

Study of Kinetics of Poly(vinyl chloride) Swelling in Cyclohexanone

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Kinetics of swelling of non-fractionated poly(vinyl chloride) in cyclohexanone has been studied on two samples of emulsion type of PVC over the temperature range 20–60°C. Values of average integral diffusion coefficients of cyclohexanone in PVC calculated from experimental data have been stated. The following average values of activation energies of the diffusion process of swelling for the referred to temperature range have been found: 7 kcal mole⁻¹ (Lonza G) and 6 kcal mole⁻¹ (Geon 121), respectively. The observed anomalous course of kinetic curves is discussed. The stepwise effect is accounted for by permeation heterogeneity as a consequence of a vigorous polymer–solvent interaction.

In the case of a sufficient mobility of macromolecular chains segments the kinetics of sorption of low-molecular penetrant is found to be controlled by the diffusion process [1–3]. The amount of penetrant Q sorbed on both the time root $t^{1/2}$ and the reciprocal value of thickness appears to be the characteristic feature of these measurements. (Isotropic sample in the shape of a thin plate is considered.) Particularly for the starting time intervals dependences $Q = Q(t^{1/2})$ determined experimentally do not substantially differ from the curves for actions with a constant diffusion coefficient. The results presented in the present paper are of this type.

Models suggested for the description of diffusion processes in solid phase are based on the supposition that the diffusion rate is controlled by that of loose “holes” formation enabling the translation motion of penetrant molecules in the negative sense of the gradient of their chemical potential [4–6].

The results presented complement the data on PVC sorption measurements published so far. 

Experimental

The cyclohexanone used was carefully purified by shaking over with anhydrous CaCl₂ and distilled in nitrogen at atmospheric pressure. The purity was checked by measuring the refractive index n_D^{20} in the range 1.4509–1.4510, what is in a good agreement with the reference data.

Polymer samples (Lonza G — Switzerland, Geon 121 — UK; both emulsion polymers of amorphous type) were deprived of the residue of both the emulgators and the catalysts by precipitation from tetrahydrofuran solutions into redistilled water and, after washing in anhydrous ethyl alcohol, dried in vacuum to constant weight. The samples are characterized by the following values of limiting viscosity numbers: 0.93 dl/g (Lonza G) and 1.17 dl/g (Geon 121) respectively, cyclohexanone, 25.0°C [7].

The kinetic measurements were carried out on a small apparatus according to *Dogadkin* [8]. An accurately weighed polymer sample of known surface and thickness over the range 0.30–0.50 mm (Lonza G) and 1.6–1.9 mm (Geon 121) was immersed into cyclohexanone of constant temperature kept within an accuracy of $\pm 0.02^\circ\text{C}$. Polymer samples were disc-like, diameter 10.0 mm. The amount of the cyclohexanone sorbed was determined in different time intervals by the measurement of volume change of the coexisting liquid phase. The volume determination of the solvent incorporated was made with an accuracy of $\pm 1 \times 10^{-3}$ ml.

In view of both the found volumes and the density of the polymer-incorporated solvent values Q , *i.e.* weight of solvent bonded by unit weight of polymer of just the same thickness l was calculated.

Results and Discussion

Differential equation for unidirectional non-stationary diffusion process has the form

$$(\partial c/\partial t) = \partial/\partial x[D(\partial c/\partial x)]. \quad (1)$$

Should the diffusion coefficient D be the function of concentration, the solution of the equation (1) might only be brought about by analytical expression of the dependence. As shown by *Crank* [9], the absorption curves $Q = Q(t)$ for even plate are of no substantial difference for the both cases, *i.e.* $(\partial D/\partial c)_t = 0$ and $(\partial D/\partial c)_t \geq 0$.

For the latter case, the equation (1) may well be rewritten in the form

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

For the case of diffusion along the half line, the following solution appears to agree with the equation (2) according to *Crank* [9]

$$Q_t/Q_\infty = (4/l) \cdot (Dt/\pi)^{1/2}, \quad (3)$$

where Q_t is the sample-incorporated amount of solvent within time t , Q_∞ the amount of solvent bonded by the sample within the final equilibrium state of swelling and l is the sample thickness. According to the relation (3), the Q_t/Q_∞ is proportional to the time

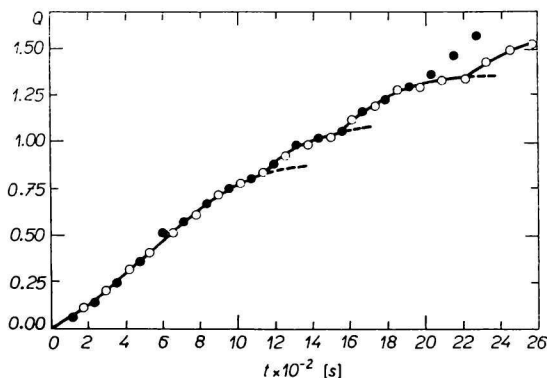


Fig. 1. Kinetic curve of PVC — Lonza G swelling in cyclohexanone at 20.0°C , two parallel experiments.

square root. The equation (3), having a limited validity, may well be applied to $Q_t/Q \leq 0.6$ under the following conditions:

1. The penetrant enters the sample by diffusion only.
2. The penetration into the solid phase is not accompanied by any chemical or physical system changes.
3. Perfect dipping of the outer sample surface occurs right after the contact with liquid penetrant has been established.
4. The penetrant enters through the sample surface only (unidirectional diffusion flow), whereas the latter is sufficiently large to neglect the flow through the walls perpendicularly to the thickness vector.

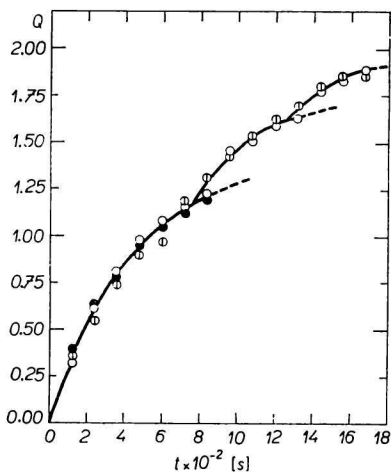


Fig. 2. Kinetic curve of PVC — Lonza G swelling in cyclohexanone at 30.0°C, three parallel measurements.

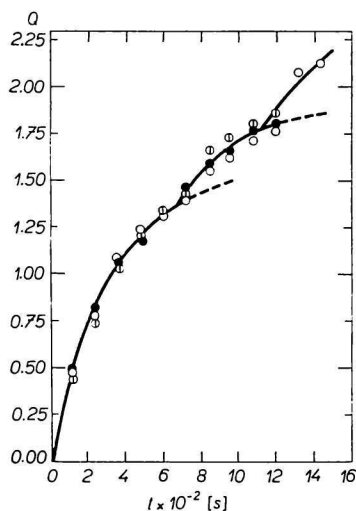


Fig. 3. Kinetic curve of PVC — Lonza G swelling in cyclohexanone at 40.0°C, three parallel measurements.

Kinetic data on PVC swelling in cyclohexanone are shown in Figs. 1—6. The dependence course $Q = Q(t)$ is in agreement with equation (3) which refers, as a matter of fact, to initial measurement stages (Fig. 7). For the calculation of diffusion coefficients first limiting values $Q_{\infty,1}$ found numerically, have been used.

The stepwise anomalous course of sorption curves is most likely due to density anisotropy within the system. It may well be assumed that in the first moments of sorption, under the influence of quite a great packing of polymer clues in solid phase, the penetrant transport corresponds to Fick's law, proceeding through loose holes resulting from thermal vibrations of polymer segments. The gradual saturation of sample surface with solvent molecules leads to the formation of the defined surface-swollen film in which, according to *Ueberreiter* and *Asmussen* [10] four characteristic sublayers (infiltration, gel, rubber-like and liquid) may well be differentiated. In the formation of the first two sublayers (infiltration and gel), later on, the kinetic process is partially affected also by mutual interaction polymer—solvent. By gradual increase of local concentration of solvent molecules in the gel sublayer the intensity increase of mutual interactions

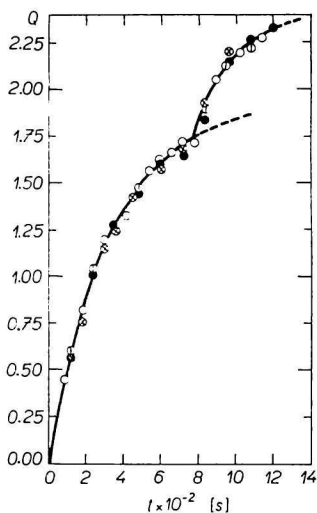


Fig. 4. Kinetic curve of PVC — Lonza G swelling in cyclohexanone at 50.0°C, four parallel measurements.

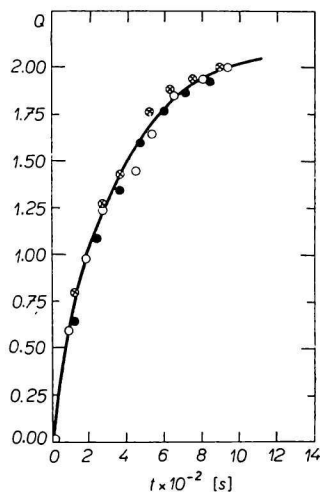


Fig. 5. Kinetic curve of PVC — Lonza G swelling in cyclohexanone at 60.0°C, four parallel measurements.

takes place getting manifest by cues expansion against both the inner and the outer pressure, which may even lead to the destruction of the mechanical medium isotropy, that is, to the formation of microcracks orientated inwardly. This results both in the acceleration of solvent penetration (suction and condensation capillary effect) and in the increase of the effective area the diffusion process proceeds along. Outwardly, it gets manifest by vivification of sorption, *i.e.* by stepwise effect. The formation of both the micropores and the craks proceeding in the course of sorption was observed by Hopfenberg *et al.* [11–13] in polystyrene, and by Vasenin, Čalych and Korobko in the

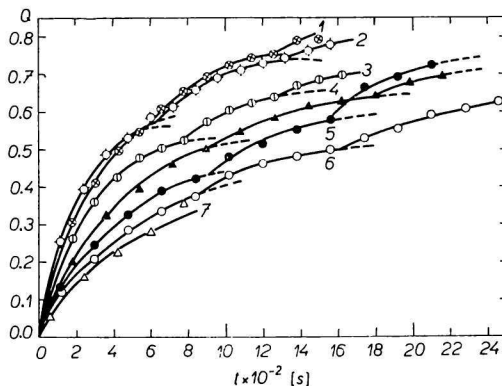


Fig. 6. Kinetic curves of PVC — Geon 121 swelling in cyclohexanone.
1. 45.0°C; 2. 45.0°C; 3. 40.0°C; 4. 35.0°C; 5. 30.0°C; 6. 25.0°C; 7. 20.0°C.

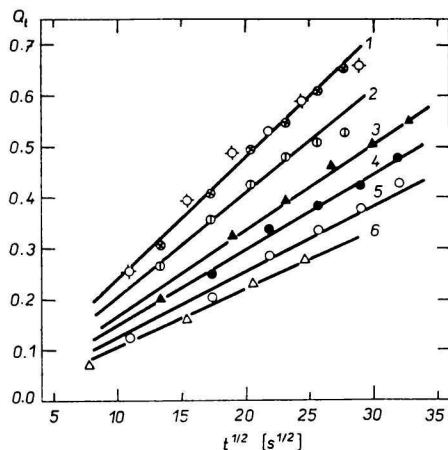


Fig. 7. Checking validity of the equation (3) for the diffusion process of PVC—Geon 121 swelling in cyclohexanone (numerical designations of the curves coincide with Fig. 6).

systems PVC—dichloroethane and polystyrene—acetone [14], respectively. With proceeding time, the optical molecular boundary between phases is acquiring increasingly a saw-like character, as may well be seen from the enclosed microinterferometrical pictures of the PVC—cyclohexanone boundary (Figs. 8—11). The results of these measurements will be published separately.

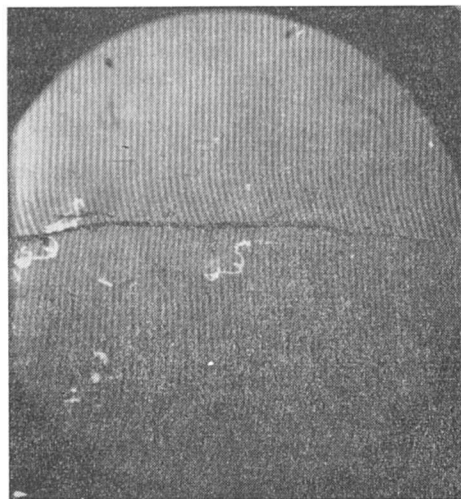


Fig. 8. Interference picture of inter-phase boundary liquid cyclohexanone—solid PVC at 21.0°C within the time $t = 9$ minutes.

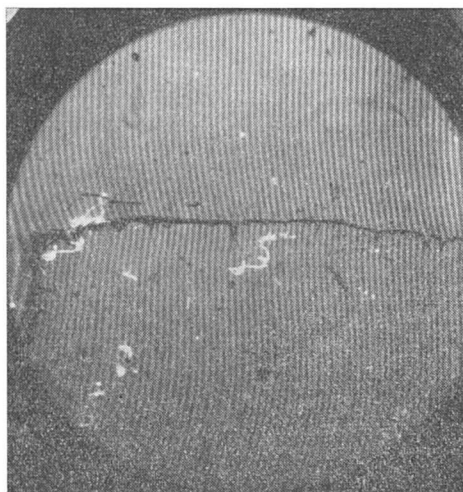


Fig. 9. Interference picture of inter-phase boundary liquid cyclohexanone—solid PVC at 21.0°C within the time $t = 28$ minutes.

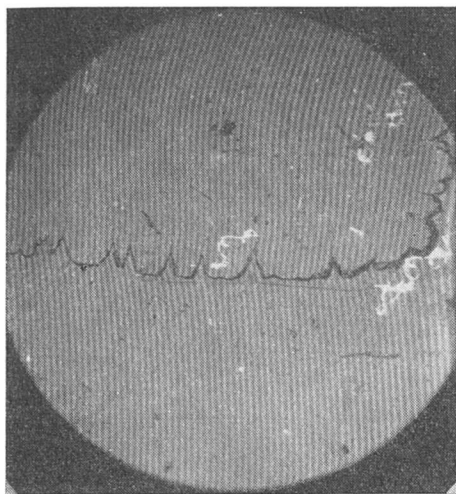


Fig. 10. Interference picture of inter-phase boundary liquid cyclohexanone—solid PVC at 21.0°C within the time $t = 85$ minutes.

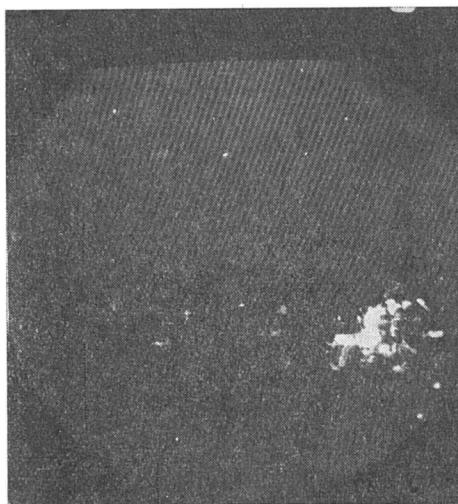


Fig. 11. Interference picture of inter-phase boundary liquid cyclohexanone—solid PVC at 21.0°C within the time $t = 115$ minutes.

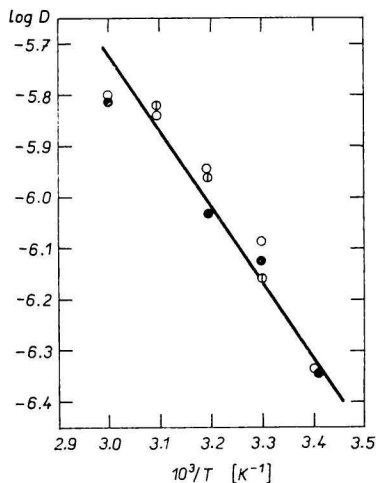


Fig. 12. Dependence of the mean integral diffusion coefficient of cyclohexanone in PVC — Lonza G on the temperature.

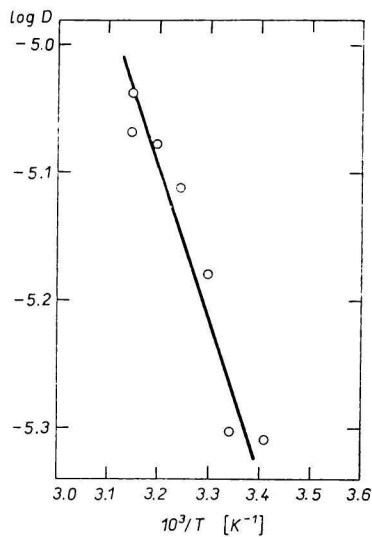


Fig. 13. Dependence of the mean integral diffusion coefficient of cyclohexanone in PVC — Geon 121 on the temperature.

The dependence of the average integral diffusion coefficient of cyclohexanone in PVC on temperature is shown in Figs. 12 and 13, respectively. Effective values of the average activation energies of the diffusion

$$E_{\text{eff}} = -R(d \ln D/d T^{-1}), \quad (4)$$

over the temperature range investigated are as follows

$$E_{\text{eff}} = 7 \pm 1 \text{ kcal mole}^{-1} \quad (\text{cyclohexanone-PVC - Lonza G}),$$

$$E_{\text{eff}} = 6 \pm 1 \text{ kcal mole}^{-1} \quad (\text{cyclohexanone-PVC - Geon 121}).$$

As stated by *Barrer* [15], the formation of loose holes in the diffusion of simple organic compounds in solid polymer phase is dependent on the molecular motion of polymer segments. Therefore, a certain relaxation time τ of the relaxation mechanism corresponds

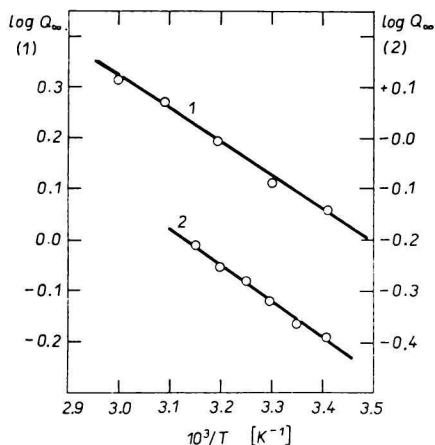


Fig. 14. Dependence of Q on the temperature.

1. Lonza G; 2. Geon 121, cyclohexanone.

to each D value. As regards the fact that the time necessary for obtaining a certain saturation degree Q_t/Q_{∞} is always proportional to the square power of the thickness or $t/l^2 = \text{const}$ [16, 17] and in view of the inversal proportionality of τ to D , the following relation for the relaxation time τ calculation has been stated by *Kanamaru* and *Sugiura* [18]

$$\tau = l^2/\pi^2 D. \quad (5)$$

The relaxation times corresponding to diffusion coefficients D (Figs. 12 and 13) are shown in Table 1.

The overall process of sorption of organic solvents into solid polymers in glassy state consists of a series of both successive and simultaneous processes:

1. transport of solvent molecules toward polymer surface has to be considered particularly in the sorption from gaseous into solid phase,
2. adsorption with successive,
3. entering of the penetrant between polymer chains,
4. change of macromolecules conformation,
5. proper diffusion of solvent molecules into the entire sample volume.

The rate of the first two processes is usually so high that it enables them to be considered as equilibrium processes; there is no concentration gradient in liquid phase, the concentration of the molecules adsorbed in polymer surface having an equilibrium value from the very beginning. Thus, the sorption rate is determined either by that of the

Table 1

Kinetic parameters of the diffusion process of PVC swelling in cyclohexanone

Sample	Temperature [°C]	Mean value of D [cm ² /s]	Mean value of τ [s]*	$D^0 \times 10^2$ [cm ² /s]**	E_{eff} [kcal mole ⁻¹]**	A^{***}	φ [kcal mole ⁻¹]**
Lonza G	20.0	4.5×10^{-7}	285	10	7 ± 1	1.9 ± 0.5	3.0 ± 0.5
	30.0	7.5×10^{-7}	175				
	40.0	1.0×10^{-6}	105				
	50.0	1.5×10^{-6}	60				
	60.0	1.6×10^{-6}	50				
Geon 121	20.0	4.9×10^{-6}	670	5	5.5 ± 1	11 \pm 1	3.3 ± 0.5
	25.0	5.0×10^{-6}	580				
	30.0	6.6×10^{-6}	570				
	35.0	7.8×10^{-6}	500				
	40.0	8.4×10^{-6}	364				
	45.0	9.2×10^{-6}	310				

* Calculated from equation (5).

** Calculated on the basis of the equation $D = D^0 \exp(-E_{\text{eff}}/RT)$.

*** Calculated from equation (6).

change of macromolecules conformation or by pure diffusivity. The results of our measurements show that in initial phases the kinetic swelling process is controlled by the rate of penetration into the surface polymer film determined by the rate of the change of PVC macrochains conformation.

The dependence of $Q_{\infty,1}$ on the temperature (Fig. 14) is quite a remarkable one. According to Hildebrand's solubility theory [19] the value Q_{∞} proves to be the function of solubility parameter δ defined as the square root of the density of cohesion energy according to the relation

$$Q_{\infty} = A \exp\{-KV_1(\delta_1 - \delta_2)^2/RT\} = A \exp(-\varphi/RT), \quad (6)$$

where V_1 is the molar volume of the penetrant, δ_1 and δ_2 are solubility parameters of both the solvent and the polymer, A and K are the constants dependent on the polarity of both components. The values φ and A (Table 1) found experimentally confirm the vigorous interaction between PVC and cyclohexanone.

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