

Kinetic study of dissolution of poly(vinyl chloride) in tetrahydrofuran, cyclohexanone, cyclopentanone, and *N,N*-dimethylformamide

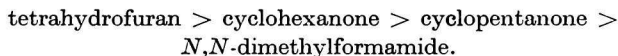
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The kinetics of dissolution of poly(vinyl chloride) (Lonza G) in tetrahydrofuran (*I*), cyclohexanone (*II*), cyclopentanone (*III*), and *N,N*-dimethylformamide (*IV*) was studied. The investigations with individual solvents were carried out in the following temperature ranges: 15–30°C (*I*), 40–70°C (*II*), 30–60°C (*III*), and 30–50°C (*IV*).

The values of induction periods of the diffusion process of dissolution t_Q and the velocity of dissolution u_{OC} of poly(vinyl chloride) in the following solvents are presented. On the basis of the measured values of t_Q and u_{OC} the values of mean integral mutual diffusion coefficients \bar{D} as well as the mean activation energies of the diffusion processes of swelling, dissolution, and mutual diffusion were calculated for particular temperature ranges. The comparison between the values of activation energy of mutual diffusion showed that the following order of the solvents under investigation could be established according to the decreasing activity with respect to the dissolution of PVC:



It has been proved experimentally as well as theoretically that the rate of dissolution of macromolecular substances is controlled by the rate of the diffusion of a low-molecular solvent into solid polymer phase [1–4]. When studying the mutual transport it is necessary to pay attention not only to the pure physical diffusion but also to some chemical changes which occur during the penetration of solvent into solid sample, in particular, the interaction between polymer and solvent as well as the heats of solution and dilution. From the point of view of the microstructure of transport phenomenon, the molecules of penetrant move discontinuously from one interstitial position into another while the frequency as well as the length of jump are controlled by the mobility of the segments of macromolecular chain.

The aim of this study is to compare the kinetic activities of some solvents (tetrahydrofuran, cyclohexanone, cyclopentanone, and *N,N*-dimethylformamide) in the dissolution of a solid polymeric film of PVC. The following kinetic parameters of the diffusion process of dissolution may be used as concrete criteria for this comparison:

- the length of induction period t_Q ,
- the rate of dissolution u_{OC} defined as the velocity of advancement of the optical interface to the centre of sample,
- the effective values of activation energies of the diffusion process of swelling ΔE_s , dissolution ΔE_d , and mutual diffusion ΔE_D .

Experimental

Polymer

The kinetic measurements were done with an amorphous polymer of emulsion type, commercial trademark "Lonza G" (Lonza Elektrizität AG, Basel, Switzerland). The non-fractionated polymer was carefully deprived of the residues of emulgators, catalysts, and other admixtures by threefold precipitation from a 1% solution in tetrahydrofuran into redistilled water. Then it was washed with anhydrous alcohol and dried *in vacuo* to constant weight. The limiting viscosity number $[\eta]$ of this polymer was $93 \pm 1 \text{ ml g}^{-1}$ (in cyclohexanone at 25°C). The number average molecular weight determined osmotically in cyclohexanone at 37°C by Dr B. Böhmer (Polymer Institute, Slovak Academy of Sciences, Bratislava) was $M_n = 44,000 \pm 2,000$ while the weight average molecular weight determined from light scattering of the polymer solutions in cyclohexanone and tetrahydrofuran by Dr T. E. Gunter (Institute of Physical Chemistry, University of Uppsala) was $M_w = 200,000$.

The investigated samples were rectangular in shape (1.5 cm \times 5.0 cm) and about 1 mm thick. The samples were cut from the films prepared by casting the polymer solutions in tetrahydrofuran on the level of mercury.

Solvents

The solvents used were of anal. grade and were freshly distilled in a distillation column with 30 theoretical plates. Before rectification, tetrahydrofuran was deprived of peroxides by boiling with solid KOH under reflux for 4 hours, all operations being carried out without direct lighting.

Apparatus

The kinetic measurements were done in an apparatus allowing to measure the refractive index of coexisting liquid phase continuously during dissolution. As shown by *Ueberreiter* and *Asmussen* [1–3], a linear relationship exists between the relative change in the refractive index of solution and the concentration of polymer in the region of low concentrations which enables us to determine the rate of dissolution on the basis of the change in the refractive index of solution with respect to that of pure solvent.

Table 1

Values of the refractive index increments $\mathfrak{R}_{546 \text{ nm}}^{25.0^\circ\text{C}}$ and the temperature increments $[\partial\mathfrak{R}/\partial T]_{546 \text{ nm}}$ for the solutions of PVC in some its solvents

Solvent	$\mathfrak{R}_{546 \text{ nm}}^{25.0^\circ\text{C}}$ [ml g ⁻¹]	$10^4 \cdot [\partial\mathfrak{R}/\partial T]_{546 \text{ nm}}$ [ml g ⁻¹ K ⁻¹]
Tetrahydrofuran	0.108 ₃	6.2
Cyclohexanone	0.076 ₇	3.9
Cyclopentanone	0.084 ₅	(3.9)*
<i>N,N</i> -Dimethylformamide	0.082 ₃	3.3

* The assumed value equals the value found for cyclohexanone.

The experimental equipment consists of two parts, *i.e.* the part for measurement and that for dissolution. Its thorough description was presented in previous paper [4].

The increments in the refractive index of investigated polymer in the above-mentioned solvents were determined experimentally with a differential refractometer [5]. The results of these measurements were published separately [6]. For completeness, the values of increments used for the calculation of u_{oc} are presented in this paper (Table 1).

Results and discussion

The kinetic curves of dissolution of poly(vinyl chloride) in tetrahydrofuran, cyclohexanone, cyclopentanone, and *N,N*-dimethylformamide have usual shape (Figs. 1–4). They are characterized by the induction period t_0 and the stationary part. The length of induction period of the diffusion process of dissolution at constant temperature increases with decreasing kinetic activity of solvent and increasing degree of the packing of polymer coils in the solid sample.

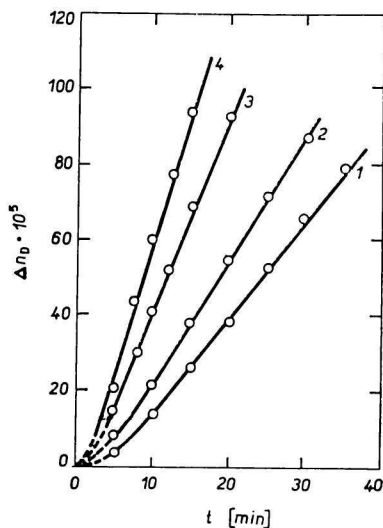
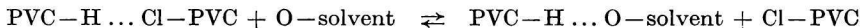


Fig. 1. Kinetic curves of dissolution of PVC (Lonza G) in tetrahydrofuran. 1. 15°C; 2. 20°C; 3. 25°C; 4. 30°C.

As shown by *Adelman* and *Klein* [7], the hydrogen bonds represent the most essential part of the PVC–PVC and PVC–solvent bonding interactions. Thus it may be assumed that the value of rate constant as well as the value on equilibrium constant of the reaction



affects considerably the length of induction period t_0 . Moreover, other factors, *e.g.* the proper volume and the structure of low-molecular solvent, distribution of electric charge, *etc.*, are operative.

The physical properties of solid polymer phase depend on the physical state of the monomer units and chains making the chemical constitution. That involves especially the amount and the intensity of bonding and non-bonding interactions between neighbouring chains (hydrogen bonds, van der Waals and Coulomb interactions) as well

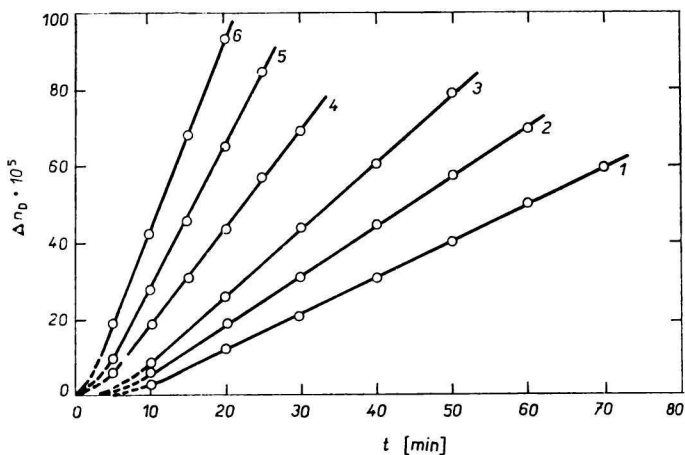


Fig. 2. Kinetic curves of dissolution of PVC (Lonza G) in cyclohexanone.
1. 40°C; 2. 45°C; 3. 50°C; 4. 55°C; 5. 60°C; 6. 70°C.

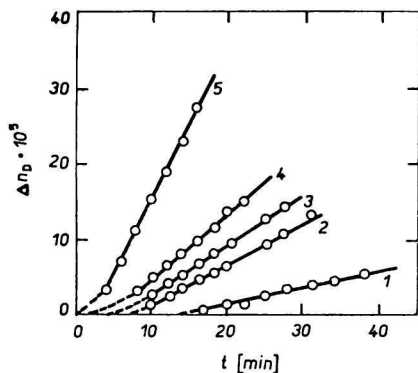


Fig. 3. Kinetic curves of dissolution of PVC (Lonza G) in cyclopentanone.
1. 30°C; 2. 40°C; 3. 45°C; 4. 50°C;
5. 60°C.

as the geometry of mutual intertwinement, and, in particular, the number of nodal points, the amount of which is strongly dependent on the thermal history of sample. The intensity of mutual mixing of polymer chains as well as the occurrence of formation and the size of "empty holes" inside the solid phase increases with temperature. From this point of view it is quite comprehensible that t_Q decreases and u_{OC} increases with temperature (Table 2).

The induction period of the process of dissolution t_Q may be regarded as a time lag L of the proper process. Then according to Daynes [10] holds

$$L = \frac{l^2}{6D}, \quad (1)$$

Table 2

Values of some kinetic parameters characterizing the diffusion process of dissolution of PVC (Lonza G)

Solvent	Temperature [°C]	t_Q [s]	$u_{oc} \cdot 10^5$ [cm s ⁻¹]	$D \cdot 10^7$ [cm ² s ⁻¹]
Tetrahydrofuran	15.00	240	2.00	5.75
	20.00	180	2.48	6.70
	25.00	120	3.70	9.80
	30.00	90	4.80	12.5
Cyclohexanone	40.00	490	0.88	2.20
	45.00	400	1.15	3.17
	50.00	330	1.48	4.35
	55.00	180	2.16	5.04
	60.00	165	3.06	9.25
	70.00	90	4.00	8.70
Cyclopentanone	30.00	900	0.21	0.24
	40.00	480	0.44	0.55
	45.00	400	0.56	0.75
	50.00	300	0.70	0.88
	60.00	150	1.51	2.05
<i>N,N</i> -Dimethylformamide	30.00	360	0.55	0.66
	35.00	180	0.88	0.85
	40.00	120	1.40	1.41
	45.00	90	1.87	1.89
	50.00	—	2.25	—

where l is the width of the membrane through which the diffusion proceeds and D is the diffusion coefficient. In this case, the relationship (1) may be applied in the following form

$$L \approx t_Q = \frac{\delta^2}{6D}, \quad (2)$$

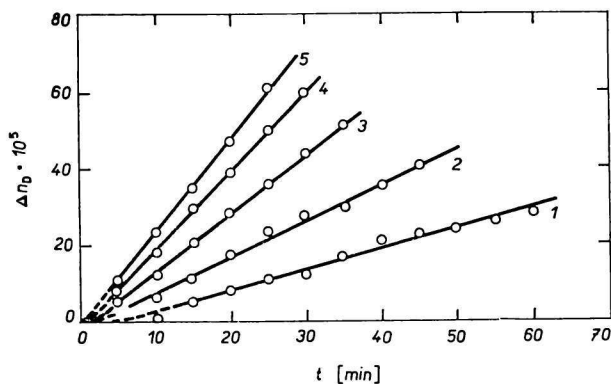


Fig. 4. Kinetic curves of dissolution of PVC (Lonza G) in *N,N*-dimethylformamide. 1. 30°C; 2. 35°C; 3. 40°C; 4. 45°C; 5. 50°C.

Table 3

Density, molar volume, electron donor capacity (EDC),
and parameter of the solubility (δ) for some solvents of PVC

Solvent	Density ^a [g cm ⁻³]	Molar volume [cm ³ mol ⁻¹]	EDC ^b [cal mol ⁻¹]	Parameter of solubility ^c δ
Tetrahydrofuran	0.8892	80.9	750	9.1
Cyclohexanone	0.9465	103.6	618	9.7
Cyclopentanone	0.9481	88.6	566	10.4
<i>N,N</i> -Dimethylformamide	0.9682	75.4	—	12.1

a) Determined pycnometrically at 20.00°C accurate to ± 0.0002 g cm⁻³.

b) Heat of mixing for a certain solvent and chloroform at 25.0°C divided by the number of contact points [7].

c) Defined as the square root of the density of cohesion energy [7, 23].

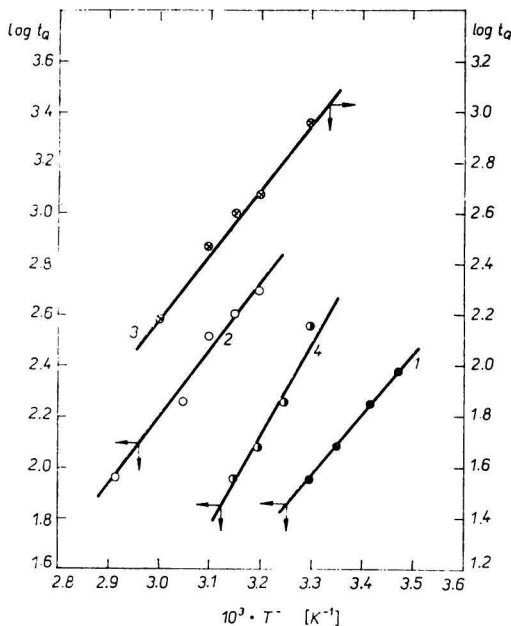


Fig. 5. Temperature dependence of the time of swelling of PVC (Lonza G) in tetrahydrofuran (1), cyclohexanone (2), cyclopentanone (3), and *N,N*-dimethylformamide (4).

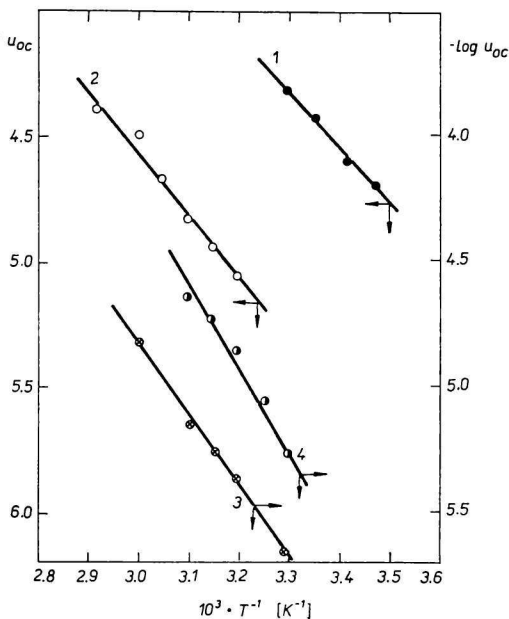


Fig. 6. Temperature dependence of the rate of dissolution of PVC (Lonza G) in tetrahydrofuran (1), cyclohexanone (2), cyclopentanone (3), and *N,N*-dimethylformamide (4).

Table 4

Values of activation energies of the diffusion processes of swelling ΔE_s , dissolution ΔE_d , and mutual diffusion ΔE_D and the corresponding frequency factors t_Q^0 , u_{0C}^0 , \bar{D}^0 (PVC — Lonza G)

Solvent	Temperature interval [°C]	ΔE_s [kcal mol ⁻¹]	ΔE_d [kcal mol ⁻¹]	ΔE_D [kcal mol ⁻¹]	t_Q^0 [s]	u_{0C}^0 [cm s ⁻¹]	\bar{D}^0 [cm ² s ⁻¹]
Tetrahydrofuran	15–30	11.5 ± 1	10.0 ± 1	10 ± 1	5.0 × 10 ⁻⁷	7.0 × 10 ²	1.8 × 10 ¹³
Cyclohexanone	40–70	12.5 ± 1	11.5 ± 1	14 ± 1	1.0 × 10 ⁻	8.5 × 10 ²	4.3 × 10 ¹⁴
Cyclopentanone	30–60	12.0 ± 1	13.0 ± 1	15 ± 2	2.2 × 10 ⁻	5.0 × 10 ⁸	3.0 × 10 ¹⁶
<i>N,N</i> -Dimethylformamide	30–50	16.0 ± 2	16.0 ± 2	17 ± 2	1.0 × 10 ⁻	1.6 × 10 ⁶	2.6 × 10 ¹⁶

where δ is the width of swollen surface layer and \bar{D} is the mean diffusion coefficient.

With respect to the definition of the rate of dissolution [4]

$$u_{oc} = \frac{\bar{D}}{\delta} \varphi_{\xi}, (\varphi_{\xi} \approx 1, \text{ provided } \xi = 0) \quad (3)$$

(where φ_{ξ} is the molar fraction of solvent in the position $x = \xi$) the mutual mean diffusion coefficient may be calculated from relationship

$$\bar{D} = 6 t_Q u_{oc}^2. \quad (4)$$

The numerical values of \bar{D} calculated from equation (4) for different temperatures and solvents are given in Table 2. The value of integral mean diffusion coefficient increases with temperature because the height of potential barrier for the molecules of solvent at the interface "liquid solvent—solid polymer" as well as the energy necessary for the formation of free vacancies decreases with increasing mobility of the segments of polymer chains. As known, the height of the potential barrier for free rotation is the fundamental factor which determines the flexibility of macromolecular chains. From a formal point of view all these effects as well as those stated before affect the values of the diffusion coefficient. Its value is determined not only by "pure diffusivity". As pointed out by *Rehage et al.* [11] it also involves the thermodynamic factor of mutual interaction

$$D_i = u_i \rho_i \left(\frac{\partial \mu_i}{\partial \rho_i} \right), \quad (5)$$

where u_i being the mobility of a certain kind of molecular (defined as the reciprocal value of the friction coefficient), *i.e.* the hydrodynamic or so-called pure transport factor; $\rho_i(\partial \mu_i / \partial \rho_i)$ is the so-called thermodynamic factor (ρ_i and μ_i being concentration in g cm^{-3} and chemical potential of a certain component, respectively).

The value of the mobility of diffusing liquid in a medium u_i is determined mainly by the proper volume and shape of diffusing molecules and in polar systems by the distribution of charge, too.

Table 3 contains the values of the molar volumes of the investigated solvents at 20.00°C. The comparison between the data of Table 2 and Table 3 shows that the influence of mutual interaction polymer—solvent on the value of diffusion coefficient in the investigated systems is greater than the influence of molar volume of the penetrant itself.

The values of formal activation energies of the diffusion processes of swelling ΔE_s , dissolution ΔE_d , mutual diffusion ΔE_D , and the corresponding frequency factors t_Q^0 , u_{oc}^0 , and \bar{D}^0 (presented in Table 4) were calculated from the equation for the temperature dependence of induction period t_Q [8], (Fig. 5)

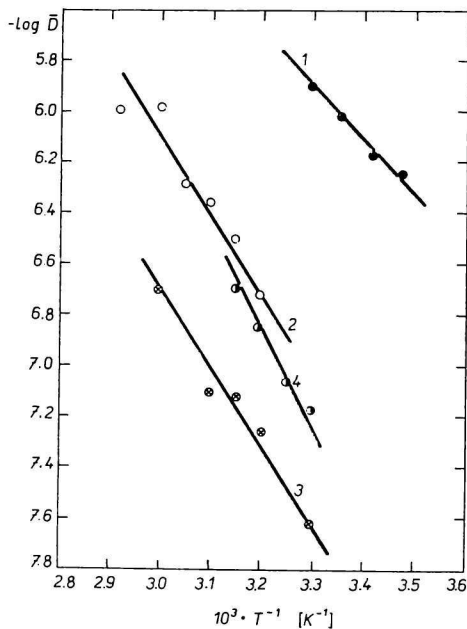
$$t_Q = t_Q^0 \exp \left(\frac{\Delta E_s}{RT} \right), \quad (6)$$

the equation for the temperature dependence of the rate of dissolution u_{oc} [4], (Fig. 6)

$$u_{oc} = u_{oc}^0 \exp \left(\frac{\Delta E_d}{RT} \right), \quad (7)$$

and the empiric equation for the temperature dependence of the diffusion coefficient D [9], (Fig. 7)

Fig. 7. Mean integral diffusion coefficient as a function of temperature. (Denotation conforms with that one in Fig. 6.)



$$D = D^0 \exp\left(\frac{\Delta E_D}{RT}\right) \quad (8)$$

According to *Ueberreiter* and *Asmussen* [1–3] the rate of dissolution of macromolecular substances is controlled by the rate of diffusion of the molecules of solvent into solid polymer phase. The effect of the nature of the molecules of diffusing substance on the rate of its transport in solid polymer was studied in a number of papers. According to statements of many authors the value of the diffusion coefficient is determined by the molecular weight of penetrant [12, 13], its molar volume [14–17], the length and shape of molecular [18–20], the amount and distribution of double bonds [21], and the polarity of a molecule [22].

The effect of the mass of molecules of penetrant on the value of diffusion coefficient is greater in the diffusion of vapours and liquids through a solid polymer membrane while the diffusion in solution is little affected. As pointed out by *Zhurkov* and *Ryskin* [14], it is the molar volume which has a greater influence on the transport of low-molecular substances in solid polymer phases. As it follows from the comparison between the data given in Tables 2 and 3, the molar volume of the investigated solvents does not unambiguously correlate with the kinetic parameters of dissolution of poly(vinyl chloride). A comparison of EDC and the parameters of solubility of the four solvents to the values of activation energies of the diffusion processes of swelling, dissolution, and mutual diffusion (Table 4) shows that the thermodynamic effect of the mutual reaction polymer—solvent affects substantially the overall kinetic process of dissolution of poly(vinyl chloride) in flowing solvent. With increasing electron donor capacity of solvent the value of the formal activation energies of mutual diffusion and diffusion process of swelling and dissolution decreases. Conversely, with increasing difference between the parameters of solubility of solvent and polymer (*Tobolsky* [24] alleges the value of $9.53^2 \text{ cal mol}^{-1} \text{ l}^{-1}$

for the density of cohesion energy of PVC) the value of activation energies increases and thus the kinetic activity decreases.

On the basis of the presented values of activation energies of the diffusion processes of swelling, dissolution, and mutual diffusion it is possible to put forward the following order of the investigated solvents according to their decreasing kinetic activity:

tetrahydrofuran > cyclohexanone > cyclopentanone > *N,N*-dimethylformamide.

The lower kinetic activity of dimethylformamide with respect to the dissolution of PVC may be explained by a greater ability of the molecules of *N,N*-DMFA to associate (which is also indicated by the much higher boiling point) as well as by a greater spatial shielding of charge vacancy.

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