The Peculiarities of Sorption Mechanism of Phenole Molecules by Films of PVA-PAA$_N$ Interpolymer Complex

Irina Lebedyeva(1), Tetyana Zheltonozhskaya(2), Valeriy Yashchuk(3),
Vladislav Kudrya(3), Ol'ga Demchenko(2)

(1)Chair of Mathematics of Ukrainian State University of Food Technology,
68, Volodymyrs'ka st., Kyiv, 01033, Ukraine;
(2)Chemical Department of Kyiv National Taras Shevchenko University,
60, Volodymyrs'ka st., Kyiv, 01033, Ukraine;
(3)Physics Department of Kyiv National Taras Shevchenko University,
6, Glushkova prosp., Kyiv, 03127, Ukraine; e-mail:
yashchuk@phys.univ.kiev.ua

SUMMARY: The peculiarities of sorption mechanism of phenole molecules by poly(vinylalcohol) and poly(acrylamide) (PVA-PAA$_N$) films are examined. An analytical model of absorption process based on diffusive character of penetration of phenole molecules in polymer film with the following spontaneous capturing by selftuning traps is proposed. The analytical results can be easy compared with experimental data obtained by spectrophotometry method. The comparison of theory and experiment gives the average value of resulting diffusion lenght of phenole molecule during «free» life-time $<l>\sim 10^{-6}$ cm.

Introduction

The processes of sorption are widely used in food, cosmetic, pharmaceutical and petrochemical industries and are the objects of corresponding applied fields of science [1]. The special polymer complexes for water purification may serve to be an example of such type of sorbents. In number of works [2-5] it was founded that grafted copolymers on the base of chemical complementary poly(vinylalcohol) and poly(acrylamide) (PVA-PAA$_N$) effective sorbed phenole and phenylalanine from water; nitrobenzene from hexane. But detailed theoretical investigations of sorption processes and getting of final results in the form suitable for comparing with experimental data (that may be obtained by means of existing methods) require the essential mathematical background.

Results and discussion

In present paper we propose following model of this process. Impurity molecules from solvent penetrate in polymer film. Their motion in it is random walks in character and

© WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 CCC 1022-1360/00/$ 17.50+.50/0

described by equation:

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2}-\frac{1}{\tau}n(x) \qquad (1)$$

where $n(x)$ - is concentration of absorbed molecules, D - diffusion coefficient, τ - lifetime of «free» guest molecules. This value determine the time from moment of guest molecule penetration in polymer film up to moment of it capturing by sorption centers. The role of these centers could play the selftuning hydrophilic (in the case of phenole sorbtion) and hydrophobic (in the case of nitrobenzene sorbtion) curvities in PVA-PAA$_N$-films.

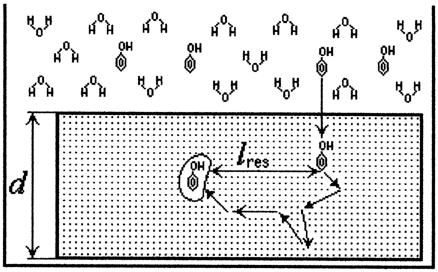

Fig. 1: The model of sorption process in PVA-PAA$_N$-film

The quantity of absorbed impurity molecules

$$N=\int_0^{t_{sat}}\int_0^{d} n(x)\,dx\,dt$$

where t_{sat} - time when sorption process reaches saturation.

Boundary conditions for equation (1)

$$n\big|_{x=0}=C_0,\ n\big|_{x=d}=0, \qquad (2)$$

initial condition

$$n\big|_{t=0}=0. \qquad (3)$$

The substitution

$$n(x,t)=e^{-t/\tau}u(x,t) \qquad (4)$$

will change the equation (1) into homogeneous equation of diffusion

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2}, \qquad (5)$$

the boundary and initial conditions are the following

$$u\big|_{x=0}=C_0e^{-t/\tau},\ u\big|_{x=d}=0, \qquad (6)$$

$$u\big|_{t=0}=0, \qquad (7)$$

when $u(x,t)$ is the new unknown function.

To get rid of nonstationary let us present unknown function $u(x,t)$ as a sum

$$u(x,t)=\frac{d-x}{d}C_0e^{t/\tau}+w(x,t) \tag{8}$$

For the function $w(x,t)$ we have the following boundary problem

$$\frac{\partial w}{\partial t}=D\frac{\partial^2 w}{\partial x^2}-\frac{d-x}{x}\frac{C_0}{\tau}e^{t/\tau}, \tag{9}$$

$$w\big|_{x=0}=0,\ w\big|_{x=d}=0, \tag{10}$$

$$w\big|_{t=0}=C_0\frac{x-d}{d}, \tag{11}$$

The solution of this problem is sought as a sum of two unknown functions

$$w(x,t)=R(x,t)+Q(x,t). \tag{12}$$

$R(x,t)$ is a solution of homogeneous differential equation under inhomogeneous initial condition:

$$\begin{cases}\dfrac{\partial R}{\partial t}=D\dfrac{\partial^2 R}{\partial x^2}, \\ R\big|_{x=0}=R\big|_{x=d}=0,\ \ R\big|_{t=0}=C_0\dfrac{x-d}{d}\end{cases} \tag{13}$$

$Q(x,t)$ is a solution of inhomogeneous differential equation under homogeneous initial condition:

$$\begin{cases}\dfrac{\partial Q}{\partial t}=D\dfrac{\partial^2 Q}{\partial x^2}-\dfrac{d-x}{d}\dfrac{C_0}{\tau}e^{t/\tau}, \\ Q\big|_{x=0}=Q\big|_{x=d};\ Q\big|_{t=0}=0\end{cases} \tag{14}$$

We can obtain the solution of the boundary problem (13) by the method of variables separating in the following form

$$R(x,t)=-\frac{2C_0}{\pi}\cdot\sum_{k=1}^{\infty}\frac{1}{k}e^{-\frac{k^2\pi^2Dt}{d^2}}\sin\frac{k\pi x}{d}. \tag{15}$$

The function $Q(x,t)$ is presented in the form of expansion in homogeneous problem (13) eigenfunctions $\sin\frac{k\pi x}{d}$:

$$Q(x,t)=\sum_{k=1}^{\infty}\gamma_k(t)\cdot\sin\frac{k\pi x}{d}. \tag{16}$$

For the unknown function of time $\gamma_k(t)$ we have the differential equation:

$$\gamma_k'(t) + \frac{k^2\pi^2 D}{d^2}\gamma_k(t) = -\frac{2C_0}{\tau k\pi}e^{t/\tau} \tag{17}$$

and initial condition

$$\gamma_k(0) = 0\ . \tag{18}$$

It is easy to show that

$$\gamma_k(t) = \frac{2C_0 d^2}{k\pi\left(d^2 + k^2\pi^2\tau D\right)}\left[e^{-\frac{k^2\pi^2 Dt}{d^2}} - e^{-\frac{t}{\tau}}\right] \tag{19}$$

($d^2 + k^2\pi^2\tau D \neq 0$, because of $\tau > 0$).

Taking into account the expressions (4),(8),(12),(15),(16),(19) one can obtain

$$\begin{aligned} n(x,t) = {} & \frac{d-x}{d}C_0 - \frac{2C_0}{\pi}\cdot\sum_{k=1}^{\infty}\frac{1}{k}e^{-\left(\frac{1}{\tau}+\frac{k^2\pi^2 D}{d^2}\right)t}\sin\frac{k\pi x}{d} + \\ & + \frac{2C_0}{\pi}\cdot\sum_{k=1}^{\infty}\frac{d^2}{k\left(d^2 + k^2\pi^2\tau D\right)}\left[e^{-\left(\frac{1}{\tau}+\frac{k^2\pi^2 D}{d^2}\right)t} - 1\right]\sin\frac{k\pi x}{d} \end{aligned} \tag{20}$$

It is easy to show that experimentally measured (with the help of spectrophotometer) optical density of polymer films $D(t)$ as a function of time (t) can be expressed in following way:

$$D(t) = \frac{\sigma\int_0^d n(x,t)dx}{\Delta S} \tag{21}$$

where σ– is crossection of optical absorption for phenole molecules, ΔS– is the spectrophotometer slit square, $n(x,t)$– linear concentration of impurity molecules absorbed by polymer film, expression for which is presented above (20). Finally, we get

$$\text{Experiment}\rightarrow\boxed{\frac{D(t)\cdot\Delta S}{\sigma} = \int_0^d n(x,t)dx =}\leftarrow\text{Theory}$$

$$\boxed{\begin{aligned} & = \frac{d}{2}C_0 - \frac{4dC_0}{\pi^2}\cdot\sum_{k=0}^{\infty}\frac{1}{(2k+1)^2}e^{-\left(\frac{1}{\tau}+\frac{(2k+1)^2\pi^2 D}{d^2}\right)t} + \\ & + \frac{4dC_0}{\pi^2}\cdot\sum_{k=0}^{\infty}\frac{d^2}{(2k+1)^2\cdot\left(d^2 + (2k+1)^2\pi^2\tau D\right)}\left[e^{-\left(\frac{1}{\tau}+\frac{(2k+1)^2\pi^2 D}{d^2}\right)t} - 1\right] \end{aligned}} \tag{22}$$

↑ Theory

$$\int_0^d n(x,t)dx\Big|_{k=0} = \frac{d}{2}C_0 - \frac{4d^3C_0}{\pi^2\left(d^2+\pi^2\tau D\right)} - \frac{4dC_0\tau D}{d^2+\pi^2\tau D}\cdot e^{-\frac{1+\pi^2 D\tau}{\tau d^2}t} \qquad (23)$$

The comparison of theory and experiment gives the approximate value of resulting diffusion length of phenole molecules $<l>=\sqrt{Dr}\approx 10^{-6}$ cm.

References

1. C.I.Berstain, E.Azuara, H.S.Garcia, E.J.Vernon-Carter, *Internat. Journ. of Food Sci. And Technology*, **31**, 379 (1996)
2. T.B.Zheltonozhskaya, O.O.Romankevich, V.G.Syromyatnikov, L.A.Bulavin, V.Yu.Kudrya, T.Yu.Ogul'chansky, V.M.Yashchuk, *Macromolecular Symp.*, **114**, 263 (1997)
3. T.B.Zheltonozhskaya, V.G.Syromyatnikov, V.M.Yashchuk, V.Yu.Kudrya, O.V.Demchenko, I.V.Filimonova, *2nd International Conference "Electronic Processes in Organic Materials". Europhysics Conference Abstracts,* **22B**, 165 (1998)
4. T.B.Zheltonozhskaya, V.G.Syromyatnikov, V.M.Yashchuk, V.Yu.Kudrya, O.V.Demchenko, I.V.Filimonova, *Functional Materials*, **5**, N 3, 398 (1998)
5. T.B.Zheltonozhskaya, O.V.Demchenko, V.G.Syromyatnikov, N.V.Strelchuk, V.M.Yashchuk, V.Yu.Kudrya, *3rd International Conference "Electronic Processes in Organic Materials". Book of Abstracts,* 208 (2000)