

## Solvent Power of Solvents for Poly(vinyl Chloride)

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### Synopsis

Osmotic, viscometric, and initial phase separation studies of dilute solutions of poly(vinyl chloride) in cyclohexanone, cyclopentanone, tetrahydrofuran, morpholine, nitrobenzene, and tetrahydropyran are reported together with some swelling measurements involving these solvents and dioxane, acetone, and methanol. Values of the polymer-solvent interaction parameter  $\chi_1$  obtained from osmotic and swelling measurements suggest the order of solvent power for poly(vinyl chloride) to be cyclohexanone > cyclopentanone > tetrahydrofuran > morpholine > nitrobenzene > tetrahydropyran. A similar order is suggested by the volumes of hexane required to cause initial phase separation. Values of intrinsic viscosity and of the viscosity slope constant  $k'$  give somewhat different orders of solvent power. Reasons for differences in order are considered. The correlation of the volume of hexane required to cause initial phase separation with  $\chi_1$  is discussed and it is suggested that the polymer is solvated in solution. Other factors affecting the solvent power of solvents for poly(vinyl chloride) would appear to include the bulk and the solubility parameter of the solvent.

### Introduction

Although there have been a number of studies of the interaction of poly(vinyl chloride) with solvents and swelling agents,<sup>1-5</sup> there seem to have been few systematic studies of the variations of such dilute solution properties as osmotic pressure, viscosity, and initial phase separation with solvents. Such studies would be of value in the assessment of the solvent power of solvents for poly(vinyl chloride). There seems to be some evidence that the order of solvent power of such solvents may vary with the method used to assess it. This paper reports results of osmotic, viscometric, and initial phase separation studies on dilute solutions of poly(vinyl chloride) in six solvents. Some swelling measurements involving these solvents and some additional liquids are also reported. Estimates of solvent power are obtained, orders of solvent power obtained by use of different criteria are compared, and reasons for variations in order are discussed. Some factors affecting the solvent power of solvents for poly(vinyl chloride) are considered.

### Experimental

The poly(vinyl chloride), Breon 121, was an unfractionated sample prepared by emulsion polymerization. Before use it was extracted with ethanol at 78°C. to remove emulsifying agent and heated under vacuum at 45°C. for 24 hr. The solvents used were cyclohexanone, cyclopentanone, tetrahydrofuran, tetrahydropyran, nitrobenzene, and morpholine. Other liquids used in swelling studies were dioxane, acetone, and methanol. The best available grades were purified, dried, and fractionally distilled before use. Tetrahydrofuran was stabilized, after distillation, by addition of 0.1% 2,4-dimethyl-6-*tert*-butylphenol. *n*-Hexane, boiling range 67–69°C., was used as precipitant in initial phase separation studies. All solutions were prepared at 20°C. and, with the exception of those involving the low boiling tetrahydrofuran and tetrahydropyran, heated for 1 hr. at 80°C. and then cooled to 20°C. before use. This preliminary heating was found to be necessary to obtain a molecular dispersion of polymer.<sup>6</sup> Osmotic pressures of unheated solutions slowly increased, and viscosities decreased over relatively long periods at 25°C., indicating slow breakdown of aggregates. Osmotic pressures and viscosities of the heated solutions showed no significant change under the same conditions. Solutions involving tetrahydrofuran and tetrahydropyran were allowed to stand before use for longer periods than the solutions which had been previously heated.

Osmotic pressures of solutions in the concentration range 0.2–1.0 g./dl. were measured statically at  $25 \pm 0.01$ °C. with Pinner-Stabin<sup>7</sup> osmometers. Diffusion of polymer occurred with regenerated cellulose membranes of different types. This was prevented by the use of Pecel 600 cellulose membranes which had been treated with 5% aqueous caustic soda for 15 min. before washing well with water and conditioning to solvent. It was not possible to measure the osmotic pressures of solutions in morpholine as this solvent swelled and gelatinized the membranes. Sufficient tetrahydropyran was not available for osmotic pressure measurements. In all other cases at least two, and usually more, determinations were made with each solvent and concentration. These did not differ by more than 5%.

Viscosities of the solvents and of solutions in the concentration range 0.2–1.0 g./dl. were measured at  $25 \pm 0.01$ °C. in suspended-level capillary viscometers. Shear effects were negligible, and duplicate measurements, for a given concentration and solvent, did not differ by more than 2%.

Hexane was used as the precipitant in initial phase separation because its nonpolar nature makes any specific interaction with the polymer improbable. For comparison between different solvents of the volumes of hexane required to just cause initial phase separation it is desirable that the concentration of polymer at this point be the same for each solvent-hexane mixture. Solutions containing 0.25, 0.5, and 1.0 g. polymer in 100 ml. solution were prepared with each solvent. Hexane, from a microburet, was added to 10 ml. of each solution at  $25 \pm 0.01$ °C. until incipient turbidity, detected by a photoelectric absorptiometer, persisted on shaking.

The percentage volume of hexane in the mixture at this point was plotted against the logarithm of the corresponding polymer concentration and the percentage volume of hexane for a polymer concentration of 0.25 g./dl. at the point of initial phase separation, denoted by  $V_n$ , obtained by interpolation. Some difficulty was experienced with morpholine as solvent. Addition of hexane caused local separation of polymer which was dispersed and redissolved with difficulty. In all other cases endpoints were quite sharp and reproducible.

Swelling measurements were made on both crosslinked and uncrosslinked films of polymer. Crosslinked films were obtained by the method of Doty and Zable.<sup>4</sup> After removal of low molecular weight material by extraction with an azeotropic mixture of acetone and methanol at its boiling point, films were prepared by casting from a solution in tetrahydrofuran and evaporation of solvent in air. The last traces of solvent were removed by heating *in vacuo* at 45°C. for 24 hr. Part of the film was crosslinked by heating for 116 hr. at 140°C., these conditions giving a degree of crosslinking such that the film imbibed about 10 times its weight of cyclohexanone at 25°C. The film darkened appreciably when heated at 140°C. The crosslinked film was extracted with tetrahydrofuran to remove any crosslinked polymer and then dried *in vacuo* at 45°C. Weighed strips of film were immersed in excess liquid at  $25 \pm 0.01^\circ\text{C}$ . and reweighed periodically until attainment of constant weight showed that equilibrium had been reached. Crosslinked films were swollen in the solvents and uncrosslinked films in the other liquids given above. Duplicate measurements did not differ by more than 5%.

## Results

Figure 1 shows plots of  $\pi/c$  against  $c$ , where  $\pi$  is the osmotic pressure and  $c$  the concentration. Values of  $\bar{M}_n$ , the number-average molecular weight, obtained by extrapolation of the linear plots to zero  $c$  are given in Table I which also includes values of the polymer-solvent interaction parameter  $\chi_1$  obtained from slopes of the plots.

TABLE I  
Osmotic Values of  $\bar{M}_n$  and  $\chi_1$

Solvent	$\bar{M}_n$	$\chi_1$
Cyclohexanone	74,000	0.18
Cyclopentanone	72,000	0.25
Tetrahydrofuran	67,000	0.26
Nitrobenzene	78,000	0.31

The values of  $\bar{M}_n$  for cyclohexanone and cyclopentanone are not significantly different, but those for nitrobenzene and tetrahydrofuran are somewhat higher and lower, respectively. Such variations may be due to some degradation of polymer which will presumably vary with the solvent. The

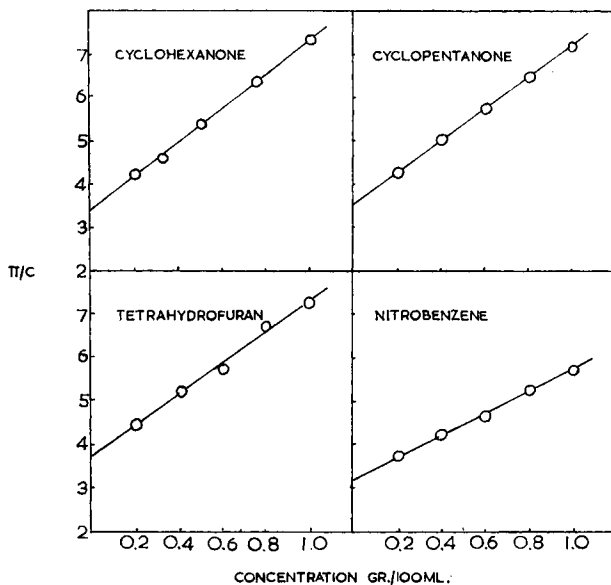


Fig. 1. Plots of  $\pi/c$  against  $c$  for dilute solutions of poly(vinyl chloride).

$\chi_1$  values for cyclohexanone, cyclopentanone, and tetrahydrofuran may be compared with Mencik's values<sup>8</sup> of 0.176, 0.253, and 0.291 respectively.

Figure 2 shows plots of viscosity number,  $\eta_{sp}/c$ , against  $c$ . Those for cyclohexanone, cyclopentanone, and tetrahydrofuran are linear, but those for tetrahydropyran, morpholine, and nitrobenzene show slight upward curvature. In these latter cases values of the intrinsic viscosity  $[\eta]$  were obtained by extrapolation of linear plots of  $\ln \eta_r/c$  against  $c$ , where  $\eta_r$  is the relative viscosity. Table II gives values of  $[\eta]$  and of the slope constant  $k'$  in the equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (1)$$

Values of  $k'$  ranging from 0.20 to 0.42 have been reported for poly(vinyl chloride)-cyclohexanone systems.<sup>9-12</sup> Most of these lie between 0.3 and 0.4. Values of 0.36 and 0.39 for poly(vinyl chloride)-tetrahydrofuran,<sup>12,13</sup>

TABLE II  
Viscosity Data

Solvent	$[\eta]$	$k'$
Cyclohexanone	1.33	0.36
Tetrahydrofuran	1.28	0.37
Cyclopentanone	1.20	0.31
Morpholine	1.17	0.41
Nitrobenzene	1.03	0.44
Tetrahydropyran	1.00	0.44

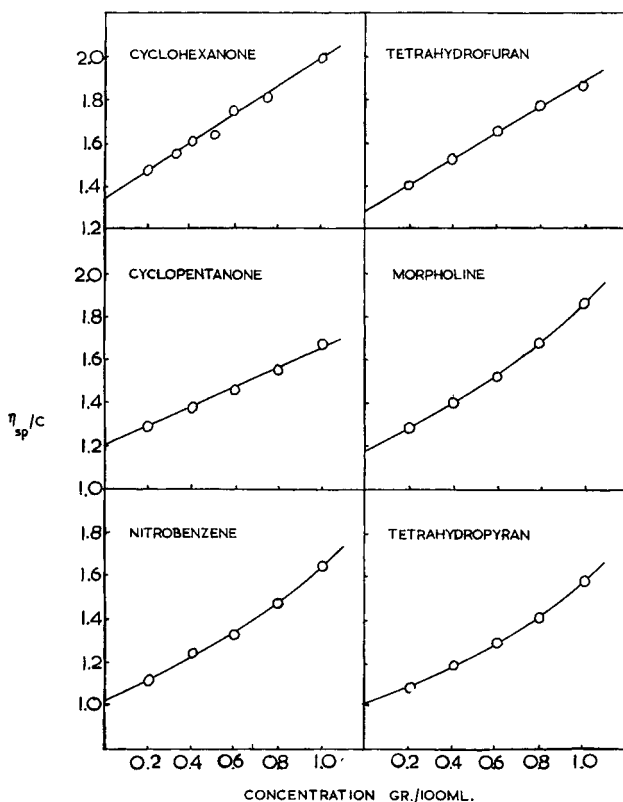


Fig. 2.  $\eta_{sp}/c$  as a function of  $c$  for dilute solutions of poly(vinyl chloride).

of 0.42 for poly(vinyl chloride)–nitrobenzene,<sup>11</sup> and 0.45–0.47 for poly(vinyl chloride)–morpholine<sup>14</sup> have also been given.

Figure 3 shows plots of the percentage of hexane in the solvent–hexane mixtures at the point of initial phase separation against the logarithm of the corresponding polymer concentration. Values of  $V_h$ , the percentage corresponding to a polymer concentration of 0.25%, are given in Table III.

Table IV gives the results of the swelling measurements in terms of  $Q_m$ , the maximum volume of liquid imbibed by unit volume of polymer at 25°C.

TABLE III  
Values of  $V_h$

Solvent	$V_h$
Cyclohexanone	53
Cyclopentanone	49
Tetrahydrofuran	44
Nitrobenzene	38
Tetrahydropyran	32
Morpholine	22.5

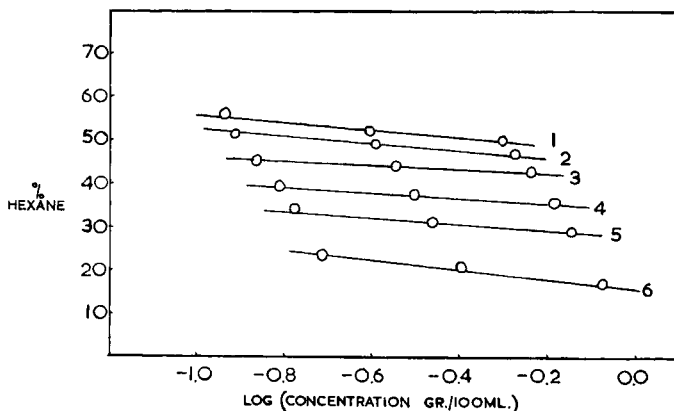


Fig. 3. Percentage of hexane in solvent-hexane mixtures as a function of polymer concentration at the point of initial phase separation: (1) cyclohexanone; (2) cyclopentanone; (3) tetrahydrofuran; (4) nitrobenzene; (5) tetrahydropyran; (6) morpholine.

TABLE IV  
Swelling Results

Film	Liquid	$Q_m$ cc. per cc. of polymer
Crosslinked	Cyclohexanone	9.02
	Cyclopentanone	8.94
	Tetrahydrofuran	8.72
	Morpholine	8.01
	Nitrobenzene	7.01
	Tetrahydropyran	6.15
Uncrosslinked	Dioxane	5.91
	Acetone	4.21
	Methanol	0.022

The value of  $Q_m$  for cyclohexanone and the value of  $\chi_1$  obtained osmotically with this solvent was used to calculate the value of  $Z$  in Mencik's equation.<sup>5</sup>

$$\chi_1 \phi_2^2 = -\ln(1 - \phi_2) - \phi_2(1 - 1/2Z) - \phi_2^{1/3}/Z \quad (2)$$

$Z$  is the average number of segments between crosslinks and  $\phi_2$  the volume fraction of polymer in the swollen film. The value of  $Z$  obtained (116.4) was then used to calculate values of  $\chi_1$  from those of  $Q_m$  for the other systems involving crosslinked film. The equation<sup>15</sup>

$$\chi_1 \phi_2^2 = -\ln(1 - \phi_2) - \phi_2 \quad (3)$$

was used to obtain  $\chi_1$  values for the systems in which uncrosslinked film was used. Table V gives values of  $\chi_1$  obtained in these ways.

TABLE V  
 Values of  $\chi_1$  from Swelling

Liquid	$\chi_1$
Cyclohexanone	0.18
Cyclopentanone	0.19
Tetrahydrofuran	0.21
Morpholine	0.24
Nitrobenzene	0.30
Tetrahydropyran	0.355
Dioxane	0.55
Acetone	0.57
Methanol	3.15

For a temperature of 53°C., Doty and Zable<sup>4</sup> give values of 0.14, 0.29, 0.48, and 0.63 for cyclohexanone, nitrobenzene, dioxane, and acetone, respectively.

### Discussion

Where comparison is possible, the values of  $\chi_1$ ,  $[\eta]$ , and  $k'$  are in reasonable agreement with those reported by other authors.  $\chi_1$  is a measure of thermodynamic solvent power; the smaller the value the greater the solvent power of the liquid concerned. Values of  $[\eta]$  and  $k'$  may also serve as measures of solvent power. The use of  $[\eta]$  in this way assumes that the better the solvent thermodynamically the more extended will be the chains so that the hydrodynamic volume and therefore  $[\eta]$  will increase with increasing solvent power.  $k'$  has been used as a measure of solvent power in the sense that the smaller its value the better the solvent.<sup>15</sup> Under certain conditions,<sup>17,18</sup> the volume of precipitant required to cause initial phase separation may also serve as a measure of thermodynamic solvent power.

The order of solvent power obtained by use of these different criteria shows some variation. Values of  $\chi_1$  obtained osmotically give cyclohexanone > cyclopentanone > tetrahydrofuran > nitrobenzene. The order from values of  $Q_m$  and the values of  $\chi_1$  derived from them: cyclohexanone > cyclopentanone > tetrahydrofuran > morpholine > nitrobenzene > tetrahydropyran, agrees with this as does that from values of  $V_h$  if the perhaps rather doubtful value for morpholine is excluded. Intrinsic viscosities and values of  $k'$  give orders which differ slightly from these and from each other. Intrinsic viscosities give cyclohexanone > tetrahydrofuran > cyclopentanone > morpholine > nitrobenzene > tetrahydropyran, while values of  $k'$  give cyclopentanone > cyclohexanone > tetrahydrofuran > morpholine > nitrobenzene = tetrahydropyran.

Osmotic values of  $\chi_1$  and those of  $[\eta]$  and  $k'$  all refer to dilute solutions and might be expected to give the same order. Although agreeing with osmotic values of  $\chi_1$  as far as cyclohexanone and nitrobenzene are concerned the values of  $[\eta]$  suggest that tetrahydrofuran is a better solvent than cyclo-

pentanone. Tetrahydrofuran solutions were not heated at 80°C. before use, and the presence of aggregates might lead to a higher intrinsic viscosity than would be obtained if the polymer was molecularly dispersed. Against this view is the fact that the molecular weight of the polymer is somewhat smaller in tetrahydrofuran than in the other solvents. Alternatively, solvation effects may lead to a larger value of  $[\eta]$ . Poly(vinyl chloride) is believed to be solvated in solution because of specific interaction between acidic hydrogen atoms of the polymer and basic solvent groups.<sup>1,2</sup> Because of steric effects, the unperturbed dimensions of solvated chains may be greater than those of unsolvated,<sup>19,20</sup> the solvated chains being more extended. This extension will vary with the solvent causing solvation and be supplementary to that resulting from interaction between solvated polymer and solvent. Combination of these two expansion effects may therefore lead to a different order of  $[\eta]$  than that expected from values of  $\chi_1$ .

Values of  $k'$  suggest that cyclopentanone is a better solvent than cyclohexanone and that nitrobenzene and tetrahydropyran are of equal solvent power. It is, however, doubtful whether  $k'$  can be regarded as a measure of solvent power, particularly where polar polymers are concerned. It depends on both polymer-solvent and polymer-polymer interaction,<sup>21</sup> and it has been suggested that it is influenced by electrical fields across the boundary between solvent and polymer<sup>22</sup> and that it is not a measure of solvent power in polar polymer-solvent systems.<sup>23</sup>

Values of  $\chi_1$  from swelling measurements give the same order of solvent power as osmotically determined values for the four common solvents, but those associated with cyclopentanone, tetrahydrofuran, and nitrobenzene are smaller. The systems concerned in swelling are more concentrated with respect to polymer than those used in osmotic measurements, and the differences might be due to variations of  $\chi_1$  with concentration for either or both the cyclohexanone and other systems. Differences in values of  $\chi_1$  might also be due to changes during crosslinking. The films were seen to darken appreciably, and some diene or fulvene structures may have been formed.<sup>24</sup> The interaction of such a modified polymer with liquids may differ somewhat from that of the uncrosslinked polymer. A value of 0.55 obtained with dioxane is consistent with the fact that dioxane is a borderline solvent in which association of polymer is known to occur.<sup>25</sup> The value of 0.57 for acetone agrees with the fact that acetone is a nonsolvent with perhaps some latent solvent power. A high value with methanol is to be expected since it may be used as a precipitant.

If the perhaps rather doubtful value for morpholine is excluded, values of  $V_h$  give the order of solvent power suggested by values of  $\chi_1$ . Tetrahydropyran appears to be the poorest solvent, and this is suggested by the other criteria of solvent power. The correlation of  $V_h$  with thermodynamic solvent power is perhaps surprising if it is considered in terms of solubility parameters. The volume of nonsolvent required to cause initial phase separation can only be a measure of thermodynamic solvent power if the



solubility parameters  $\delta$  of the solvents and of the nonsolvent all lie on the same side of that of the polymer.<sup>17,18</sup> Values of 9.7<sup>26</sup> and 9.9<sup>27</sup> have been given for the solubility parameter of poly(vinyl chloride) at 25°C. Values of  $\delta$  at 25°C. for the solvents and hexane, calculated in the absence of complete vapor pressure data by use of the Hildebrand Rule,<sup>28</sup> are given in Table VI.

TABLE VI  
Solubility Parameters

Liquid	$\delta_1$ , (cal./cc.) <sup>1/2</sup>
Nitrobenzene	11.0
Cyclopentanone	10.45
Morpholine	10.2
Cyclohexanone	9.7
Tetrahydrofuran	9.1
Tetrahydropyran	8.7
<i>n</i> -Hexane	7.4

Some of these values exceed 9.9, although  $V_h$  appears to follow the order of solvent power given by values of  $\chi_1$ . It has been pointed out that the polymer is likely to be solvated and solvated polymer may separate in initial phase separation. The solubility parameter of a solvated polymer will differ from that of the unsolvated and will also vary with the solvent solvating the polymer. In such a case it is difficult to predict the variation of  $V_h$  with solvent, and the apparent correlation of  $V_h$  and  $\chi_1$  may be fortuitous. The calculation of solubility parameters by use of the Hildebrand Rule may give values differing from those obtained from vapor pressures. The latter method is to be preferred if vapor pressures are known.<sup>28</sup> This, and the possibility of some desolvation on addition of hexane may further complicate interpretation. The thermodynamic solvent power of solvents for polar polymers which are solvated in solution seems unlikely to be simply related to their solubility parameters but the solubility parameter of the solvent must not be too different from that of the solvated polymer if solution is to occur.

The view that poly(vinyl chloride) is solvated in solution is supported by the relatively low values of  $\chi_1$  associated with the solvents. The largest value, 0.355 obtained with the poorest solvent tetrahydropyran, is well below the theoretical upper limit of approximately 0.5.  $\chi_1$  may be expressed in terms of heat and entropy contributions by:

$$\chi_1 = \chi_h + \chi_s \quad (4)$$

The entropy contribution  $\chi_s$  is theoretically equal to  $1/z$ , where  $z$  is the lattice coordination number, but experimental values for many polymer-solvent systems lie between 0.3 and 0.5. Low values of  $\chi_1$  may be the result of negative values of the heat contribution  $\chi_h$  arising from evolution of heat in solvation. Doty and Mischuck<sup>29</sup> obtained values of  $\chi_h$  and  $\chi_s$  from

the temperature dependence of osmotic values of  $\chi_1$  for poly(vinyl chloride) in cyclohexanone and dioxane. Mencik<sup>8</sup> obtained values with cyclopentanone in a similar way. The results of these authors, adjusted to 25°C., are given in Table VII.

TABLE VII  
Values of  $\chi_a$  and  $\chi_s$

Solvent	$\chi_a$	$\chi_s$
Cyclohexanone	-0.22	0.46
Cyclopentanone	-0.09	0.38
Dioxane	0.34	0.16

The low values of  $\chi_1$  associated with cyclohexanone and cyclopentanone are clearly a consequence of the negative values of  $\chi_b$ .

Solvation is therefore likely to be an important factor in the interaction of poly(vinyl chloride) and solvents. In the cases of cyclohexanone and cyclopentanone, solvation may involve specific interaction between acidic hydrogen atoms of the polymer adjacent to C-Cl groups and carbonyl oxygen atoms of the ketones. Similar interaction may involve the ether oxygen groups in dioxane which are capable of short range interaction with acidic hydrogen atoms but this might be weaker and it should be noted that the mixing of solvated polymer and solvent may be endothermal. With the ketones endothermal effects may be less, so that exothermal ones predominate. Association of polymer in dioxane<sup>25</sup> may also affect the value of  $\chi_1$ . With the other solvents, solvation may also involve specific interaction between hydrogen atoms of polymer and oxygen atoms of solvent. In the case of morpholine the nitrogen atom might alternatively be involved.

It may also be noted that the solvents used are cyclic or aromatic suggesting that bulk or steric effects may also influence solvent power.<sup>2</sup> The factors influencing the solvent power of liquid for poly(vinyl chloride) would thus seem to include the presence of groups in solvent molecules capable of specific interaction with groups of the polymer causing solvation, the solubility parameter of the solvent which should not be too different from that of the solvated polymer if solution is to occur, and solvent bulk of steric effects. Similar conclusions were reached by Adelman and Klein and by Anagnostopoulos et al.<sup>2</sup> The necessity for an appropriate combination of these and perhaps other factors may account for the rather limited range of solvents for poly(vinyl chloride).

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### Résumé

Des études osmotique, viscométrique et de séparation initiale de phase de solutions diluées de chlorure de polyvinyle dans la cyclohexanone, cyclopentanone, tétrahydrofuranne, morpholine, nitrobenzène et tétrahydrofuranne sont décrites ensemble avec plusieurs mesures de gonflement incluant ces solvants ainsi que le dioxanne, l'acétone et le méthanol. Les valeurs du paramètre  $\chi_1$  dû à l'interaction polymère-solvant et obtenu par des mesures osmotiques et par celles de gonflement, suggèrent l'ordre suivant: cyclohexanone > cyclopentanone > tétrahydrofuranne > morpholine > nitrobenzène > tétrahydrofuranne pour la force du solvant à l'égard du chlorure de polyvinyle. Un ordre similaire est suggéré pour les volumes d'hexane nécessaires à provoquer la séparation initiale de phase. Les valeurs de la viscosité intrinsèque et de la constante  $k'$  de la pente pour la viscosité donnent des ordres quelque peu différents pour la force du solvant. On a considéré les raisons pour ces différences dans l'ordre précité. Une comparaison du volume d'hexane exigé pour provoquer la séparation de la phase initiale avec  $\chi_1$  est discutée et il est suggéré que le polymère est solvaté en solution. D'autres facteurs affectant la puissance de dissolution des solvants pour le chlorure de polyvinyle englobent un paramètre de masse et de solubilité du solvant.

### Zusammenfassung

Über osmotische, viscosimetrische und Phasentrennungsuntersuchungen an verdünnten Lösungen von Polyvinylchlorid in Zyklohexanon, Zyklopentanon, Tetrahydrofuran, Morphinol, Nitrobenzol, und Tetrahydrofuran wird zusammen mit einigen Quellungsmessungen unter Verwendung dieser Lösungsmittel sowie Dioxan, Aceton, und Methanol berichtet. Die aus osmometrischen und Quellungsmessungen erhaltenen Werte des Polymer-Lösungsmittel-Wechselwirkungsparameters  $\chi_1$  deuten darauf hin, dass die Reihenfolge der Lösungsmittelwirksamkeit für Polyvinylchlorid Zyklohexanon

> Zyklopentanon > Tetrahydrofuran > Morpholin > Nitrobenzol > Tetrahydropyran ist. Eine ähnliche Reihenfolge wird durch die zur Phasentrennung nötigen Hexanvolumina nahegelegt. Werte der Viscositätszahlen und der Viscositätsneigungskonstanten  $k'$  geben eine etwas andere Reihenfolge der Lösungsmittelwirksamkeit. Gründe für den Unterschied werden diskutiert. Die Beziehung des zur Phasentrennung benötigten Hexanvolumens zu  $\chi_1$  wird diskutiert und es wird angenommen, dass das Polymere in Lösung solvatisiert wird. Andere Faktoren, die die Lösungsmittelwirksamkeit von Lösungsmitteln für Polyvinylchlorid beeinflussen, scheinen der Bulk- und Löslichkeitsparameter des Lösungsmittels zu sein.

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