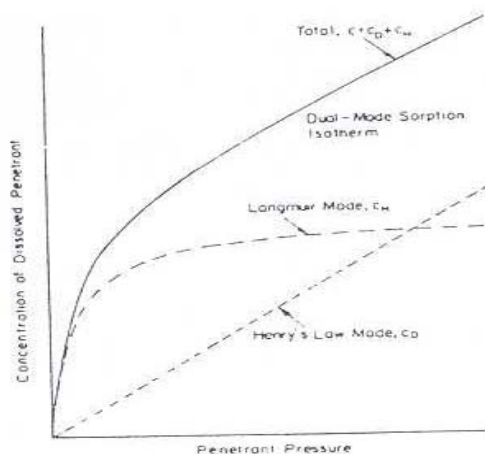
**Fig. 3: Pore flow model.**

As illustrated below (Fig. 4a-d), mechanism of gas molecules flow depends upon the size of the pores in relation to the mean free path of gas molecules. In viscous flow, flow is inversely proportional to the viscosity of the fluid (gas). In contrast, flow is inversely proportional to the molecular mass of diffusing species in Knudson flow. Ultra micro porous molecular sieving membrane has higher productivities and selectivities than solution diffusion

mechanics. The gas sorption to a homogenous polymer has been classified into two categories. For sorption to a rubbery polymer membrane, the sorption behaviour was described by Henry's law. Recently a more complex BET type sorption isotherm which describes multilayer sorption has also been reported (Fig. 5). This combines two isotherms, a Henry type isotherm for matrix absorption and a Langmuir type isotherm for site absorption [7].



**Fig. 4: Mechanism of flow of gas molecules (a) Viscous flow, (b) Knudson flow, (c) molecular sieving & (d) solution diffusion.**



**Fig.5: Typical dual-mode sorption isotherm & its components.**

The difference in the transport and solution behaviour of gases in rubbery and glassy polymers is due to the fact that glass is not in a state of true thermodynamic equilibrium. Rubbery polymers have a short relaxation time and responds very rapidly to stress. Thus a change in temperature causes an immediate adjustment to a new equilibrium. On the other hand, glassy polymers have very long relaxation times. Therefore in presence of a penetrant, the motions of a whole polymer chain or a portion are not sufficiently rapid to completely homogenize the penetrant environment. Penetrant (gas molecules) can thus potentially sit in holes or irregular cavities with very different intrinsic diffusional mobilities [10]. Similarly, the gas transport in polymer blend is directly affected by the morphology and chemical uniformity of the material.

## CONCLUSIONS

In this paper we have presented how simple mathematical relations help in explaining the behaviour and/or mechanism of the diffusion of molecules through polymer membranes and organic coatings. The diffusion of small molecules through the polymeric membranes influences several industrial processes. These membranes are used to separate or chemically convert and modify the permeate stream. The physical properties and appearance of coatings is modified by even the presence of trace amounts of volatile components. It has been proved beyond doubt that molecular diffusion process is a key step in the design process and often governs the utility and manufacture of commercial products which will include the controlled

release of pesticides, drugs and fertilizers. Hence, we can safely conclude that the progress of separation industry is directly dependent on understanding and developing the better synergy between the chemistry and mathematics of diffusion processes through polymeric membranes and coatings.

## REFERENCES

- [1] George, S.C. & Thomas, S. (2001), "Transport phenomenon through polymeric systems", *Prog. Polym. Sci.*, Volume 26, pp 985-1017.
- [2] Premkumar, S.R. & Ford, D.M. (2000), "Permeation of small molecules through polymers confined in mesoporous media", *J. Membr. Sci.*, Volume 171, pp 239-252.
- [3] Aggarwal, L.K., Thapliyal, P.C. & Karade, S.R. (2004), "Anti corrosive paints for the protection of steel structures", *Proc. International Conference on Corrosion, CORCON-2004, NACE, New Delhi, December 2-4, Paper No.101*, pp. 1-11.
- [4] Aggarwal, L.K., Thapliyal, P.C. & Karade, S.R. (2007), "Anticorrosive properties of the epoxy-cardanol resin based paints", *Prog. Org. Coat.*, Volume 59, pp 76-80.
- [5] Thapliyal, P.C. & Dhawan, Astha (2007), "A protective coating prospective for the sustainable design of the buildings", *Proc. National Seminar on Modern Trends in Architectural & Civil Engineering Practices, Roorkee, November 23-24*, pp. 54-56.
- [6] Jia, L., Fu, H., Xu, J., Hirai, A. & Odani, H. (2003), "Studies on the sulfonation of poly (phenylene oxide) (PPO) and permeation behavior of gases and water vapor through sulfonated PPO membranes. III. Sorption behavior of water vapor in PPO and sulfonated PPO membranes", *J. Appl. Poly. Sc.*, Volume 52, pp 29-37.
- [7] Castro, E.F., Gonjo, E.E. & Gottifredi, J.C. (1996), "The analysis of sorption data of organic vapours in polymeric membranes through novel theories", *J. Membr. Sci.*, Volume 113, pp 57-59.