

Study of the diffusion process in the dissolution of poly(vinylidene chloride) in streaming organic solvents

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The kinetics of dissolution of powdered poly(vinylidene chloride) prepared by emulsion polymerization under optimum reaction conditions have been investigated. The values of the mean integral diffusion coefficient of the process of dissolution of the solid particles of poly(vinylidene chloride) in cyclohexanone, dioxan, *o*-dichlorobenzene, tetrahydrofuran, and tetrachloroethane found on the basis of the calculated rates of dissolution and the measured width of swollen surface layer are presented.

Для исследования кинетики растворения поливинилиденхлорида был использован его порошок, приготовленный эмульсионной полимеризацией при оптимальных условиях реакции. На основании вычисленных скоростей растворения и измеренной толщины набухаемого поверхностного слоя, в работе приводятся значения среднего интегрального коэффициента диффузии для процесса растворения твердых частиц поливинилиденхлорида в циклогексаноне, диоксане, *o*-дихлорбензоле, тетрагидрофуране и тетрахлорэтаноле.

Many operations in the field of the processing of macromolecular substances demand knowledge of the phenomena occurring during dissolution of the solid polymer phase in liquid solvents.

The dissolution itself has been investigated in the preparation of polymer solutions in the liquids for further processing operations, in rheology from the view-point of reducing the pressure loss by friction, in liquid flow after an addition of polymer admixtures as it is practicable in crude oil industry, or at the raising of the viscosity index by dissolving macromolecular substances in oils, in the fractionation of polymers or extraction of a certain polymer fraction from mixtures, *e.g.*

homopolymer from its mixture with copolymer, *etc.* This brief and incomplete account of processes demonstrates the importance of the research in this field.

From the view-point of the theory of general hydrodynamics and the theory of diffusion processes, the mechanism of the effect of solvent on solid polymer is relatively complicated. The ignorance of exact mechanism of the segment—solvent molecule interaction results from the incompetence of quantum chemistry to describe the physical interaction among molecules precisely. Therefore, up to the present, most authors have used simplified model ideas based on a phenomenological description in terms of the theory of absolute reaction rates elaborated by Eyring.

Theoretical

The rate of dissolution of polymers in liquid medium is determined by the rate of diffusion of solvent molecules into the solid polymer. The kinetic process of the effect of liquid solvent on the surface of polymer may be divided into two stages [1—9]. In the first stage the diffusion of the molecules of solvent into the solid macromolecular substance takes place owing to which a swollen surface layer is formed on the polymer—solvent interface. From the hydrodynamic point of view, the motion of the liquid particles in the boundary layer is given by the velocity distribution in the range from the zero value on the solid surface of polymer to the value equal to the velocity of flowing solvent on the external surface of the arising swollen surface layer. The growth of the width of layer is a nonsteady diffusion phenomenon for which the density of diffusion flow of the solvent molecules into the swollen surface layer is a function of time. In the second stage the transport of macromolecules into solution sets in after the swollen surface layer has reached a certain constant width. Thus, the diffusion of macromolecules into solution begins after a certain induction period of the diffusion dissolution process t_0 which is necessary for the formation of a swollen surface layer. Then, under constant thermodynamic conditions, the whole process is steady and the flow densities of the liquid solvent into the swollen surface layer and of the macromolecules into solution are constant.

Ueberreiter and *Asmussen* [1—6] studied the dissolution process of polymers in great detail. They used the second Fourier—Fick law for mathematical description. They derived equations for the rate of advance of interface which is proportional to the value of the pertinent diffusion coefficient and inversely proportional to the width of the swollen surface layer. *Lapčík* [7] and *Valko* [8] used a modified *Ueberreiter—Asmussen* method for the study of dissolution kinetics of the fractions of poly(vinyl chloride) in cyclohexanone. *Valko* [9] derived equations describing the relationships among the values of induction periods, rates of

dissolution, temperature, and the length of macromolecular chain. *Lapčík* and *Valko* [10] explained the physical sense of the exponent occurring in the equations describing the dependence of t_0 on the rate of dissolution u_{RC} defined as the velocity of advance of interface.

In the monograph by *Crank* and *Park* [11] the results of the study of diffusion dissolution process by *Ueberreiter* and *Asmussen* [1—6] are summarized and their significance is discussed. A more detailed knowledge of the relationships between the properties of the solutions of chain macromolecules and the individual properties of components may be obtained on the basis of a more exact approach from the view-point of conformational statistics and statistical thermodynamics which is presented in detail for instance in the monograph by *Flory* [12].

On the basis of the cited papers [1—12], we present the results of experimental study of the dissolution of poly(vinylidene chloride) in five organic solvents.

The second Fourier—Fick law as a constitutive eqn (1) expresses the dependence of the density of substance flow on concentration gradient

$$\frac{\partial c}{\partial t} = \nabla[D(c) \nabla c] \quad (1)$$

The phenomenological coefficient in eqn (1) is the coefficient of diffusion which depends on the concentration of individual components, temperature, pressure, and other variables. The solution of modified eqn (1) for many cases is given in monographs [13, 14]. Subsequently, we are going to present only a concise solution for one-dimensional problem in order to obtain the resulting expression suited for the determination of the coefficient of diffusion from experimental data available.

In a steady state, i.e. provided t is greater than t_0 , the density of polymer substance flow is

$$J_{p,x} = -D_{p,r} v_p \frac{\partial c_p}{\partial x} \quad (2)$$

and the density of solvent flow is

$$J_{r,x} = -D_{r,p} v_r \frac{\partial c_r}{\partial x}$$

Simultaneously, it holds

$$D_{r,p} \equiv D_{p,r} = D \quad (3)$$

The rate of dissolution expressed as the rate of advance of the optical interface into the solid sample is

$$u_{RC} = J_{r,x} \quad (4)$$

Thus it follows from eqns (2—4) that

$$u_{RC} = -D v_r \frac{\partial c_r}{\partial x} \quad (5)$$

and on integration we obtain

$$u_{RC} d = -v_r \bar{D} \Delta c_r \quad (6)$$

where the mean integral coefficient of diffusion is defined by the expression

$$\bar{D} = \frac{1}{\Delta c_r} \int_{c_2}^{c_1} D(c) dc \quad (7)$$

and d is the width of the swollen surface layer.

As $v_r \Delta c_r = \Delta \Phi$, where $\Delta \Phi$ is the difference of volume fractions of solvent on the interfacial area between polymer and the surface of the swollen surface layer, we can obtain from eqn (6)

$$u_{RC} = -\left(\frac{\bar{D}}{d}\right) \Delta \Phi \quad (8)$$

The volume fraction of solvent on the interface between the swollen surface layer and polymer equals zero while it is equal to one on the interface between the swollen surface layer and solvent. Hence, it follows from eqn (8) that

$$u_{RC} = \frac{\bar{D}}{d} \quad (9)$$

The dependence of the mean integral coefficient of diffusion \bar{D} on temperature is to be described by the expression

$$\bar{D} = \bar{D}_0 \exp \left[-\frac{E_D}{RT} \right] \quad (10)$$

where E_D is the effective activation energy of diffusion and \bar{D}_0 is the preexponential factor.

Experimental

The powdered poly(vinylidene chloride) prepared according to [15] was used for the study of dissolution kinetics. The density of the particle size distribution was determined by measuring particle diameters with a Zeiss—Abbé comparator accurate to $\pm 1.5 \mu\text{m}$.

Cyclohexanone, *o*-dichlorobenzene, dioxan, tetrahydrofuran, and tetrachloroethane (anal. grade chemicals, Lachema, Brno) were used as solvents. The experimental equipment consisted of a dissolution cell thermostated at a constant temperature accurate to $\pm 0.1^\circ\text{C}$. By intensive stirring of the polymer—solvent mixture a turbulent flow was achieved in the whole volume of the cell and a homogeneous concentration field in the solution could be

assumed while the resistance against diffusion in the liquid phase outside the swollen surface layer could be considered equal to zero.

The effective rate of dissolution was determined by means of the equation derived in [7] in the form

$$u_{RC} = \frac{k_1}{S} \frac{dm}{\rho_p dt} \quad (11)$$

where dm/dt is the rate of dissolution expressed by the amount of the substance dissolved in unit time, S is the total surface of polymer, and ρ_p is the density of polymer at a given temperature.

For very dilute solutions it holds

$$\frac{dm}{dt} = k_2 \left[\frac{d(\Delta n)}{dt} \right] \quad (12)$$

The numerical value of the constant k_2 was determined experimentally by measuring the change in the index of refraction Δn as a function of the concentration of poly(vinylidene chloride) in the above-mentioned solvents at varying temperature.

On inserting eqn (12) into eqn (11) we obtain

$$u_{RC} = \frac{k_1 k_2}{S} \frac{d(\Delta n)}{\rho_p dt} \quad (13)$$

Thus, the amount of the polymer dissolved may be found from the relationship $m = f(\Delta n)$ where m is the mass in a volume unit of solvent which determines Δn unambiguously. The accuracy of measurement of the index of refraction with an immersion refractometer (Zeiss, Jena) was $\pm 1 \times 10^{-5}$.

The width of the swollen surface layer was determined from the mass of original polymer m_p , dissolved polymer m_1 , and from the mass of polymer augmented by the content of solvent contained in the swollen surface layer m_2 .

Results and discussion

Fig. 1 shows a typical course of kinetic curves expressing the dissolution of poly(vinylidene chloride) in tetrachloroethane. On the basis of this figure the values of u_{RC} have been determined by means of eqn (13). Moreover, it has enabled to extrapolate and thus to find the time t_0 necessary for reaching a constant width of the swollen surface layer. These data are given as a function of $1/T$ in Fig. 2.

The course of curves in Fig. 1 is in agreement with the results obtained by Ueberreiter and Asmussen. If we extrapolate the linear part of the plot $\Delta n = f(t)$ up to the axis of time, we obtain the value of t_0 . It is obvious that the time t_0 decreases with increasing temperature.

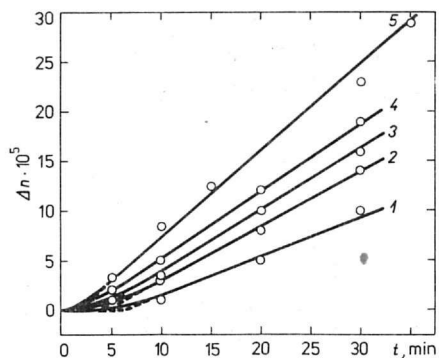


Fig. 1. Kinetic curves of the dissolution of poly(vinylidene chloride) in tetrachloroethane. 1. 20°C; 2. 30°C; 3. 35°C; 4. 40°C; 5. 50°C.

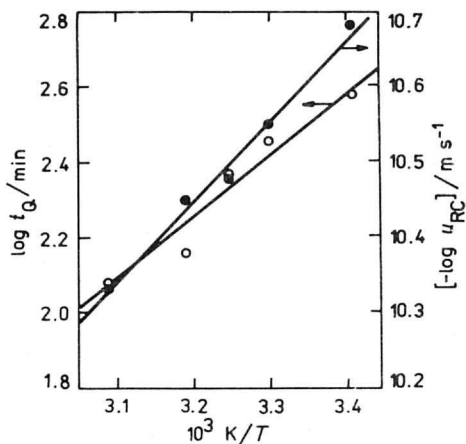


Fig. 2. Plots of $\log u_{RC}$ and $\log t_G$ vs. $1/T$ for poly(vinylidene chloride) in tetrachloroethane.

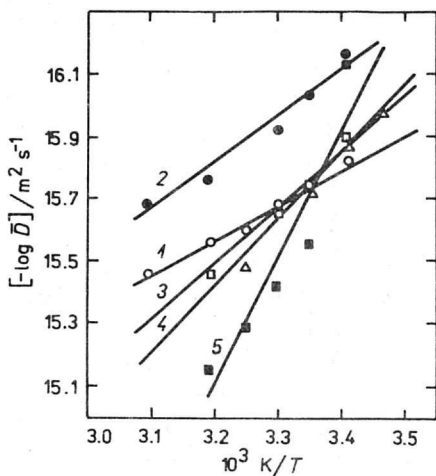


Fig. 3. Plots of $\log \bar{D}$ vs. $1/T$. 1. Tetrachloroethane; 2. dioxan; 3. cyclohexanone; 4. tetrahydrofuran; 5. *o*-dichlorobenzene.

Table 1 contains the fundamental parameters of the diffusion process of poly(vinylidene chloride) dissolution in individual solvents, namely the width of the swollen surface layer d and the value of the mean integral coefficient of diffusion \bar{D} .

The relationship according to eqn (10), *i.e.* the dependence of $\log \bar{D}$ on $1/T$ is presented in Fig. 3.

The suitability of the approximative solution according to eqn (10) was tested by the coefficient of correlation r . The values of the effective activation energy E_D ,

Table 1

Values of the total width of swollen surface layer d and the mean integral coefficient of diffusion \bar{D}

T °C	Tetrachloroethane		Dioxan		Cyclohexanone		Tetrahydrofuran		<i>o</i> -Dichlorobenzene	
	$d \cdot 10^6$ m	$\bar{D} \cdot 10^{17}$ $\text{m}^2 \text{s}^{-1}$	$d \cdot 10^6$ m	$\bar{D} \cdot 10^{17}$ $\text{m}^2 \text{s}^{-1}$	$d \cdot 10^6$ m	$\bar{D} \cdot 10^{17}$ $\text{m}^2 \text{s}^{-1}$	$d \cdot 10^6$ m	$\bar{D} \cdot 10^{17}$ $\text{m}^2 \text{s}^{-1}$	$d \cdot 10^6$ m	$\bar{D} \cdot 10^{17}$ $\text{m}^2 \text{s}^{-1}$
15	—	—	—	—	—	—	3.24	10.6	—	—
20	7.39	15.4	5.63	6.9	7.78	12.4	3.37	13.7	7.12	7.1
25	—	—	5.78	9.2	8.01	18.0	3.49	18.5	7.55	27.8
30	7.54	21.4	5.93	11.8	8.24	20.8	3.63	21.4	7.61	38.1
35	7.62	25.3	—	—	8.47	24.3	3.76	32.8	7.66	51.3
40	7.69	27.5	6.22	16.8	8.69	34.5	—	—	7.71	69.6
50	7.83	35.7	6.50	20.7	—	—	—	—	—	—

preexponential factor \bar{D}_0 as well as the values of the coefficient of correlation r are given in Table 2 and confirm the validity of eqn (10) for the systems studied.

It ensues from the results that the kinetic activity of dissolution according to E_D falls in this sequence: tetrachloroethane > dioxan > cyclohexanone > tetrahydrofuran > *o*-dichlorobenzene.

Table 2

Values of the preexponential factor \bar{D}_0 , effective activation energy of diffusion E_D , and coefficient of correlation r

Solvent	\bar{D}_0 $\text{m}^2 \text{s}^{-1}$	E_D kJ mol^{-1}	r
Tetrachloroethane	1.27×10^{-12}	21.8	0.9968
Dioxan	9.93×10^{-12}	28.5	0.9871
Cyclohexanone	3.1×10^{-10}	35.6	0.9841
Tetrahydrofuran	1.73×10^{-9}	39.8	0.9895
<i>o</i> -Dichlorobenzene	1.54×10^{-2}	79.1	0.9304

The plots in Fig. 1 show that the character of dissolution is nonsteady at the time $t < t_Q$. The solvent attacks the polymer and first of all, the width of the swollen surface layer increases until it reaches a certain final value d which corresponds to a steady state at $t_Q < t$. It means that the diffusion of macromolecules from the polymer surface into solution is constant and independent of time. The diffusion and the rate of dissolution are significantly influenced by the molar volume of solvent. Besides, the diffusion of solvent into polymer and the rate of dissolution also depend on molecular structure of polymer and physicochemical properties of solvent. Since poly(vinylidene chloride) is a high-crystalline polymer, only very polar organic solvents are suitable for the dissolution of this polymer.

Symbols

- c concentration
- c_p concentration of polymer
- c_s concentration of solvent
- D coefficient of diffusion
- \bar{D} mean integral coefficient of diffusion
- \bar{D}_0 preexponential factor in eqn (10)
- $D_{p,r}$ coefficient of polymer diffusion into solvent
- $D_{r,p}$ coefficient of solvent diffusion into polymer
- d width of swollen surface layer

E_D	effective activation energy of diffusion
$J_{p,x}$	diffusion flow of polymer
$J_{r,1}$	diffusion flow of solvent
k_1	constant in eqn (11)
k_2	constant in eqn (12)
m	mass of polymer in a volume unit of solvent
m_p	mass of polymer
m_1	mass of dissolved polymer
m_2	mass of swollen polymer
Δn	change in the index of refraction
S	total surface of polymer
t	time
t_O	time of swelling
u_{RC}	rate of dissolution
v_p	partial specific volume of polymer
v_r	partial specific volume of solvent
$\Delta\Phi$	difference between mole fractions of solvent
ρ_p	density of polymer

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