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DIFFUSION COEFFICIENT AND SOLUBILITY OF VINYL ACETATE MOLECULES IN POLY(VINYL ACETATE) MATRICES

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Abstract—Diffusion coefficient and equilibrium solubility for poly(vinyl acetate)/vinyl acetate system (VAc) were determined by measuring the rate of uptake or loss of VAc. The amount of residual VAc, as well as temperature, affected the mutual diffusion coefficient. Free volume theory, proposed recently by Vrentas and Duda, represented the behaviour of diffusion coefficients reasonably well over a wide range of temperature and VAc concentration.

INTRODUCTION

Since monomer conversion in polymerization processes may be far from complete, it is necessary to remove the unreacted monomer in order to improve the physical properties of the polymer and to meet environmental regulations. This removal can usually be done in separators such as flash evaporators or devolatilizers with film-forming devices depending upon the viscosity of the polymers [1]. Diffusion coefficient and equilibrium solubility of the monomer in the polymer matrices are the most essential parameters to be considered for an appropriate selection or design of the separators. Many papers have reported results about equilibrium solubilities and diffusion coefficients [2–7] of polymer–volatile solute systems.

The diffusion coefficient is observed to rise with temperature of the system, while it goes up and then falls as the content of the volatile solute increases [8]. Concentration dependence of diffusion coefficients has been expressed by various empirical equations [2]. However, these equations lack physical significance, so that it is uncertain to extrapolate the experimental data.

Fujita [3] has proposed a free volume theory to explain the peculiar behaviour of the diffusion coefficients in concentrated polymer solution. Recently Vrentas and Duda [4–6] proposed a new free volume theory eliminating many of the shortcomings of Fujita's theory. It is based on the fact that diffusion of monomer molecules depends on the probability that a free volume of sufficient size will occur in the polymer matrices and on the probability that monomer molecules have enough energy to jump into this hole. In this work, we determined absorption and desorption diffusion coefficients and equilibrium solubility for the poly(vinyl acetate)/vinyl acetate (PVAc/VAc) system using a weighing method, and analysed the predictability of the free volume theory.

EXPERIMENTAL PROCEDURES

1. PVAc preparation

PVAc was bulk polymerized with AIBN (0.001 g/g of VAc) at 50 ± 1°C in a shaking water bath for 12 hr. The resulting polymer was dissolved in methanol to cast into a film, which was dried under vacuum at room temperature for several weeks. Number-average molecular weight and polydispersity of the polymer were 1.5×10^5 and 5.4 respectively.

2. Absorption and desorption

The schematic diagram of the experimental apparatus is shown in Fig. 1. A sample film was cast on a flat quartz plate in a sample bucket and loaded in the sorption chamber, the temperature of which was kept constant by circulating silicone oil through the jacket. Vacuum was applied to the sorption chamber after several times of repeated introduction and removal of pure N_2 and then the system was brought to sorption temperature. When extension of the quartz spring loaded with a sample film was monitored to be time invariant, VAc vapour was introduced into the sorption chamber.

Linear variation of the quartz spring due to absorption and desorption of VAc molecules was detected using a cathetometer to 10 μm precision. The sample bucket must be maintained horizontally to keep the molten sample uniform in thickness.

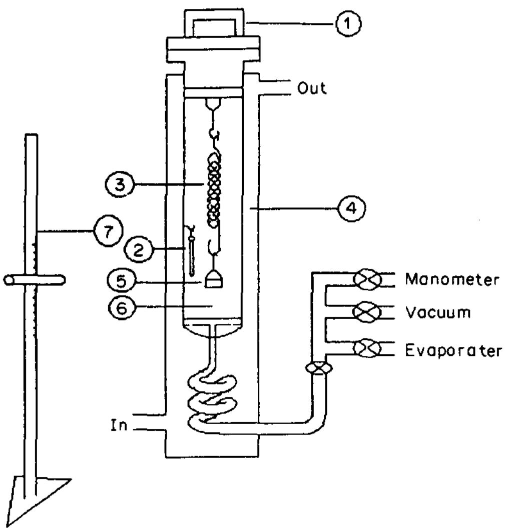
RESULTS AND DISCUSSION

The one dimensional diffusion is governed by:

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

with the associated initial and boundary conditions:

$$C(x, 0) = C_0$$
$$C(L, t) = C_s$$
$$\left.\frac{\partial C}{\partial t}\right|_{x=0} = 0. \qquad (2)$$



1 : Cap
2 : Thermometer
3 : Quartz spring
4 : Heating medium
5 : Bucket
6 : Sorption chamber
7 : Cathetometer

Fig. 1

The diffusion coefficient in equation (1) is an average corresponding to the range of solute concentrations appropriate to the experiments, which can be approximated by [13]

$$\bar{D} = \frac{\int_{C_0}^{C_s} D\,\mathrm{d}C}{C_s - C_0} \tag{3}$$

where C_s and C_0 are equilibrium and initial solute concentrations respectively. By integration of the concentration profile obtained by solving equations (1) and (2) [2], the weight of the solute absorbed or desorbed can be expressed as [8]:

$$\frac{M_t}{M_\infty} = 2\left(\frac{\bar{D}t}{L^2}\right)^{1/2}\left(\frac{1}{\pi^{1/2}} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\frac{nL}{(\bar{D}t)^{1/2}}\right). \tag{4}$$

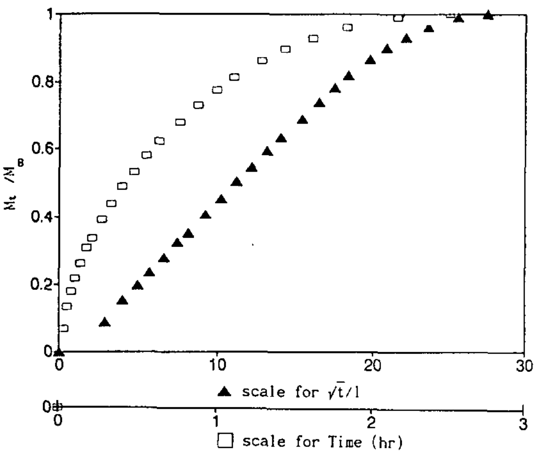


Fig. 2. Absorption and reduced conjugated absorption curves for PVAc at 100°C, 0.7 atm.

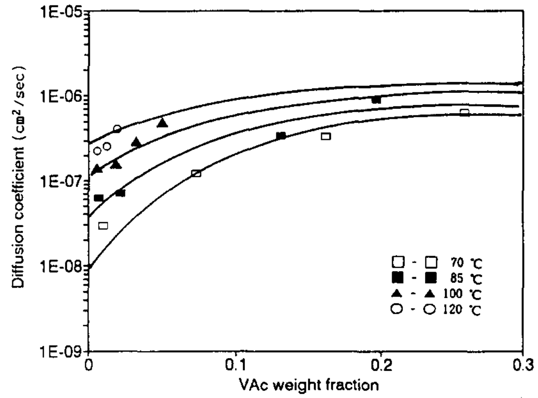


Fig. 3. Absorption diffusion coefficients for PVAc/VAc system. Solid lines, prediction using equations (3) and (7) employing values of parameters in Table 1.

In the early stages, the average diffusion coefficient can be determined as:

$$\bar{D} = \frac{\pi}{4}\left(\frac{\mathrm{d}\left(\frac{M_t}{M_\infty}\right)}{\mathrm{d}\left(\frac{\sqrt{t}}{l}\right)}\right)^2 \tag{5}$$

obtained by approximation of equation (4).

Absorption and reduced conjugated absorption curve of PVAc/VAc system at 100°C and under 0.7 atm of VAc vapour are plotted in Fig. 2.

As the reduced conjugated curve was almost linear for a long period of time, initial fluctuation of the spring due to sudden change in the pressure of the sorption chamber did not hinder the determination of the diffusion coefficients using equation (5).

Figures 3 and 4 represent respectively absorption and desorption diffusion coefficients as a function of equilibrium VAc concentration. It can be seen that diffusion coefficient depends on VAc concentration as well as temperature.

Its dependence on solute concentration has been expressed in a number of empirical forms [2], such as equation (6):

$$D = D_0 \exp(\alpha C) \tag{6}$$

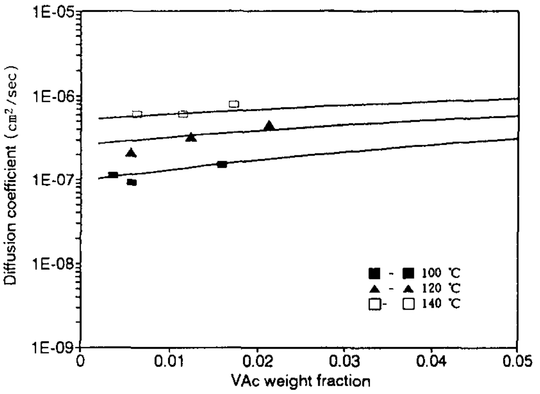


Fig. 4. Desorption diffusion coefficients for PVAc/VAc system. Solid lines, prediction using equations (3) and (7) employing values of parameters in Table 2.

Table 1. Values of the parameters of the free volume theory for absorption diffusion coefficients

D_{01}(cm²/sec)	$\frac{\gamma\hat{V}_2^*}{K_{12}}$(K)	$K_{22}-T_{g2}$	ξ	$\frac{\gamma\hat{V}_1^*}{K_{11}}$(K)	$\hat{V}_1^*$	$\hat{V}_2^*$	$K_{11}-T_{g1}$	χ
2.9×10^{-5}	1681.4[a]	−280.0[a]	0.31	328.0[b]	0.9[b]	0.84[a]	−114.0[b]	0.45

[a,b]Values are taken from Refs [7] and [14] respectively.

Table 2. Values of the parameters of the free volume theory for desorption diffusion coefficients

D_{01}(cm²/sec)	$\frac{\gamma\hat{V}_2^*}{K_{12}}$(K)	$K_{22}-T_{g2}$	ξ	$\frac{\gamma\hat{V}_1^*}{K_{11}}$(K)	$\hat{V}_1^*$	$\hat{V}_2^*$	$K_{11}-T_{g1}$	χ
2.6×10^{-5}	1681.4[a]	−280.0[a]	0.31	328.0[b]	0.9[b]	0.84[a]	−114.0[b]	0.45

[a,b]Values are taken from Refs [7] and [14] respectively.

These equations predict reasonably well only over a narrow range of solute concentration.

Vrentas and Duda's simplified version [4, 5] of the free volume theory for binary mutual diffusion coefficient can be written as:

$$D = D_{01}\exp\left(\frac{w_1\hat{V}_1^* + w_2\hat{V}_2^*\xi}{V_{\mathrm{FH}}^*/\gamma}\right) \times [(1-2\chi\phi_1)(1-\phi_1)^2]$$

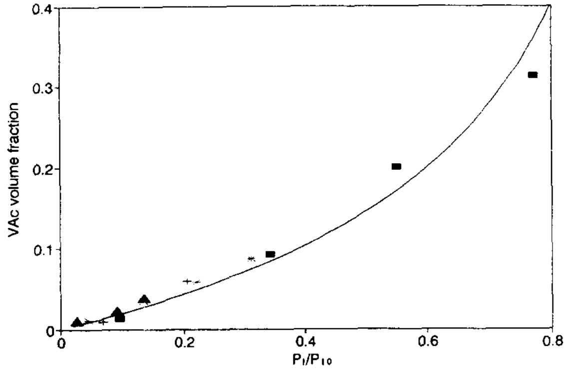


Fig. 5. Equilibrium solubility of VAc in PVAc as a function of VAc pressure. The solid line represents equation (8) with $\chi = 0.45$. ■, 70°C; +, 85°C; *, 100°C; ▲, 120°C.

$$\frac{V_{\mathrm{FH}}^*}{\gamma} = w_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} + T - T_{g1}) + w_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} + T - T_{g2}) \quad (7)$$

$\hat{V}_1^*$, K_{11}/γ and $K_{11} - T_{g1}$ are properties of pure VAc while $\hat{V}_2^*$, K_{12}/γ and $K_{22} - T_{g2}$ are those of pure PVAc. ξ, D_{01} and χ depend on mixture properties. Duda *et al.* [7, 8] clearly present methods of determination of all these parameters. Tables 1 and 2 summarize values of the parameters for absorption and desorption of the PVAc/VAc system respectively.

χ, the reciprocal interaction parameter of the Flory–Huggins' equation (8), was determined from data of equilibrium absorption solubility as shown in Fig. 5

$$\frac{P_1}{P_1^\circ} = \phi_1\exp(\phi_2 + \chi\phi_2^2). \quad (8)$$

It can be noted from Fig. 5 that equilibrium solubility deviates significantly from Henry's law at high pressures of VAc vapour and that χ is nearly independent of temperature [15].

Solid lines in Figs 3 and 4 represent the predicted average diffusion coefficient using equations (3) and (7) employing values of parameters in Table 1 and 2, which seems to coincide reasonably with the experimental data.

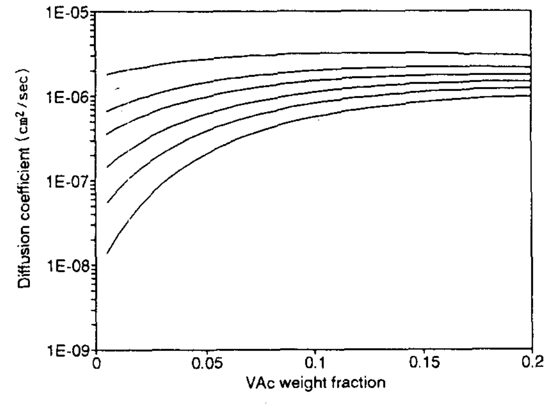


Fig. 6. Absorption diffusion coefficients predicted by equation (7) derived from free volume theory. Temperatures are 190, 140, 120, 100, 85 and 70°C respectively from the top.

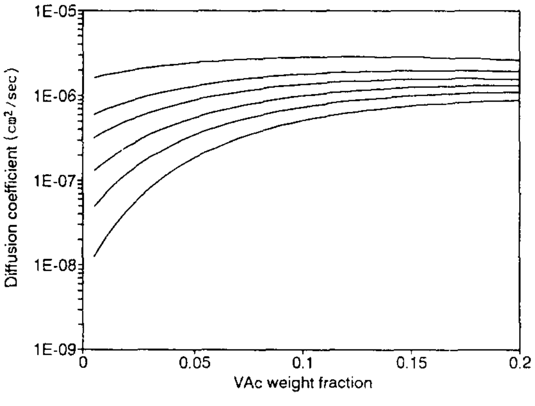


Fig. 7. Desorption diffusion coefficients predicted by equation (7) derived from free volume theory. Temperatures are 190, 140, 120, 100, 85 and 70°C respectively from the top.

It is interesting to observe that values of parameters for absorption diffusion coefficient are identical with those for desorption diffusion coefficient except for D_{01}. This keeps the physical meaning of the free volume theory. Predictions of diffusion coefficient as a function of VAc concentration were made using equation (7) and are shown in Figs 6 and 7. Its dependence upon VAc concentration decreased as temperature and VAc content increased.

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