

Solution properties of poly(vinyl chloride) in tetrahydropyran

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Received 30 July 1976

Accepted for publication 7 October 1976

Dedicated to Professor A. Blažej, DrSc, on his 50th birthday

The solution properties of the system poly(vinyl chloride)—tetrahydropyran were quantitatively characterized by the methods of viscometry and sedimentation velocity. The Mark—Houwink relationship was determined as a function of temperature in the region of 20—50°C. Moreover, the unperturbed dimensions ($K_0 = 14.0 \times 10^{-4}$) and their temperature coefficient ($d \ln \bar{r}_0^2/dT = -1.5 \times 10^{-3} \text{ K}^{-1}$) were ascertained. From the thermodynamic point of view tetrahydropyran is a poorer solvent for poly(vinyl chloride) than cyclohexanone and tetrahydrofuran.

Методами вискозиметрии и скорости седиментации были количественно характеризованы свойства растворов системы поливинилхлорид—тетрагидропиран. Была определена Маркова—Гоувинкова формула как функция температуры в области от 20 до 50°C. Дальше определились невозмущенные размеры ($K_0 = 14,0 \times 10^{-4}$) и их температурный коэффициент ($d \ln \bar{r}_0^2/dT = -1,5 \times 10^{-3} \text{ K}^{-1}$). С точки зрения термодинамики является тетрагидропиран более плохим растворителем для поливинилхлорида чем циклогексанон и тетрагидрофуран.

The study of the solution properties of polymer substances gives a lot of information about the size, shape, and structure of the macromolecules in solution as well as the interactions occurring in a system. Though poly(vinyl chloride) belongs among important industrial polymers, its solution properties have not been

investigated extensively. It seems that its structural peculiarities (presence of associates and microgels) represent the limiting factor in this sense. In most studies hitherto published [1—7] cyclohexanone and tetrahydrofuran were used as solvents, whereas the behaviour of poly(vinyl chloride) in other solvents was described only qualitatively.

Therefore our investigations were concerned with a quantitative description of the behaviour of different fractions of poly(vinyl chloride) in tetrahydropyran. For this purpose, the methods of sedimentation velocity and viscometry were used.

Experimental

Materials

A linear poly(vinyl chloride) of the emulsion type of Czechoslovak production (CHZWP, Nováky) was used for the investigations. Particular fractions were prepared by fractional precipitation of a 1% solution in tetrahydrofuran which was carefully deprived of peroxides by refluxing over solid KOH. Distilled water was used as a precipitating agent. The fractions obtained were twice precipitated and dried to constant weight *in vacuo*. The solvent used, *i.e.* tetrahydropyran was distilled immediately before measurement. The fraction with b.p. 88°C, refractive index $n_D^{20} = 1.4190$, and density $\rho_{20} = 0.88612 \pm 0.0005 \text{ g cm}^{-3}$ was employed. Considerable attention was paid to the preparation of solutions. Before use the solution was heated at 50°C for 1 h and afterwards it was rapidly cooled to the temperature of measurement.

Sedimentation measurements

For the determination of sedimentation coefficients the method of sedimentation velocity in an ultracentrifuge Spinco E (Beckman) was used. A rotor of the type A4-D with a 12 mm cell was applied. In all measurements the schlieren peak was taken from a distance shorter than 3 mm from meniscus so that the correction for pressure and radial dilution was as small as possible. The temperature of rotor was held at the constant value of 20°C accurate to $\pm 0.2^\circ\text{C}$. For the calculation of molecular weight the modified Flory—Mandelkern equation was used [8] (as tetrahydropyran is a good solvent, we assumed that the relation $k_s = 1.66 [\eta]$ was fulfilled)

$$M = 9.2 \times 10^{24} \eta_0^{\frac{3}{2}} \bar{v}_2^{\frac{3}{2}} \frac{s_0^{\frac{3}{2}} k_s^{\frac{1}{2}}}{(1 - \bar{v}_2 \rho_0)^{\frac{3}{2}}} \quad (1)$$

where η_0 , ρ_0 , s_0 , k_s , and \bar{v}_2 are viscosity of solvent, density of solvent, sedimentation coefficient at infinite dilution, coefficient of the concentration dependence of sedimentation coefficients, and partial specific volume of polymer, respectively. All quantities refer to the temperature of measurements, *i.e.* 20°C.

Viscometry

For the measurement of viscosities an Ubbelohde dilution viscometer modified according to Berger and Deckert [9] was used. The minimum amount of solution necessary for measurement was 0.5 ml. With respect to the concentrations used, molecular weights of samples and capillary bore of viscometers all corrections (for kinetic energy, curvature of capillary, density of solutions, and velocity gradient) could be omitted.

The fundamental solution of each fraction was prepared in such concentration that the relative viscosity of the solutions prepared from it by diluting was in the range 1.1—1.7. The solutions prepared were filtered through a fritted glass G4 and the temperature of measurement was held constant accurate to $\pm 0.01^\circ\text{C}$. For the evaluation of the data obtained the Huggins relationship [10] was used

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad (2)$$

where η_{sp} , $[\eta]$, c , and k_H stand for specific viscosity, limiting viscosity number, concentration, and the Huggins constant, respectively.

Results and discussion

The measured values of limiting viscosity numbers of the fractions of poly(vinyl chloride) in tetrahydropyran and their molecular weights are summarized in Table 1. By the method of least squares the coefficients of the Mark—Houwink relationship were calculated for the system poly(vinyl chloride)—tetrahydropyran as a function of temperature (Table 2).

On the basis of the Mark—Houwink exponent a it may be stated that tetrahydropyran is a little poorer solvent for poly(vinyl chloride) than cyclohexanone and tetrahydrofuran ($a = 0.77$ — 0.78 [3]).

Table 1

Solution characteristics of the fractions of poly(vinyl chloride) in tetrahydropyran as a function of temperature

Fraction	$M \cdot 10^{-4}$	20°C		30°C		40°C		50°C		$d \ln [\eta]/dT \cdot 10^3$
		$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	
1	4.70	0.64	0.28	0.63	0.29	0.62	0.28	0.605	0.30	-1.9 ₀
2	5.72	0.73	0.26	0.74	0.28	0.71	0.27	0.68	0.31	-2.1 ₈
3	8.85	1.07	0.27	1.05	0.26	1.02	0.29	1.00	0.30	-2.2 ₇
4	14.5	1.48	0.24	1.45	0.26	1.41	0.26	1.38	0.27	-2.0 ₃
5	29.1	2.43	0.23	2.40	0.24	2.37	0.26	2.31	0.25	-2.0 ₁
6	34.7	2.80	0.22	2.76	0.20	2.71	0.23	2.65	0.20	-1.9 ₂

Table 2

Coefficients of the Mark—Houwink relation for the system
poly(vinyl chloride)—tetrahydropyran

$T, ^\circ\text{C}$	$K \cdot 10^4$	a	χ
20	2.46 ₂	0.73 ₂	0.37 ₆
30	2.53 ₇	0.72 ₈	0.37 ₃
40	2.27 ₃	0.73 ₆	0.37 ₂
50	2.13 ₉	0.73 ₉	0.36 ₉

Unperturbed dimensions

The quality of the solvent used necessitates an application of the extrapolation methods to the determination of the unperturbed dimensions of poly(vinyl chloride) in tetrahydropyran. These methods are most frequently used for the determination of these dimensions for poly(vinyl chloride) because the only hitherto described one-component Θ solvent is benzyl alcohol at 155°C [11].

For the determination of the unperturbed dimensions we used the subsequent extrapolation procedures.

- 1. The procedure according to *Stockmayer, Fixman and Burchard* [12, 13]

$$\frac{[\eta]}{M^{\frac{1}{2}}} = K_{\theta} + C_1 M^{\frac{1}{2}} \quad (3)$$

where K_{θ} is the Mark—Houwink constant valid for Θ solvent (it is proportional to unperturbed dimensions or to the product $\Phi_0(\bar{r}_0^2/M)^{\frac{3}{2}}$ and C_1 is a constant dependent on the polymer—solvent system used. It has been pointed out [14, 15] that this simple relationship is valid only if the values applied fulfil the inequality $1 < [\eta]/K'_{\theta} M^{\frac{1}{2}} < 1.6$ where K'_{θ} is the section on the axis of ordinates. If this condition is not fulfilled, empirical corrections are needed. For $1 < [\eta]/K'_{\theta} M^{\frac{1}{2}} < 2.5$ it is $K'_{\theta}/K_{\theta} = 1.05$ and for $1.3 < [\eta]/K'_{\theta} M^{\frac{1}{2}} < 2.9$ the value $K'_{\theta}/K_{\theta} = 1.4$ has been recommended [14].

Our data fulfil the last mentioned inequality and the application of this method is presented in in Fig. 1. The value $K_{\theta} = 13.6 \times 10^{-4}$ has been obtained.

- 2. The procedure according to *Berry* [14]

$$\left(\frac{[\eta]}{M^{\frac{1}{2}}}\right)^{\frac{1}{2}} = K_{\theta}^{\frac{1}{2}} + C_2 \frac{M}{[\eta]} \quad (4)$$

where C_2 is a constant dependent on the polymer—solvent system. The application of this procedure is presented in Fig. 2 and $K_{\theta} = 14.1 \times 10^{-4}$.

- 3. The procedure according to *Bohdanecký* [16]

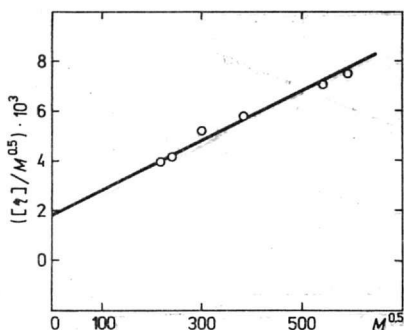


Fig. 1. Values of K_θ according to the Stockmayer—Fixman—Burchard relation at 20°C.

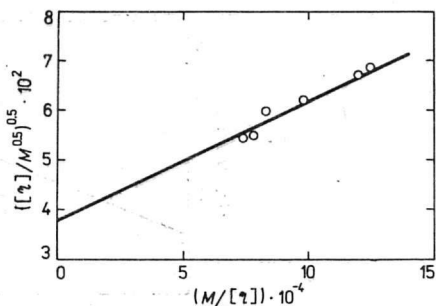


Fig. 2. Values of K_θ according to the Berry relation at 20°C.

$$\frac{[\eta]}{M^{\frac{1}{2}}} = 0.80 K_\theta + C_3 M^{0.35} \quad (5)$$

This procedure which is presented in Fig. 3 gives the value $K_\theta = 14.4 \times 10^{-4}$.

The mean value $K_\theta = 14 \times 10^{-4}$ is somewhat higher than the values hitherto published $(10-13) \times 10^{-4}$ [4, 6] but because of the limitation of graphical procedures it may be assumed that the agreement is satisfactory.

The temperature coefficient of unperturbed dimensions $d \ln \bar{r}_0^2 / dT$ where $(\bar{r}_0^2)^{\frac{1}{2}}$ is the end-to-end distance of chain in unperturbed state, is an important quantity for the characterization of the Θ state. This quantity has been estimated from the temperature coefficients of $[\eta]$ (Table 1) by using the proposition of Bohdanecký [17] which is a modification of the method described by Flory *et al.* [18]. It is based on the following relation

$$\left(\frac{P}{Q}\right) \frac{d \ln [\eta]}{dT} = Q^{-1} \frac{d \ln \bar{r}_0^2}{dT} + \frac{d \ln (\bar{v}_2^2 / V_1)}{dT} + \frac{d \ln \left(\frac{1}{2} - \chi\right)}{dT} \quad (6)$$

where

$$P = \left(\frac{1}{\alpha_n^2}\right) \left(\frac{5}{3} \alpha_n^2 - 1\right) \quad (6a)$$

$$Q = \left(\frac{1}{\alpha_n^2}\right) (\alpha_n^2 - 1) \quad (6b)$$

$$\alpha_n^3 = \frac{[\eta]}{K_\theta M^{\frac{1}{2}}} \quad (6c)$$

The symbols V_1 , χ , and α_n denote molar volume of solvent, interaction parameter polymer—solvent, and viscometric expansion coefficient, respectively.

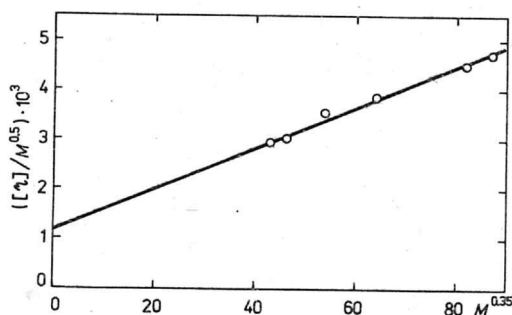


Fig. 3. Value of K_θ according to the Bohdanecký relation at 20°C.

The application of this method to the system poly(vinyl chloride)—tetrahydropyran is presented in Fig. 4. The value obtained ($-1.5 \times 10^{-3} \text{ K}^{-1}$) is equal to the value obtained with the solutions in cyclohexanone and nitrobenzene [19], which evidences a similarity of these solvents as regards the temperature dependence of unperturbed dimensions.

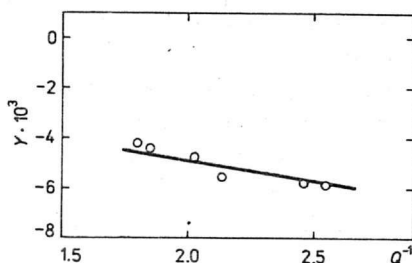


Fig. 4. Coefficient $d \ln \bar{r}_0^2/dT$ according to eqn (6), $Y = P/Q d \ln [\eta]/dT$.

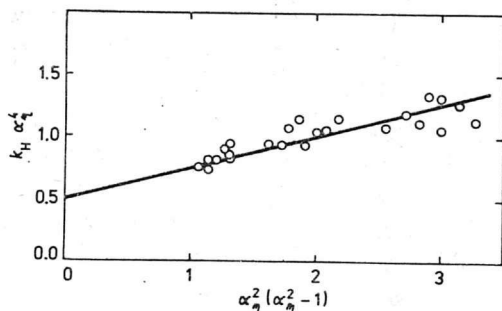


Fig. 5. Determination of the parameters of eqn (8).

Interaction polymer—solvent

For the determination of the interaction parameters of the system studied the Flory—Fox relation [20] modified by Stockmayer [21] has been used. Since the quantities \bar{v}_2 , V_1 , and K_θ are a temperature function, it holds

$$\frac{1}{2} - \chi = 2.49 \times 10^2 \frac{V_1}{\bar{v}_2^2} K_\theta (\alpha_n^5 - \alpha_n^3) M^{-\frac{1}{2}} \quad (7)$$

The values obtained are listed in Table 2 and do not contradict the statement that tetrahydropyran is a good solvent for poly(vinyl chloride) from the thermodynamic

point of view. As obvious from Table 2, the parameter χ decreases slowly with increasing temperature, which indicates a slightly endothermic character of the system studied.

Huggins constant

The constant k_H in the Huggins equation which correlates the specific viscosity of solution with its concentration is a function of the expansion coefficient α_η [22, 23]

$$k_H \alpha_\eta^4 = k_H^0 + C_0(\alpha_\eta^4 - \alpha_\eta^2) \quad (8)$$

The application of the values measured in the temperature interval 20—50°C is presented in Fig. 5. The values of the parameters k_H^0 and C_0 obtained (0.50 and 0.26) are in good agreement with the values hitherto published (0.50 and 0.28—0.30) [23] for different polymer—solvent systems.

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Translated by R. Domanský