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Studies of Poly-2-vinylpyridine. II. Solubilities in Various Solvents

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The viscosity and osmotic pressure of a fraction of poly-2-vinylpyridine have been measured in various solvents, and the parameters concerning the solubility of this polymer, that is, the osmotic second virial coefficient, A_2, the polymer-solvent interaction parameter, μ, and the solubility parameter, δ_2, have been obtained. From the values of these parameters, the following conclusions have been obtained: poly-2-vinylpyridine has a solubility parameter of ca. 10.4 (cal./cc.)$^{1/2}$ and acts as an electron donor. As a result of the specific interaction between a solvent and the pyridine nitrogen of this polymer, the solvent power is greater in an acidic solvent and smaller in a basic than would be expected from the solubility parameter alone. An especially strong interaction between poly-2-vinylpyridine and aliphatic alcohols, chloroform and nitroethane has been observed and its nature has been discussed.

The interaction between a polymer and a solvent is the very important factor which influences the behavior of the polymer in solution.[1,2] The nitrogen atom which is situated at the α-position of pyridine ring of poly-2-vinylpyridine has a lone

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[1] T. Alfrey, Jr., A. I. Goldberg and J. A. Price, *J. Colloid Sci.*, **5**, 251 (1950).

[2] H. Daoust and M. Rinfret, ibid., **7**, 11 (1952).

electron-pair and, consequently, shows a fairly strong basic character. The solubilities of this polymer in various solvents are much influenced by the basicity and the structural position of nitrogen. In the present study, the viscosity and osmotic pressure of a fraction of poly-2-vinylpyridine was measured in various solvents, and the nature of the polymer-solvent interaction will be discussed using the various solubility parameters obtained by these measurements.

Experimental

Polymer.—A fraction of poly-2-vinylpyridine, our sample number H-2, was used for this investigation. The procedure of the polymerization of this polymer has been described in Part I,[3] while that of the fractionation will be given in Part III.[4]

Solvents.—The solvents used were treated by the usual procedure and distilled before use.

The Viscosity and the Osmotic Pressure.—All parts of the apparatus and all procedures for the measurement of the viscosity and the osmotic pressure were the same as in Part I.[3] In order to measure the intrinsic viscosity of one fraction in various solvents, many viscometers with capillaries of different diameters were used; the correction of kinetic energy could be neglected. The osmotic pressure was measured by the static method with a gel cellophane membrane No. 300.

Results and Discussion

Huggins' Polymer-Solvent Interaction Parameter.—According to Huggins,[5] the partial molar free energy of dilution, ΔF_1, is given by the expression:

$$\Delta F_1 = \boldsymbol{R}T\{\ln(1-v_2) + (1-1/x)v^2 + \mu v_2{}^2\} \qquad (1)$$

where v_2 is the volume fraction of the polymer; x, the ratio of the molar volume of polymer to that of solvent, and μ, a polymer-solvent interaction parameter which is independent of the molecular weight and the concentration of the polymer. The μ value is related to the osmotic second virial coefficient, A_2, by the following equation[6]:

$$A_2 = \bar{v}_2{}^2/\boldsymbol{N}V_1'(1/2-\mu) \qquad (2)$$

where $\bar{v}_2$ is the specific volume of the polymer; $\boldsymbol{N}$, the Avogadro number, and V_1', the molecular volume of the solvent.

The results of osmotic pressure measurements of the H-2 fraction in ethanol, methanol, isopropanol, benzene and ethyl methyl ketone at 25±0.003°C are shown in Fig. 1. The relation between the π/c and c values in each solvent is shown by a linear line, from the slope of which the values of A_2 and μ were calculated by using Eq. 2. As for the value of $\bar{v}_2$, the observed value of 0.856 ml./g. was used. The value of π/c in a benzene solution is small over the whole range of concentration. From the observed value of the intrinsic viscosity in benzene, this abnormality of π/c is considered to be caused by the leak of solute molecules through the membrane, and not by such an abnormality of the molecular dispersion state as association[7] in solution. The leak of solute molecules, however, may not influence the value of A_2 very much.[8] The values of A_2 and μ are shown in columns 4 and 5 of Table I.

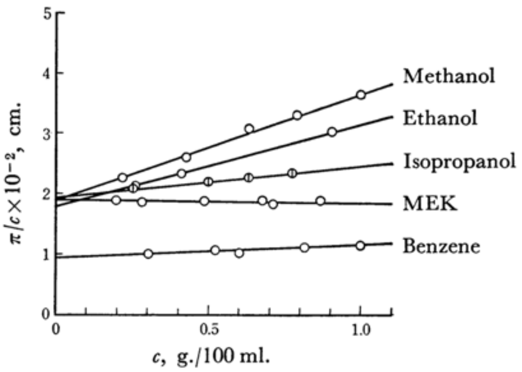

Fig. 1. Plots of reduced osmotic pressure vs. concentration of poly-2-vinylpyridine (fraction H-2) in various solvents at 25°C.

The value of μ can also be evaluated from the data of the intrinsic viscosity.[9] From the theory of Flory and Fox,[10,11] the relation between the intrinsic viscosity $[\eta]$ in a solvent and the $[\eta]_\theta$ value in a θ-solvent is expressed by Eq. 3 for a homogeneous fraction of the polymer:

$$[\eta] = [\eta]_\theta \alpha^3 \qquad (3)$$

where α is the viscosity expansion factor, which can be expressed by Eq. 4:

$$\alpha^5 - \alpha^3 = 2C_{\mathrm{m}}(1/2-\mu)M^{1/2} \qquad (4)$$

where C_{m} is a constant which depends on the specific volume of the polymer, $\bar{v}_2$, and on the molar volume of solvent, V_1; it can be expressed by: $C_{\mathrm{m}} = (27/2^{5/2}\pi^{3/2})(\bar{v}_2{}^2/\boldsymbol{N}V_1)(\langle L^2\rangle_0/M)^{-3/2}$, where $\langle L^2\rangle_0$ is the mean-square displacement length of the chain in a θ-solvent. By rearranging Eqs. 3 and 4, the following equation can be obtained:

$$(1/2-\mu) = (V_1/2C_{\mathrm{m}}'\Phi_0 M)([\eta]^{5/3}/[\eta]_\theta{}^{2/3}-[\eta]) \qquad (5)$$

where C_{m}' is a constant expressed by $(27/2^{5/2}\pi^{3/2})$ $(\bar{v}_2{}^2/\boldsymbol{N})$ and Φ_0, a universal constant.

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[3] S. Arichi, S. Mitsuta, N. Sakamoto and H. Murata, This Bulletin, **39**, 428 (1966).

[4] S. Arichi, ibid., **39**, 439 (1966).

[5] M. L. Huggins, *Ann. New York Acad.*, **43**, 9 (1942).

[6] P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

[7] P. Doty, H. Wagner and S. Singer, *J. Phys. & Colloid Chem.*, **51**, 32 (1947).

[8] H. Tompa, "Polymer Solutions," Butterworths Scientific Publications, London (1956).

[9] G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1742 (1958).

[10] P. J. Flory and T. G. Fox, Jr., *J. Am. Chem. Soc.*, **73**, 1904 (1951).

[11] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

TABLE I. SOLUBILITY DATA FOR POLY-2-VINYLPYRIDINE[a)]

No.	Name	$[\eta]$ dl./g.	A_2 cm.^{3} mol./g.^{2} $\times 10^4$	μ[b)]	μ[c)]	δ_1[d)] (cal./cc.)$^{1/2}$	k'	k_s
1	Nitroethane					11.1		
2	92.01 wt. % Ethanol	1.30					0.20	0.16
3	Chloroform	1.23			0.443	9.3	0.23	0.13
4	*n*-Heptanol	1.22			0.400	10.6	0.28	0.11
5	*i*-Butanol	1.17			0.441	9.8	0.23	0.09
6	*n*-Pentanol	1.16			0.402	10.9	0.27	0.11
7	Methanol	1.16	6.29	0.45	0.474	13.4	0.29	0.12
8	*n*-Butanol	1.15			0.445	10.1	0.37	0.14
9	*n*-Propanol	1.09			0.460	11.9	0.32	0.13
10	Ethanol	1.03	5.52	0.45	0.473	11.6	0.29	0.11
11	Pyridine	0.867			0.476	11.5	0.25	0.10
12	Nitrobenzene	0.853			0.471	10.0	0.36	0.14
13	Dimethylformamide	0.701			0.467	11.8	0.36	0.15
14	Tetramethyleneoxide	0.673			0.489	9.3	0.53	0.17
15	Isopropanol	0.670	2.18	0.47	0.490	10.2	0.33	0.13
16	Chlorobenzene	0.670			0.486	9.5	0.42	0.17
17	Benzene	0.530	0.96	0.49	0.495	9.2	0.31	0.13
18	Dioxane	0.470			0.498	10.0	0.60	0.19
19	Ethyl methyl ketone	0.385	−0.25	0.50	0.500	9.3	0.61	0.22

a) Our sample number, H-2.
b) The values from measurement of osmotic pressure, Eq. 2.
c) The values from measurement of viscosity, Eq. 5.
d) The values of δ_1 are taken from Hildebrand and Scott[14)] for most of the solvents and are calculated with the aid of Hildebrand's rule[14)] for the rest.

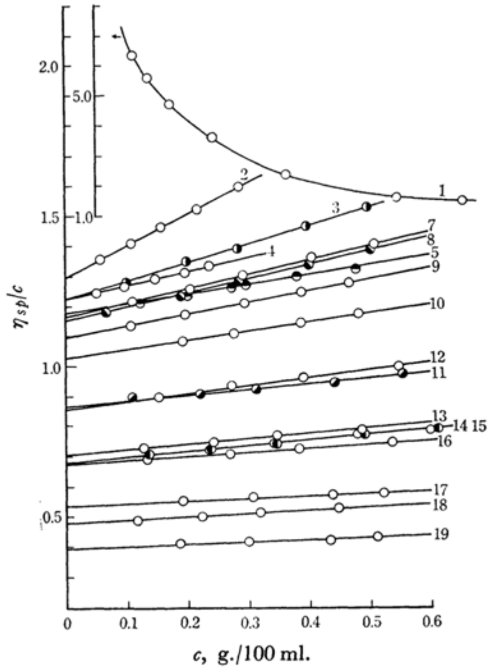

Fig. 2. Plots of reduced viscosity vs. concentration of poly-2-vinylpyridine (fraction H-2) in various solvents at 25°C. The number on each line corresponds to that of solvent cited in Table I.

The value of μ was evaluated by Eq. 5. The results of the viscosity measurements of the H-2 fraction in various solvents at 25±0.01°C are shown in Fig. 2 and are listed in Table I. The value of $[\eta]_\theta$ was evaluated by the following equation of Krigbaum[12)]:

$$[\eta] = [\eta]_\theta + 5.0\times 10^{-3} A_2 M \qquad (6)$$

The values of A_2 and $[\eta]$ are plotted in Fig. 3,

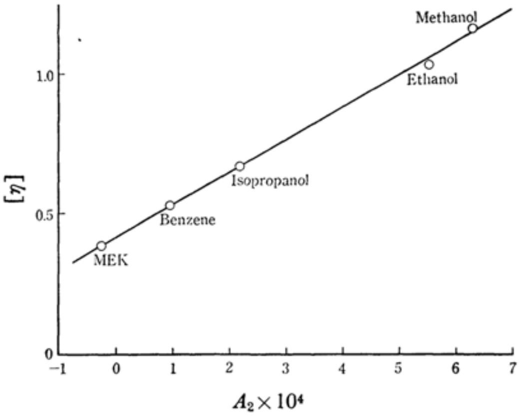

Fig. 3. Plots of intrinsic viscosity vs. osmotic second virial coefficient of poly-2-vinylpyridine (fraction H-2) in various solvents at 25°C.

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12) W. R. Krigbaum, *J. Polymer Sci.*, **28**, 213 (1958).

from which the value of $[\eta]_\theta$ can be found to be 0.415. The measurement of the molecular weight, $M_w(30.08\times 10^4)$, of this polymer will be described in Part III.[4] The values of μ in various solvents, which were calculated by inserting these data in Eq. 5, are shown in column 6 of Table I.

The values of the intrinsic viscosities, the osmotic second virial coefficients and the interaction parameters cited in Table I show that Lewis bases such as ethyl methyl ketone and dioxane and neutral solvents such as benzene are poor solvents, while Lewis acids such as nitroethane, chloroform and aliphatic alcohols are good solvents.

The Cohesive Energy Density of Poly-2-vinylpyridine.—According to the theory of Huggins,[13] μ can be divided into the term of entropy, μ_s, and that of the heat of mixing, μ_h:

$$\mu = \mu_s + \mu_h \tag{7}$$

When the contribution of μ_h is endothermic, it is related to the solubility parameters of the solvent, δ_1, and to that of the polymer, δ_2, as follows[14]:

$$\mu_h = V_1/\boldsymbol{R}T(\delta_1-\delta_2)^2 \tag{8}$$

where δ_1 and δ_2 are the square roots of the cohesive energy densities of the solvent and the polymer respectively. Equation 8 shows that the closer the value of δ_2 gets to δ_1, the stronger the solvent power becomes. Therefore, δ_2 is a useful key in selecting the solvent for the polymer.[15]

The method for evaluating the δ_2 value for the linear polymer has also been proposed by Bristow and Watson,[16] who obtained the following equation by combining Eqs. 7 and 8:

$$\begin{aligned}\delta_1{}^2/\boldsymbol{R}T &= \mu/V_1 \\ &= 2(\delta_2/\boldsymbol{R}T)\delta_1 - (\delta_2{}^2/\boldsymbol{R}T+\mu_s/V_1)\end{aligned} \tag{9}$$

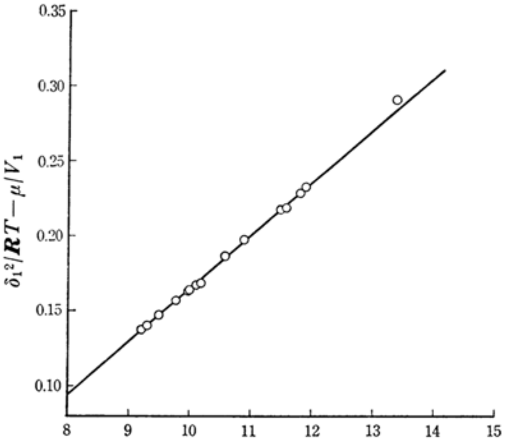

Fig. 4. Plots of $(\delta_1{}^2/\boldsymbol{R}T-\mu/V_1)$ vs. solubility paremeter of solvents for poly-2-vinylpyridine (fraction H-2).

$(\delta_1{}^2/\boldsymbol{R}T-\mu/V_1)$ was plotted against δ_1 in Fig. 4 using the values of μ and δ_1 cited in columns 6 and 7 of Table I. The value of δ_2 evaluated from the slope of the line and that evaluated from the intercept at the ordinate, neglecting the term of μ_s/V_1 are 10.4 and 10.5 (cal./cc.)$^{1/2}$ respectively.

In principle Eq. 8 should be applied to the system in which the heat of mixing, μ_h, is only endothermic. If this is the case for poly-2-vinylpyridine-solvents systems, the solvent which has a value of δ_1 closer to 10.4 (cal./cc.)$^{1/2}$ should have a stronger solvent power. Consequently, the intrinsic viscosities in such solvents must be large.

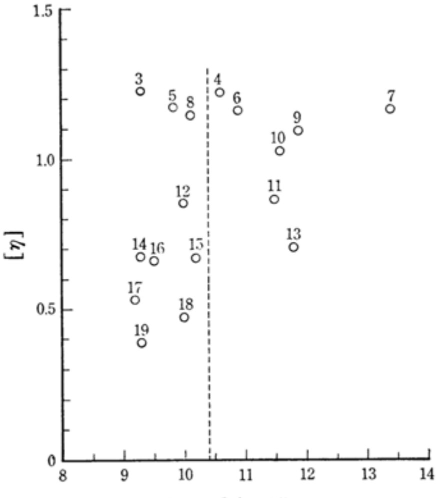

Fig. 5. Plots of intrinsic viscosity vs. solubility parameter of solvents for poly-2-vinylpyridine (fraction H-2). The number on each point corresponds to that of solvent cited in Table I.

In Fig. 5 the intrinsic viscosities in Table I are plotted against the δ_1 values of the corresponding solvents. From this figure no clear correlation can be seen between $[\eta]$ and δ_1. Thus, it may be considered that there exists some exothermic interaction between poly-2-vinylpyridine and some solvents.

Interaction between Poly-2-vinylpyridine and Solvents.—The nature of the specific interaction between poly-2-vinylpyridine and solvents described above was investigated from the viewpoint of Spurlin.[17] The nitrogen atom at the α-position of the pyridine ring has a lone electron-pair and acts as an electron donor, and so poly-2-vinylpyridine is quite a strong base. When a solvent is a Lewis acid or can act as an electron acceptor, its solvent power with regard to the

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[13] M. L. Huggins, ibid, **16**, 209 (1955).

[14] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold, New York (1950).

[15] R. Johannsen, *Deut. Farben-Z.*, **17**, 264 (1963).

[16] G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).

[17] H. M. Spurlin, *J. Polymer Sci.*, **3**, 714 (1948).

polymer may be increased because of solvation.

A typical example of such solvents is alcohols. As may be seen in Table I, it is remarkable that all the intrinsic viscosities of the polymer in various aliphatic alcohols are quite high except that in isopropanol. The intrinsic viscosities in methanol, ethanol and *n*-propanol are much higher than those which would be predicted on the basis of their solubility parameters alone. It is known that the lower aliphatic alcohol can act as a Lewis acid.[18,19] Alcohols, as a result, may be solvated to pyridine nitrogen, probably through the hydrogen bond.

The intrinsic viscosity of the H-2 fraction in chloroform, which has an acidic hydrogen atom, is also much higher than that which would be predicted on the basis of its solubility parameter alone. In contrast to this, carbon tetrachloride, which has no hydrogen atom, is nonsolvent of poly-2-vinylpyridine. These facts may be explained by the solvation of chloroform through hydrogen bonding to the polymer. A similar effect of solvated chloroform on the intrinsic viscosity was reported for polymethyl methacrylate.[20]

The existence of the hydrogen bond between the pyridine nitrogen in the polymer and alcohol or chloroform was supported by the following experiments. When the precipitant, *n*-hexane, was added to a poly-2-vinylpyridine solution in isopropanol or chloroform, and also when water was added to the solution in methanol, the lower the temperature, the larger the volume of the precipitant required for the first appearance of turbidity, as may be seen in Table II. Furthermore, the turbid solution thus produced became clear when it was cooled while this clear solution again became cloudy when heated. Obviously the temperature coefficient of the solubility of this polymer in these mixed solvents is negative; this may lead us to the conclusion that the polymer forms a hydrogen bond with the alcohol and chloroform.

TABLE II. PRECIPITATION MEASUREMENT OF POLY-2-VINYLPYRIDINE SOLUTION[a]

Solvent	Isopropanol		Methanol		Chloroform	
Precipitant	*n*-Hexane		Water		*n*-Hexane	
	Temp. °C	φ[b]	Temp. °C	φ[b]	Temp. °C	φ[b]
	20	40.26	10	53.98	10	55.75
	30	40.19	25	52.47	25	55.04
	40	39.02	40	51.10	35	54.02
	50	37.88			50	52.58

a) Our sample No. 5. Concentration was 1.0 g./100 ml.

b) Volume per cent of precipitant at the time of the first appearance of turbidity.

In the process of hydrogen bonding, it is probable that there is a steric hindrance for the orientation of solvent molecules. The fact that the H-2 fraction is practically insoluble in *t*-butanol is considered to be due to the steric hindrance. Such a steric hindrance may be small in the case of poly-4-vinylpyridine, in which the nitrogen atom is located at the γ-position of the pyridine ring. In fact, poly-4-vinylpyridine dissolves even *t*-butanol, and Strauss[21] has recognized the existence of hydrogen bonding in the poly-4-vinylpyridine-*t*-butanol system because of the negative temperature coefficient of the solubility of this polymer in a *t*-butanol - benzene mixture.

An extreme case of the specific interaction between poly-2-vinylpyridine and an acidic solvent is seen in the results of the viscosity measurement of the H-2 fraction in nitroethane. As may be seen in Fig. 2, the relation between the reduced viscosity and the concentration is similar to that of typical polyelectrolyte.[22] A similar result has been obtained by Cashin[23] in the case of poly-2-vinylpyridine in nitromethane. Nitroalkyl is tautomerized into nitro and acid forms, the latter of which behaves as an acid.[24] Nitroalkyl in the acid form may, therefore, quaternize the pyridine nitrogen. Thus, poly-2-vinylpyridine in nitroalkyl behaves as a polyelectrolyte.

The oxygen of the carbonyl group in ethyl methyl ketone has two lone electron-pairs, and so this solvent can act as a typical Lewis base.[18] Dioxane and nitrobenzene also act as bases to Lewis acid.[18] As may be seen in Fig. 5 the intrinsic viscosities in these solvents are lower than would be predicted on the basis of their solublity parameters alone. These results may also be explained as resulting from the interaction between pyridine

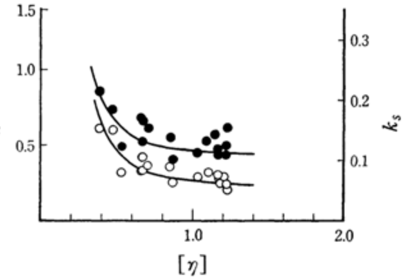

Fig. 6. Plots of Huggins' constant (○) and Spurlin's constant (●) vs. intrinsic viscosity of poly-2-vinylpyridine (fraction H-2) in various solvents.

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[18] S. G. Cohen, "Progress in Physical Organic Chemistry," Vol. 1, Interscience, New York-London (1964).

[19] R. P. Bell, "Acids and Bases," Methuen, London, John Wiley and Sons, New York (1952).

[20] W. R. Moore and R. J. Fort, *J. Polymer Sci.*, Part **A1**, 929 (1963).

[21] A. G. Boyes and U. P. Strauss, ibid., **22**, 463 (1956).

[22] R. M. Fuoss and U. P. Strauss, ibid., **3**, 246 (1948); R. M. Fuoss, ibid., **3**, 603 (1948).

[23] W. M. Cashin, *J. Colloid Sci.*, **6**, 271 (1951).

[24] D. Turnbull and S. H. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943).

nitrogen and solvents.

The intrinsic viscosity of the H-2 fraction in isopropanol is relatively low in spite of the value of δ_1 being closer to 10.4 (cal./cc.)$^{1/2}$ and in spite of its acidity. This is considered to be due to the steric hindrance to hydrogen-bond formation described previously.

Benzene is a typical neutral solvent, and the viscosity behavior of the polymer in this solvent coincides with that which is to be expected from its solubility parameter.

Huggins' Constant and Spurlin's Constant. —It has generally been recognized that Huggins' constant, k', defined by Eq. 1 in Part I3) and Spurlin's constant, k_s, the ratio of the slope in the plots of $\log(\eta_{sp}/c)$ against c to the intrinsic viscosity, decrease with solvent power.20,25) The values of k' and k_s obtained from the measurement of viscosity for the H-2 fraction in various solvents are cited in columns 8 and 9 of Table I and are plotted against the corresponding intrinsic viscosity in Fig. 6, which shows that the general rule described above is applicable to the present results.

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25) L. H. Cragg and R. J. Sones, *J. Polymer Sci.*, **9**, 585 (1952).