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Studies of Poly-2-vinylpyridine. V. Temperature Dependence of the Intrinsic Viscosity and Osmotic Pressure of an Ethanol Solution

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The viscosity of a series of 10 fractions of poly-2-vinylpyridine and the osmotic pressure of a fraction of the same polymer in ethanol were measured at several temperature. The temperature coefficients of the intrinsic viscosities of all the fractions measured were found to be completely negative. The Mark-Houwink equations for molecular-weight-homogeneous samples were obtained in ethanol at 10, 25, 40, and 65°C. The Flory constant, $K=[\eta]_\theta/M^{1/2}$, obtained by the method of Fixman was found to be 13.0×10^{-4} at 25°C; this value is considerably larger than those estimated from the intrinsic viscosity data of this polymer in non-acidic solvents. The K value lowered to an ordinary level when it contained 2.7 N of dry ammonia in ethanol at 25°C. The values of the thermodynamic interaction parameters for dilution, ψ_1 and θ, were obtained from the viscosity data; the former was negative, but nearly zero (-0.02), while the latter was unusually large (397°C). The excess molar entropy of dilution obtained from the measurements of the temperature dependence of the osmotic pressure was found to be negative, but almost zero, which was in accordance with the value of ψ_1 described above; the excess molar heat of dilution obtained in the same way was found to be completely negative. Thus, the exothermic interaction and negative excess entropy for dilution in this system were studied somewhat quantitatively.

In preceding papers[1-4] some results of the investigation of the solution properties of poly-2-vinylpyridine have been reported as a part of a series of studies of this polymer. Recently, several other papers concerning the solution properties of this polymer[5] and of a related polymer, poly-2-methyl-5-vinylpyridine[6,7] have also been reported. These papers have indicated that the Flory constants, $K=[\eta]_\theta/M^{1/2}$, of polyvinylpyridine homologues are exceptionally larger in alcohols or chloroform than those in the other solvents.[3,4,6,7] It has been also suggested that the thermodynamic interactions of polyvinylpyridine homologues with alcohols are peculiar; for example, in the cases of poly-4-vinylpyridine and poly-2-vinylpyridine, it has been suggested qualitatively that the contributions of enthalpy and entropy to the relative polymer-solvent interaction in alcohols are negative.[2,8]

The present investigation was intended to clarify more completely the solvent effects on the unperturbed dimension, and the thermodynamic interactions between poly-2-vinylpyridine and ethanol, by measuring the temperature dependence of the intrinsic viscosity of a series of fractions in ethanol, and also by measuring the temperature dependence of the osmotic pressure of a fraction in the same solvent.

Experimental

Materials. The poly-2-vinylpyridine fractions used in the viscosity and osmotic pressure measurements were all the same to those used in a previous study.[3] The ethanol was refluxed with freshly-burned calcium oxide and was then carefully distilled with the apparatus described in a previous paper.[1] Ethanol and methanol containing dry ammonia were prepared by introducing ammonia gas into these solvents. The ammonia gas was generated by slightly warming 32% ammonia water and was dried with soda lime, potassium hydroxide, and phosphorus pentoxide successively. The concentration of ammonia was determined by titration with hydrochloric acid.

Viscosity and Osmotic Pressure. The viscosity measurements were carried out with Ubbelohde-type capillary viscometers. The flowing volume was about 2 m*l*, and the flow time of ethanol for one of viscometers at 10, 25, 40, and 65°C were 187.5, 141.8, 109.5 and 74.3 sec, respectively. Nearly the same flow time was required for the other three viscometers. All the solutions were filtered through a glass filter immediately

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

[2] S. Arichi, H. Matsuura, Y. Tanimoto and H. Murata, *ibid.*, **39**, 439 (1966).

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

[4] S. Arichi, *J. Sci. Hiroshima Univ., Ser. A-II,* **29**, 97 (1965).

[5] A. J. Hyde and R. B. Taylor, *Polymer,* **4**, 1 (1963).

[6] G. B. Gechele and L. Crescentini, *J. Polymer Sci.*, **A-3**, 3599 (1965).

[7] C. Garbuglio, L. Crescentini, A. Mula and G. B. Gechele, *Makromol. Chem.*, **97**, 97 (1966).

[8] A. G. Boyes and U. P. Strauss, *J. Polymer Sci.*, **22**, 463 (1956).

before measurement. The initial concentrations of the solution ranged from 0.5 to 2.5 g/d*l* according to the molecular weight of the fractions measured; they were determined by the weight method at 25°C and were corrected for thermal expansion or contraction. The kinetic-energy correction was neglected.

The measurements of osmotic pressure were carried out with an apparatus of the type proposed by Sands and Johnson.⁹⁾ The detailed procedure and the complete construction of the equipment were described in their paper. Almost the same equipment was constructed; fifteen measurements could be carried out at the same time in the same water bath using a turntable. The membranes used were gel cellophane, ♯300, kindly supplied by the Tokyo Cellophane Co., Ltd. At least 10 hr were required to attain equilibrium, regardless of the concentration of the solution, at 15°C. The lowering of height difference, $h-h_0$, between the head in the measuring capillary, h, and that in the reference capillary, h_0, after the equilibrium had been attained were not observed during the 15 days the solution was kept at 15°C. With an increase in the temperature, the linear line in $h-h_0$ *versus* the time plots inclined slightly, but when measurements were continued for at least 10 days, a sufficiently accurate extraporation to zero time could be made.

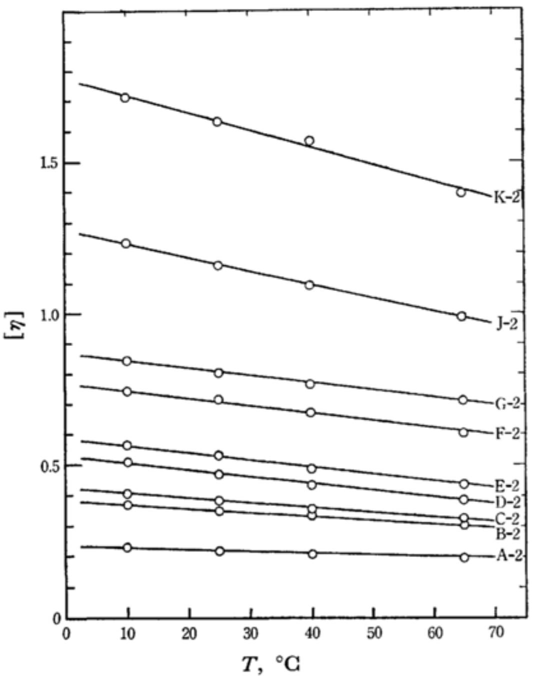

Fig. 1. Plots of intrinsic viscosity of poly-2-vinyl-pyridine fractions in ethanol *vs.* temperature.

Results and Discussion

The Mark-Houwink Equation. The results of viscosity measurements for a series of fractions at 10, 25, 40, and 65°C in absolute ethanol are summarized in Table 1, while plots of the intrinsic viscosity number, $[\eta]$, *versus* the temperature are shown in Fig. 1. The fraction numbers in Table 1 and Fig. 1 correspond to those described in a previous paper,³⁾ where the measurement of the weight-average and the number-average molecular weight, M_w and M_n, for each fraction are described. The slopes of the line in Fig. 1, namely, the temperature coefficients of the intrinsic viscosity, are all negative, in contrast to the case in ordinary polymer-solvent systems.

Figure 2 shows plots of $[\eta]$ at four temperatures against M_w in double logarithmic scales. The Mark-Houwink equation at each temperature was obtained by the method of least squares as follows:

$$[\eta] = 1.03\times 10^{-4}\, M_w^{0.74_6} \qquad \text{at } 10°\text{C}$$

$$[\eta] = 1.09\times 10^{-4}\, M_w^{0.72_9} \qquad \text{at } 25°\text{C}$$

$$[\eta] = 0.99\times 10^{-4}\, M_w^{0.73_3} \qquad \text{at } 40°\text{C}$$

$$[\eta] = 1.06\times 10^{-4}\, M_w^{0.71_8} \qquad \text{at } 65°\text{C}$$

TABLE 1. THE WEIGHT AVERAGE MOLECULAR WEIGHT AND THE INTRINSIC VISCOSITY NUMBER AT VARIOUS TEMPERATURE FOR A SERIES OF FRACTIONS OF POLY-2-VINYLPYRIDINE IN ABSOLUTE ETHANOL, AND IN ETHANOL CONTAINED 2.7 N DRY AMMONIA

Fraction No.	M_w $\times 10^{-4}$	$[\eta]$ in ethanol at				$[\eta]$ in ethanol contained 2.7 N NH_3 at 25°C
		10°C	25°C	40°C	65°C	
A-2	3.40	0.231	0.219	0.210	0.199	0.160
B-2	6.28	0.370	0.354	0.332	0.300	0.225
C-2	7.27	0.409	0.384	0.356	0.325	0.259
D-2	9.30	0.511	0.466	0.440	0.385	0.280
E-2	12.01	0.562	0.526	0.484	0.437	0.398
F-2	16.05	0.747	0.713	0.678	0.601	—
G-2	21.95	0.849	0.800	0.767	0.712	0.528
J-2	30.75	1.235	1.156	1.096	0.986	0.815
K-2	52.06	1.715	1.637	1.577	1.397	0.932
M-1	81.29	2.487	2.205	2.075	1.825	1.642
L-1	84.97	—	—	—	—	1.785

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9) G. D. Sands and B. L. Johnson, *Anal. Chem.*, **19**, 261 (1947).

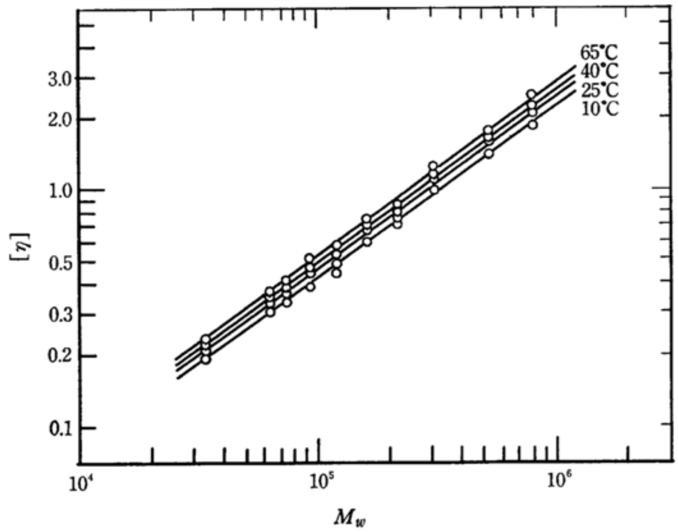

Fig. 2. Log-log plots of intrinsic viscosity of poly-2-vinylpyridine fractions in ethanol *vs.* weigt average molecular weight at 10, 25, 40 and 65°C.

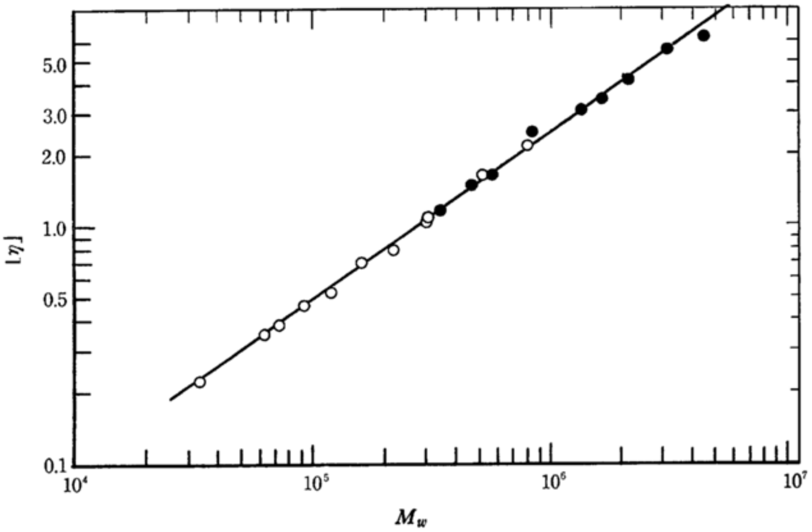

Fig. 3. Log-log plots of intrinsic viscosity of poly-2-vinylpyridine fractions in ethanol *vs.* weight average molecular weight at 25°C; (●): data obtained by Hyde and Taylor,[5] (○): data obtained in this study.

The Mark-Houwink equation for poly-2-vinylpyridine in absolute ethanol has already been reported by Hyde and Taylor[5] as follows:

$$[\eta] = 2.8\times 10^{-4}\, M_w^{0.66} \qquad \text{at } 25^\circ\text{C}$$

The values of the two constants in this equation seem to be considerably different from those in our equation at the same temperature described above. However, if all the data for $[\eta]$ and M_w obtained by Hyde and Tailor and those obtained in this study are plotted together, the relation between $\log [\eta]$ and $\log M_w$ are sufficiently represented by a linear line for a very wide range of molecular weight, as is shown in Fig. 3. The line is consistent with the following equation, obtained by the method of least squares:

$$[\eta] = 1.50\times 10^{-4}\, M_w^{0.70_3} \qquad \text{at } 25^\circ\text{C}$$

with the point of the lowest-molecular-weight sample, $M_w = 8.6\times 10^4$, in the data of Hyde and Taylor being excepted.

The Mark-Houwink equations for the molecular-weight-homogeneous samples were obtained in the

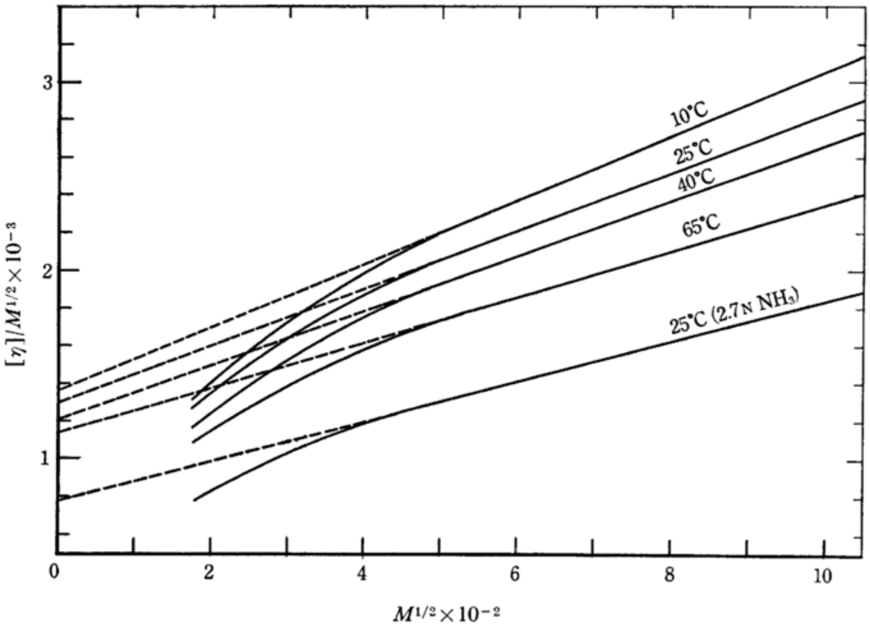

Fig. 4. Plots of $[\eta]/M^{1/2}$ *vs.* $M^{1/2}$ for poly-2-vinylpyridine in ethanol at 10, 25, 40 and 65°C and of those in ethanol contained ammonia (2.7 N) at 25°C.

same manner as before,[3] assuming that the molecular-weight distribution of each fraction is represented by the logarithmic normal-type molecular-weight-distribution function[10]:

$$w(M) = MA\exp\{-p^2(\ln M/M_0)^2\}$$

where the parameters are the same as in a previous paper.[3] The results are as follows:

$$[\eta] = 1.10\times10^{-4}\,M^{0.74_0} \quad \text{at } 10°\text{C}$$

$$[\eta] = 1.18\times10^{-4}\,M^{0.72_9} \quad \text{at } 25°\text{C}$$

$$[\eta] = 1.06\times10^{-4}\,M^{0.73_3} \quad \text{at } 40°\text{C}$$

$$[\eta] = 1.15\times10^{-4}\,M^{0.71_8} \quad \text{at } 65°\text{C}$$

These equations were used for the following evaluations of the Flory constants and of the thermodynamic interaction parameters.

The Flory Constant. The Flory constant, K, is defined by the following equations:

$$[\eta]_\theta = KM^{1/2} \tag{1}$$

$$K = \Phi_0(\langle L^2\rangle_0/M)^{3/2} \tag{2}$$

where $[\eta]_\theta$ and $\langle L^2\rangle_0$ are the intrinsic viscosity and the mean square of the end-to-end distance of a polymer molecule in the θ-solvent respectively; M, the molecular weight, and Φ_0, the universal constant (2.87×10^{21} for the molecular-weight-homogeneous polymer). The values of K were estimated according to the equation of Stockmayer and Fixman:[11]

$$[\eta]/M^{1/2} = K + 0.51\Phi_0 BM^{1/2} \tag{3}$$

where B is the long-range-interaction parameter. In spite of recent attempts to improve the graphical method for obtaining the unperturbed dimension, the Stockmayer and Fixman relation is still recommended as the most versatile form.[12]

Plots of the left-hand side of Eq. (3) against $M^{1/2}$ are drawn in Fig. 4. The calculations were carried out for a number of pairs of ideal values of M and $[\eta]$ obtained from the Mark-Houwink equation for molecular-weight-homogeneous poly-2-vinylpyridine in ethanol at each temperature described previously. The full lines show the range of molecular weight over which the original Mark-Houwink equations can be applied. Although the samples used in this study have quite a large inhomogeneity of molecular-weight distribution about their average values,[3] the corrected values of K may be obtained by the way of plotting shown in Fig. 4. A similar plotting method has been used by Gechel and others[7] in obtaining the value of K.

Because the lines in Fig. 4 show an appreciable downward curvature in the low-molecular-weight region, where, unfortunately, it is most important to extrapolate the lines to zero molecular weight, the values of K at each temperature were estimated by the extrapolation of the linear part of the lines in the relatively higher molecular-weight region.

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10) R. Koningsveld and C. A. F. Tuijinman, *J. Polymer Sci.*, **39**, 445 (1959).

11) W. H. Stockmayer and M. Fixman, *ibid.*, *C*-**1**, 137 (1963).

Recently, the deviation from linearity in the Fixman plots has been discussed by several authors.[12,13] Berry[14] has proposed a new approximate expression instead of Eq. (3). However, most of these discussions have been based on the data of considerably higher-molecular-weight samples in good solvents. In this study, the molecular weights of the samples are not so large (less than 10^6), and the expansion coefficients, α_η, were mostly less than 1.4. Consequently, no correction has been applied further.

The values of K estimated from Fig. 4 are shown in Table 2; they are extraordinary large when compared with those estimated from the data in non-alcoholic solvents.[4] Gechel and others[6,7] reported just the same situation as to the trend of downward curvature shown in Fig. 4, and as to the estimation of the large value of K from the intrinsic viscosity data of poly-2-methyl-5-vinylpyridine in methanol and chloroform. They attributed these results to the association of solution components due to the polarity of the solvents.

TABLE 2. THE FLORY CONSTANT, K, OBTAINED FROM Fig. 4 FOR POLY-2-VINYLPYRIDINE AT VARIOUS TEMPERATURE

Temp. (°C)	Solvent	$K\times10^4$
10	Ethanol	13.7
25	Ethanol	13.0
40	Ethanol	12.2
65	Ethanol	11.5
25	Ethanol - 2.7 N NH_3	7.9

Attempts were made to clarify the effect of the acidity of methanol and ethanol on the values of the intrinsic viscosity of poly-2-vinylpyridine fractions in these solvents. Figure 5 shows the plots of the intrinsic viscosity of poly-2-vinylpyridine fractions in methanol and ethanol containing varying amounts of ammonia *versus* the concentration of ammonia in these solvents.

The sensitive lowering of the intrinsic viscosity with the increase in the concentration of ammonia, namely, with the decrease in the acidity of the solvent, is shown in Fig. 5. The plots of the intrinsic viscosity of the fractions in ethanol contained 2.7 N of dry ammonia *versus* M_w at 25°C; for purposes of comparison, those in absolute ethanol at 25°C *versus* M_w are shown in Fig. 6. The Mark-Houwink equation for the fractions of molecular-weight-homogeneous poly-2-vinylpyridine in ethanol containing 2.7 N dry ammonia were obtained in the same way as before to be as follows:

$$[\eta]=0.64\times10^{-4}\,M^{0.74} \tag{4}$$

The lowest line in Fig. 4 resulted from the combination of Eq. (3) and Eq. (4); the value of K was estimated to be 7.9×10^{-4}, which is very close to the values obtained from the data of the intrinsic viscosity in non-acidic solvents.

The results obtained above are considered to be sufficient to show that the unperturbed dimension of poly-2-vinylpyridine in alcohols is influenced by the acidity of solvents.

Parameters for Thermodynamic Interaction. The thermodynamic interaction parameters for dilution, ψ_1 and θ, were obtained using

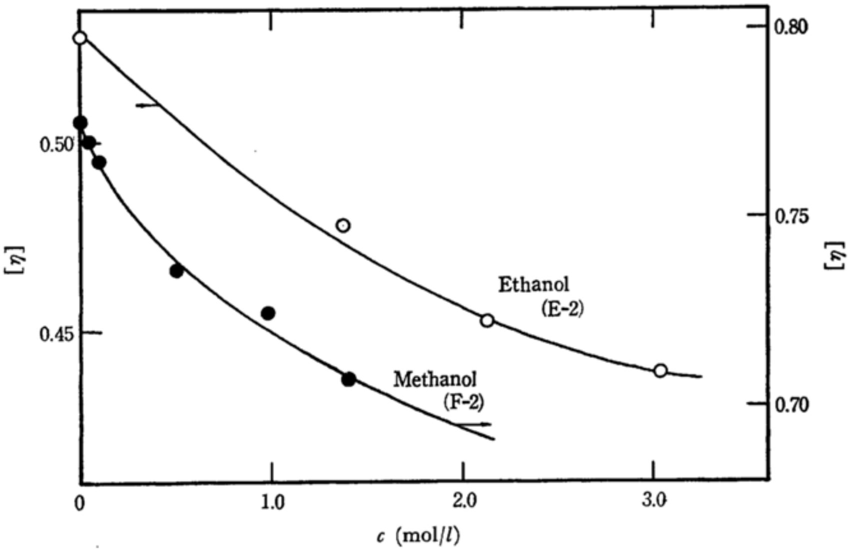

Fig. 5. Plots of intrinsic viscosity of poly-2-vinylpyridine fractions *vs.* concentration of ammonia contained in solvent at 25°C; (○): data for the fraction E-2 in ethanol, (●): data for the fraction F-2 in methanol.

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12) J. M. G. Cowie, *Polymer*, **7**, 487 (1966).

13) H. Inagaki, H. Suzuki, M. Fujii and T. Matsuo, *J. Phys. Chem.*, **70**, 1718 (1966).

14) G. C. Berry, *J. Polymer Sci.*, ***B*-4**, 161 (1966)

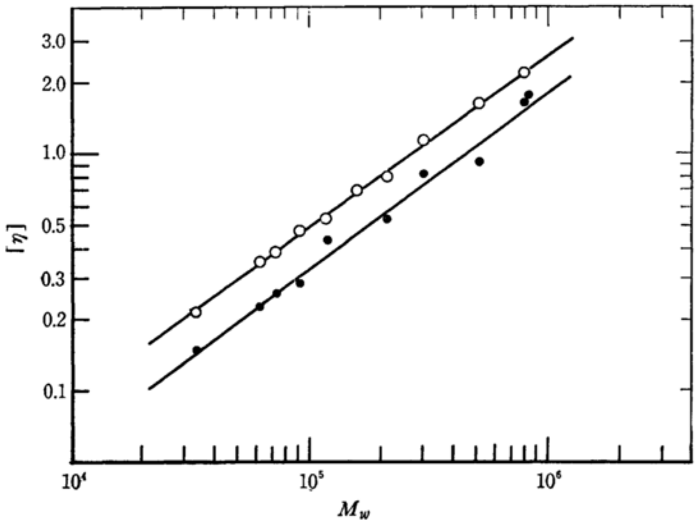

Fig. 6. Log-log plots of intrinsic viscosity of poly-2-vinylpyridine fractions in absolute ethanol (○), and in ethanol contained ammonia (2.7 N) (●), *vs.* weight average molecular weight at 25°C.

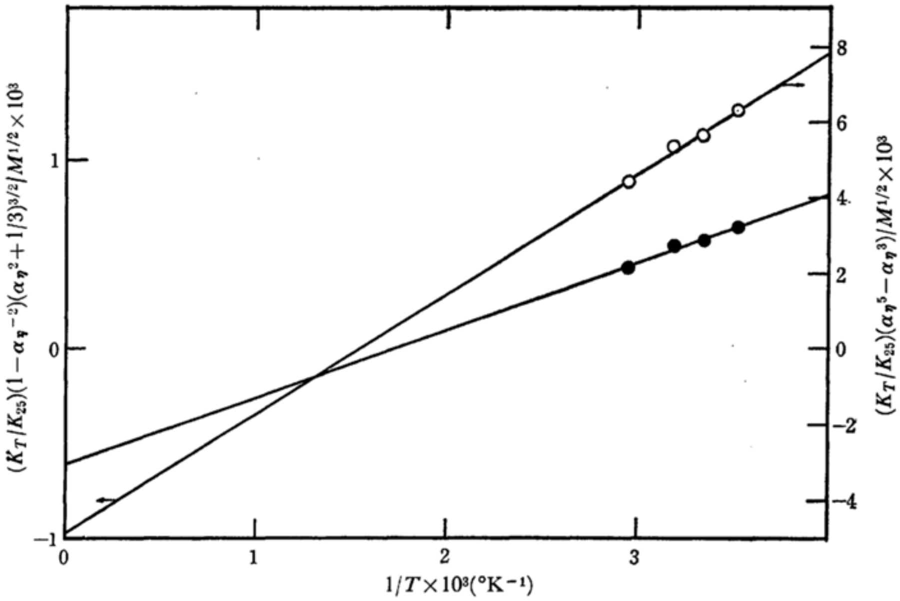

Fig. 7. Plots of $(K_T/K_{25})(\alpha_\eta^5-\alpha_\eta^3)/M^{1/2}$, (●), and $(K_T/K_{25})(1-\alpha_\eta^{-2})(\alpha_\eta^2+1/3)^{3/2}/M^{1/2}$, (○), *vs.* $1/T$ for poly-2-vinylpyridine in ethanol.

the data of the intrinsic viscosities at four different temperatures. The basic equations used for this purpose were the equation of Flory and Fox15) and that of Kurata and Stockmayer:16)

$$(K_T/K_{25})(\alpha_\eta^5-\alpha_\eta^3)/M^{1/2} = 2C_M\psi_1(1-\theta/T) \quad (5)$$

$$(K_T/K_{25})(1-\alpha_\eta^{-2})(\alpha_\eta^2+1/3)^{3/2}/M^{1/2} = (2^5/3^3)1.10C_M\psi_1(1-\theta/T) \quad (6)$$

where:

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta$$

and

$$C_M = ((3^3/2^{5/2}\pi^{3/2})v^2/NV_1)(M/\langle L^2\rangle_0)^{3/2}$$

and where K_T and K_{25} are the Flory constants at T°C and 25°C respectively; v, the specific volume

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15) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

16) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymer. Forsch.*, **3**, 196 (1963).

of the polymer; V_1, the molar volume of the solvent, and $\boldsymbol{N}$, the Avogadro number.

With the aid of the Mark-Houwink equations for the molecular-weight-homogeneous samples at each temperature, we calculated the values of $[\eta]$ and $[\eta]_\theta$ and, consequently, the α_η value for an ideal polymer fraction whose molecular weight $M=10^6$; the values of the left-hand side of Eq. (5) and Eq. (6) are plotted against $1/T$ in Fig. 7. Apparently the slopes of the lines are the reverse of those for ordinary polymer-solvent systems. The values of ψ_1 and θ obtained by the method of least squares are summarized in Table 3.

Table 3. The thermodynamic interaction parameters for dilution of poly-2-vinylpyridine in ethanol

Method	ψ_1	θ (°C)
Flory and Fox, Eq. (5)	-0.02	287
Kurata and Stockmayer, Eq. (6)	-0.02	397

The values of the entropy parameter obtained by the two equations are both very small, but negative, while the theta temperatures thus evaluated are unusually high. Such an anomaly as the occurrance of precipitation upon the heating of the solution can be predicted when the solution process is characterized by a negative excess entropy.[17]

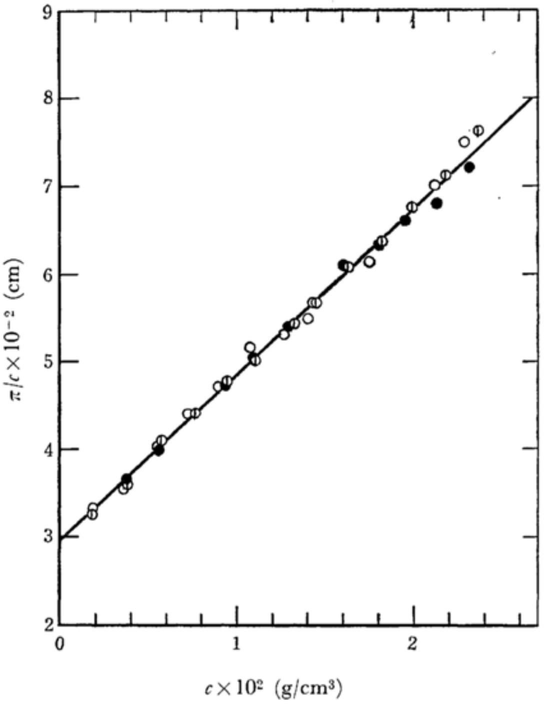

Fig. 8. Plots of reduced osmotic pressure *vs.* concentration of poly-2-vinylpyridine fraction, E-2, in ethanol at 15°C (⦶), 30°C (●), and 45°C (○).

The extraordinariness of the thermodynamic interaction between polyvinylpyridine and ethanol was further studied by investigating the temperature dependence of the second and the third virial coefficient, A_2 and A_3, of this polymer-solvent system.[18]

Figure 8 shows plots of the reduced osmotic pressure, π/c, *versus* the concentration, c. In spite of the measurements of the osmotic pressure over the range of very wide concentration, the temperature dependence of π/c is very small, as may be seen in Fig. 8; however, the data were treated with the method of Flory and Krigbaum,[19] assuming that the following equation is valid for this polymer-solvent system:

$$(\pi/c)^{1/2} = (\pi/c)_0^{1/2}[(1+\Gamma_2/2)c] \tag{7}$$

The values of A_2 and A_3 were calculated from the values of $(\pi/c)_0$ and Γ_2 as evaluated by the method of least squares; they are plotted against the temperature in Fig. 9.

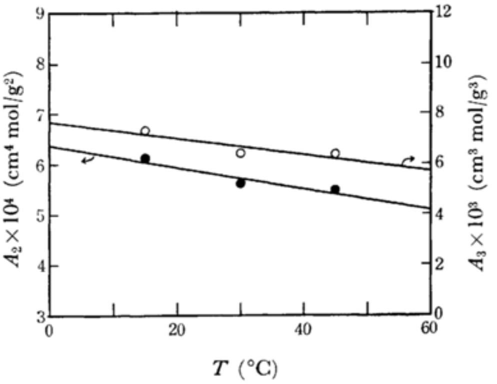

Fig. 9. Plots of osmotic the second, (●), and the third virial coefficient, (○), *vs.* temperature for poly-2-vinylpyridine fraction, E-2, in ethanol.

The excess thermodynamic functions of dilution for this system at 25°C were calculated by the following equations:

$$\Delta\mu_1{}^{\mathrm{E}}/c^2V_1 = -\boldsymbol{R}T(A_2+A_3c)$$

$$\Delta h_1{}^{\mathrm{E}}/c^2V_1 = \boldsymbol{R}T^2\{(\partial A_2/\partial T)+(\partial A_3/\partial T)c\}$$

$$T\Delta s_1{}^{\mathrm{E}}/c^2V_1 = \boldsymbol{R}T\{A_2+T(\partial A_2/\partial T)+A_3c + T(\partial A_3/\partial T)c\}$$

where $\Delta\mu_1{}^{\mathrm{E}}$ represents the excess free energy of dilution; $\Delta h_1{}^{\mathrm{E}}$, the excess molar heat of dilution, and $\Delta s_1{}^{\mathrm{E}}$, the excess molar entropy of dilution. The results are summarized in Table 4.

Here again, it was confirmed that the contributions of both enthalpy and entropy to the relative polymer-solvent interaction in this system are

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[17] H. Morawetz, "Macromolecules in Solution," Interscience Publishers, N. Y. (1965).

[18] K. Takamizawa, This Bulletin, **39**, 1186 (1966).

[19] P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949); P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

TABLE 4. THE EXCESS THERMODYNAMIC FUTNCTIONS OF DILUTION FOR POLY-2-VINYLPYRIDINE IN ETHANOL AT 25°C (cal cm^3/g^2)

$c\times 10^2$ g/100 cm^3	$\Delta\mu_1^E/c^2V_1$	$\Delta h_1^E/c^2V_1$	$T\Delta s_1^E/c^2V_1$
0	−0.346	−0.376	−0.030
1	−0.387	−0.433	−0.046
2	−0.428	−0.489	−0.061

negative, indicating a very strong specific interaction between polymer and solvent upon their being mixed, and also, a very high degree of order in the packing of ethanol molecules and of the polymer segments (this is probably due to the hydrogen bond formation).17)

The existence of some exothermic interaction between poly-2-vinylpyridine and aliphatic alcohols or chloroform, and the resulting possibility of hydrogen-bond formation between the polymer and solvent, has been already suggested by investigations of the data of the intrinsic viscosity in many solvents at a constant temperature, 25°C, and those of the precipitation measurements of this polymer in mixed solvents consisting of alcohol and hexane, and of chloroform and hexane.2) However, the parameters and the functions for the relative thermodynamic interactions between poly-2-vinylpyridine and absolute ethanol obtained by the data of the temperature dependence of intrinsic viscosity and osmotic pressure in this study confirm more directly and quantitatively the suggestions described above.

The author wishes to express his thanks to Professor Daisei Yamamoto of this University for his continued advice and encouragement in this work.