Pergamon

PII: S0014-3057(96)00140-1

Eur. Polym. J. Vol. 33, No. 6, pp. 943–948, 1997

Printed in Great Britain
0014-3057/97 \$17.00 + 0.00

SOLUTION PROPERTIES OF POLYVINYLPYRIDINE IN ACID—II. SOLUTION PROPERTIES OF POLY(4-VINYLPYRIDINE) IN AQUEOUS SOLUTION OF HYDROCHLORIC ACID

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(Received 18 October 1995; accepted in final form 11 January 1996)

Abstract—The total electrostatic free energy change, ΔG_{el}, for poly(4-vinylpyridine) (P4VP) was evaluated from the apparent dissociation constant, p$K(\alpha)$, by means of UV spectra in an aqueous solution of hydrochloric acid (aq. HCl). The intrinsic viscosity ($[\eta]$) of P4VP was measured in aqueous solutions of 2×10^{-3}, 4×10^{-3}, 10^{-2}, 10^{-1}, 1, 3 and 6 M hydrochloric acid, methanol and *N,N*-dimethylformamide (DMF) at 25°C. Linear relations between $[\eta]$ and weight-average molecular weights (M_w) were observed in 10^{-1}, 1, 3 and 6 M HCl, methanol and DMF. It was found that the unperturbed dimension of P4VP evaluated from the Stockmayer–Fixman plot was dependent on the concentration of HCl. The characteristic ratios, C_∞, in these solutions of HCl are larger than those in organic solvents. However, in 2×10^{-3}, 4×10^{-3} and 10^{-2} M HCl, the double logarithmic plots of $[\eta]$ and M_w show a concave-downward curvature. The persistence length (q) and the molar mass per contour length (M_L) were evaluated from viscosity data in 2×10^{-3}, 4×10^{-3} and 10^{-2} M HCl according to the theory of the worm-like chain model. When the diameter of the cylinder (d) was assumed to be 1.0 nm, the agreement between $[\eta]$ experimentally obtained and calculated by means of the Yamakawa–Fujii–Yoshizaki theory is satisfactory. © 1997 Elsevier Science Ltd

INTRODUCTION

Since P4VP is soluble only in very polar solvents, reports on the solution properties of P4VP are very limited [1, 2]. However, the solution properties of P4VP quaternarized with alkyl halide in aqueous solution were reported by Fuoss *et al.* in the 1940s [3, 4]. When the aqueous acid for P4VP is used as a solvent, this polymer is protonated and soluble in aqueous solution. Since protonated P4VP is a polyelectrolyte, as is well-known, the solution properties of P4VP in aqueous solution of acid are dependent on the kind of acid, pH and the concentration of added salt, i.e. polyion charge density and solution ionic strength. We have investigated the influence of the solution properties of polyvinylpyridine (P4VP and P2VP) on the kind of acid and the concentration of acid [2, 5]. For example, solutions of P4VP in aqueous solution of H_2SO_4 cause a phase separation and the aqueous solution of 0.75 M H_2SO_4 at 25°C is a theta solvent for P4VP [2].

In this paper, the solution properties of P4VP using HCl as an acid were investigated. The first purpose of this study is to evaluate the total electrostatic free energy (ΔG_{el}) for the removal of an equivalent of a proton from a pyridine residue of P4VP in an aqueous solution of HCl. The second purpose is to evaluate several molecular parameters of P4VP from M_w and $[\eta]$ at several concentrations of HCl. The so-called short range interaction parameter (unperturbed dimension) was evaluated by means of the Stockmayer–Fixman theory [6]. The parameters were obtained in methanol and DMF in order to compare the effect of protonation on the parameters of P4VP. In several concentrations of HCl, values of the persistence length (q) and the molar mass per unit contour length (M_L) were evaluated by means of the theory of a worm-like model chain [7–9]. The measured values of $[\eta]$ were compared with the theoretical values assuming $d = 1.0$ nm.

EXPERIMENTAL

Materials

The 4-vinylpyridine monomer was purchased from Kouei Kagaku Co. Ltd, and was distilled under reduced pressure immediately before the polymerization. The monomer was polymerized with butyllithium as an inhibitor in tetrahydrofuran at −78°C. However, the molecular weight of P4VP obtained by this method was not high enough. High molecular weight samples (samples a and b in Table 1) were additionally obtained by the method of usual radical polymerization with azobisisobutyronitrile at 50°C. Both of the polymer samples were purified by the precipitation method using *tert*-butanol–benzene as a solvent–precipitant pair.

Light-scattering measurement

Light-scattering measurements were carried out with a Fica 50 automatic light-scattering photometer with vertically polarized incident light of 436 nm at 10 or 11 different angles ranging from 30° to 145 or 150°. The optical purification of each solution and solvent was carried out through a Millipore membrane filter "FG" (pore size

Table 1. Limiting viscosity number [η] measured for P4VP fractions in each solvent

				$[\eta]/(\mathrm{dLg^{-1}})$						
				[HCl]						
Sample	$M_w \times 10^{-4}$	MeOH	DMF	2×10^{-3}	4×10^{-3}	10^{-2}	10^{-1}	1	3	6
a	223	5.97	3.18	72.6	53.3	39.5	14.9	6.15	5.28	6.25
b	186	5.70	2.91	61.3	49.3	37.1	13.2	5.73	—	—
c	58.0	2.17	1.23	33.6	24.4	17.4	5.63	2.19	2.20	2.24
d	32.7	1.47	0.811	21.5	16.5	12.4	4.00	1.64	1.44	1.60
e	13.7	0.815	0.474	11.8	8.83	5.40	2.17	0.926	0.785	0.870
f	8.40	0.561	0.365	5.50	4.09	2.49	1.37	0.608	0.550	0.593
g	4.17	0.340	0.215	3.69	2.24	1.77	0.767	0.310	—	—
h	3.42	0.288	0.201	2.31	2.18	1.27	0.544	0.280	0.279	0.302

0.2 μm). An antifluorescence filter of 436 nm was also used to protect the fluorescence effect. The weight-average molecular weight (M_w) was estimated from the Zimm plot in methanol. The specific refractive-index increment was measured with a Shimadzu DR-3 type refractometer.

Viscosity measurement

The dependence of reduced viscosity on the shear rate. It is reported that the reduced viscosity of polyelectrolyte showed a shear rate dependence [10, 11]. However, there is no report on the shear rate dependence of the reduced viscosity of P4VP. A variable shear viscometer, which was basically a modification of the viscometer reported by Vink [10] and Yamanaka *et al.* [11], was constructed. The height of the meniscus of this viscometer was read with a traveling microscope to 0.01 cm. Viscosity measurement was carried out in a water bath controlled within ±0.01°C at 25°C.

The average shear rate (q_v) at the capillary wall was calculated with Rabinowich's equation as follows: The high meniscus is at height H and $H - \mathrm{d}H$ at time t and $t + \mathrm{d}t$, then:

$$q_v = (R'/R^3)(\mathrm{d}H)(3/\mathrm{d}t) + h\mathrm{d}(1/\mathrm{d}t)/\mathrm{d}h \qquad (1)$$

where R is the radius of the capillary, R' is the radius of the measuring tube and h is the mean height difference $[h = H - (1/2)\mathrm{d}H]$. The differential coefficient $\mathrm{d}(1/\mathrm{d}t)/\mathrm{d}h$ was obtained by applying the least-squares method to a $1/\mathrm{d}t$ vs h plot. Figure 1 shows the reduced viscosity as a function of the shear rate for the three concentrations of P4VP fraction ($M_w = 186 \times 10^4$) in 4×10^{-3} M HCl at 25°C. As shown in Fig. 1, a shear rate dependence of the reduced viscosity was not observed, namely, the shear rate correction was unnecessary in our viscosity measurement. The shear rate independence of viscosity was reported for poly(isobutyl vinyl ether-co-maleic anhydride) [12].

Evaluation of [η]. Since the measurement of [η] by a variable shear viscometer took a long time, the measurements of [η] were carried out with a Ubbelohde-type viscometer. [η] was estimated by using the Huggins or the Mead–Fuoss plots and is presented in Table 1.

pH measurements

The value of pH was measured using a Horiba pH meter. F-8 AT.

UV spectra

The measurements of UV spectra of the solutions of P4VP in HCl at room temperature were carried out using a UVIDEC-670 spectrophotometer from Japan Spectroscopic Co., Ltd.

RESULTS AND DISCUSSION

The dissociation equilibrium of the ionizable groups of a polyacid (including the conjugate acid of base) is co-operative and complicated, due to the strong electrostatic interaction among the charged groups densely fixed to the chain. Generally, the apparent dissociation constant, p$K(\alpha)$, of protonated pyridinium ions is estimated by:

$$\mathrm{p}K(\alpha) = \mathrm{pH} - \log[(1 - \alpha)/\alpha] \qquad (2)$$

$$= \mathrm{p}K_0 + (0.434/RT)G_{\mathrm{el}}(\alpha) \qquad (3)$$

where α is the degree of protonation. pK_0 is the intrinsic dissociation constant when electrostatic interactions with other charged groups are absent. This value (p$K_0 = 5.0 \pm 0.3$) was reported by Satoh *et al.* [13]. $G_{\mathrm{el}}(\alpha)$ is the electrostatic free energy due to the removal of an equivalent of a proton at a given α. The total change ($\alpha = 0 - 1$) ΔG_{el} can be obtained from the area under a plot of p$K(\alpha)$ vs $1 - \alpha$. In this study, α was evaluated from the UV spectra in several concentrations of HCl at 230 nm [14]. In the range of higher concentration of HCl (pH < 1), the accurate absorption coefficient per monomer unit of P4VP was not evaluated due to the absorbability of the solvent. In this region (pH < 1), it was assumed that α is equal to 1. Further, the value of p$K(\alpha)$ of this polymer cannot be evaluated in the whole range of α, since P4VP precipitates in the range of lower α. The value of ΔG_{el}, accordingly, was evaluated assuming that a conformational transition in the lower range of α does not occur. The relations between p$K(\alpha)$ and α are shown in Fig. 2. The value of p$K(\alpha)$ decreased monotonously with increasing α. These behaviors of p$K(\alpha)$ vs α were similar to those obtained by means of the titration method for P4VP in aqueous ethanol [13]. It is difficult to assume that P4VP exhibits any marked co-operative transition taken part in the hydrogen bond or hydrophobic side chain in the course of transition, as observed in the case of poly(methyl acrylic acid) [15].

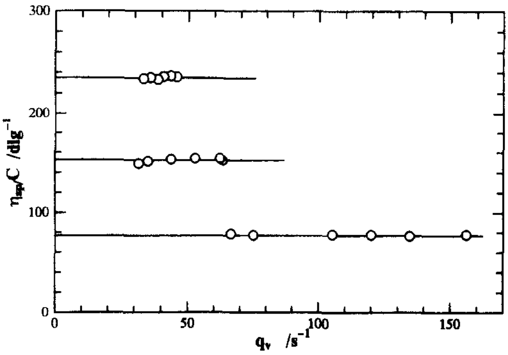

Fig. 1. Dependence of specific viscosity (η_{sp}/C) on the shear rate (q_v) of P4VP ($M_w = 186 \times 10^4$) in 4×10^{-3} M HCl.

ΔG_{el} evaluated from $G_{el}(\alpha)$ vs α was -13.8 ± 0.1 kJ mol^{-1}, assuming $pK_0 = 5.0$. Ochiai *et al.* reported that ΔG_{el} for poly(allylammonium) cation is -9.42 kJ mol^{-1} in 0.05 M NaCl [16]. The magnitude of ΔG_{el} of P4VP is fairly large. With respect to the release of a proton from a protonated residue, a pyridine residue is more favorable than an allylamine residue.

In the well-known modified Henderson–Hasselbach plots (not shown as a figure), an approximately linear relationship was found between pH and log $[\alpha/(1-\alpha)]$ over a wide range of α ($pK(\alpha)$ at $\alpha = 0.5$ is 2.97).

Relationship between $[\eta]$ *and* M_w

Since there are few organic solvents for P4VP, there is only a report on the Mark–Houwink–Sakurada (M–H–S) equation of P4VP in ethanol [1]. The double logarithmic plots for P4VP in the acidic aqueous solution at several concentrations of HCl, methanol and *N,N*-dimethylformamide (DMF) at 25°C are shown in Fig. 3. The points in 3 M HCl almost coincided with those in methanol reported by Fuoss *et al.* [1]. The M–H–S equations in 10^{-2}, 4×10^{-3} and 2×10^{-3} M HCl undoubtedly deviate downwards in the range of higher molecular weight from the linear relationship. A similar curve with upward curvature is reported for the relation between M_w and $[\eta]$ for poly(hexyl isocyanate) in toluene [17] and poly(diisopropyl fumarate) in benzene [18]. The values of K and ν in the M–H–S equation ($[\eta] = KM^{\nu}$) were calculated by the least-squares method, with the exception of the curved lines, and are presented in Table 2. The values of ν in the concentration range of HCl from 10^{-1} M to 6 M are 0.764–0.702 and comparable to those of a random coil in very good solvents. The value of $[\eta]$ decreases as the concentration of HCl increases and increases after passing through a minimum.

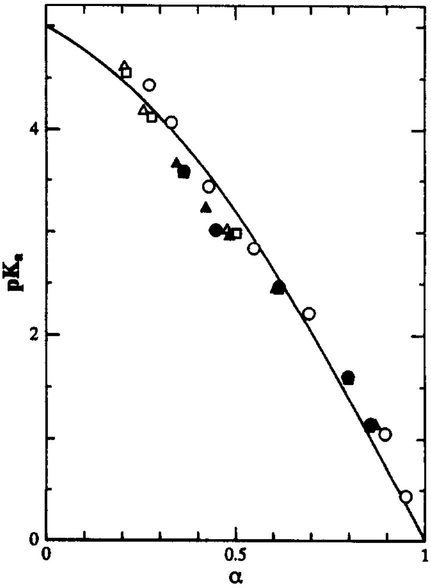

Fig. 2. Dependence of p*K* on α in an aqueous solution of HCl. Molecular weight: ●: 223×10^4; △: 13.4×10^4; ○: 58.0×10^4; ▲: 186×10^4; □: 32.7×10^4.

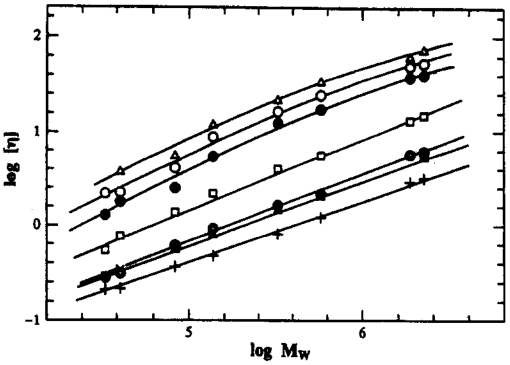

Fig. 3. Double logarithmic plots of $[\eta]$ vs M_w in different concentrations of HCl (△: 2×10^{-3} M; ◎: 4×10^{-3} M; ●: 10^{-2} M; □: 10^{-1} M; ○: 1 M; ▲: 3 M; and ■: 6 M) ×: methanol and +: DMF.

Evaluation of unperturbed dimension

The value of pH of the polymer solution in 10^{-1} M HCl was 1.1 at room temperature. From the measurement of UV in this solvent, the value of α was found to be larger than 0.9. Consequently, in the following evaluation of the short range interaction parameters in the range from 10^{-1} M to 6 M HCl, the molecular weight and the concentration with relation to reduced viscosity of P4VP were corrected assuming that the polymer was fully protonated. In this study, the unperturbed dimension was evaluated using the equation derived from widely accepted theory, the Stockmayer–Fixman equation [6]:

$$[\eta]/M_w^{1/2} = K_\Theta + 0.51\Phi_0 B M_w^{1/2} \qquad (4)$$

where Φ_0 is the Flory constant (2.87×10^{21}), B is the long-range interaction parameter and K_Θ is the parameter related to the mean-square end-to-end distance ($\langle r^2 \rangle_0$) by:

$$K_\Theta = \Phi_0(\langle r^2 \rangle_0 / M)^{3/2} \qquad (5)$$

The typical Stockmayer–Fixman plots of P4VP in 10^{-1} and 1 M HCl, methanol and DMF are shown in Fig. 4. The linear relation of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ is observed in the range of lower molecular weight, as seen in a usual polymer–solvent system. The value of K_Θ was evaluated from these linear relations. K_Θ of P4VP is listed in Table 2, together with the characteristic ratio C_∞ and σ. C_∞ was calculated using the following equation:

$$C_\infty = (\langle r^2 \rangle_0 / nl^2)_{n=\infty} = (K_\Theta/\Phi_0)^{2/3}\{M_u/(2l^2)\} \qquad (6)$$

Here, n is the bond number, l is the bond length in the main chain ($l = 0.154$ nm for C—C bond) of the

Table 2. The constant in the Mark–Houwink–Sakurada equation, unperturbed dimension parameter (K_θ), characteristic ratio (C_∞) and steric hindrance parameter (σ)

Solvent	$K \times 10^4$/ (dLg^{-1})	ν	$K_\theta \times 10^4$/ (dLg^{-1})	C_∞	σ
Methanol	1.4_3	0.72_9	11.0_0	11.0_7	2.4_2
DMF	1.8_0	0.66_8	9.0_0	10.0_2	2.2_6
10^{-1} M HCl	2.2_6	0.76_3	20.0_9	24.0_2	3.4_8
1 M HCl	1.3_3	0.73_8	9.4_1	14.0_2	2.6_6
3 M HCl	1.9_7	0.69_9	10.0_2	15.0_0	2.7_4
6 M HCl	2.1_1	0.70_0	9.8_6	14.0_7	2.7_1

vinylpolymer and M_u is the monomer molar mass. σ is defined as the ratio of $\langle r^2\rangle_0^{1/2}/M$ to $\langle r^2\rangle_{0f}^{1/2}/M$ of the hypothetical chain with free rotation around the C—C bond in the main chain. The values of K_Θ of P4VP are almost constant regardless of the concentration of HCl, except for 0.1 M HCl and the organic solvents. However, the values of C_∞ or σ in aq. HCl are larger than those in organic solvent. It can be seen that the unperturbed dimension is influenced by the protonation of pyridine residue in aq. HCl. Namely, it is found that the large values of C_∞ or σ result from the larger monomer molecular weight, independently of the electrostatic interaction. The value of σ in organic solvents is comparable to those of P2VP(2.2) in organic solvents [19, 20]. The value of σ in aqueous solutions of hydrochloric acid, also, is comparable to that of poly(N-methylpyridinium chloride) (2.8) in aq. NaCl solution [21].

There are several reports on the behavior of $[\eta]$ accompanying the change of concentration of a salt (c_s) [22, 23]. The value of $[\eta]$ is in proportion to $c_s^{-0.5}$. However, in this study, the behavior of $[\eta]$ against the concentration of HCl is found to have a minimum at 3M HCl. There are some reports on the value of $[\eta]$ which increases with increasing c_s [2, 24]. In these reports, such behavior was explained in terms of a breakdown of intra- and inter-chain association. However, since a specific association for P4VP can not be expected in HCl, it is difficult to explain the behavior in terms of an association, although poly(sulphopropylbetaine) can be explained in terms of it [25]. The behavior that $[\eta]$ decreases with increasing concentration of HCl can be explained if HCl shields charged segments of P4VP from electrostatic repulsion, like a salt. However, the behavior of $[\eta]$ in the range of 3–6 M HCl can not be explained in this way.

The relation between M_w *of P4VP and* $[\eta]$ *in aqueous solution of* 10^{-2}, 4×10^{-3} *and* 2×10^{-3}*M HCl*

An anomalous Zimm plot was observed in the light-scattering measurement in dilute concentration of HCl ($<10^{-1}$ M). Forster and Schmidt also reported anomalous light-scattering of quaternized P2VP in aqueous solution [26]. A typical example in 4×10^{-3} M HCl is presented in Fig. 5. The z-average radius of gyration ($\langle s^2\rangle_z$) and second virial coefficient (A_2) of these polymer fractions from direct measurement could not be evaluated. For that reason, the expansion factor of P4VP from $\langle s^2\rangle_z$ in these solutions could not be discussed directly.

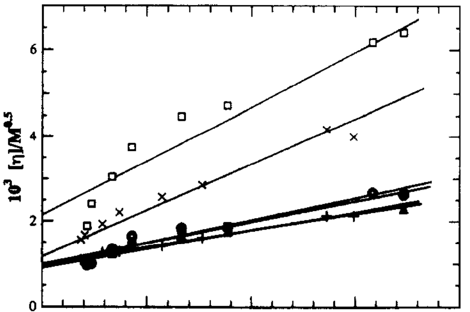

Fig. 4. Stockmayer–Fixman plots for P4VP in 10^{-1} M, 1 M, 3 M and 6 M HCl, methanol and DMF. The symbols are the same as those in Fig. 3.

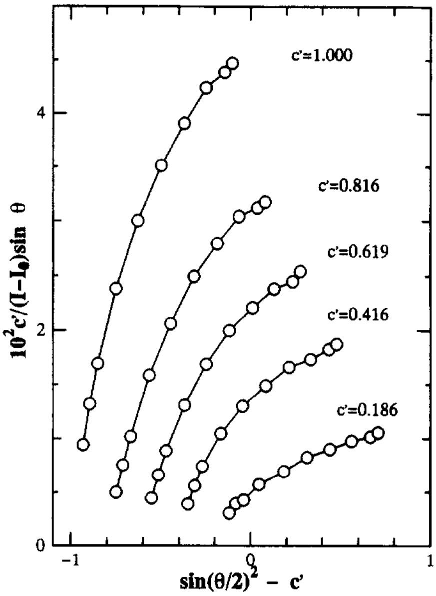

Fig. 5. Anomalous Zimm plot of P4VP ($M_w = 186 \times 10^4$) in 4×10^{-3} M HCl at 25°C. c' is the reduced value.

M_w and $[\eta]$ in Table 1 might be corrected for the protonation of pyridine nitrogen. From the UV data of P4VP in dilute HCl solution ($<10^{-1}$ M), it was found that the value of α in 10^{-2} M HCl was 0.80, in 4×10^{-3} M HCl it was 0.67, and in 2×10^{-3} M HCl it was 0.58. The values of M_w and $[\eta]$ were corrected for the protonation and the relationship between M_w and $[\eta]$ is presented in Fig. 6. Hodgson and Amis reported that the conformation of P2VP in 2.3×10^{-3} M HCl–ethylene glycol was represented by a worm-like model [27]. As can be seen from the relationship of M_w and $[\eta]$ in Fig. 6, the conformation of P4VP in these solvents ($<10^{-1}$ M HCl) may be represented by a worm-like model. However, the dimension of P4VP in dilute solution of HCl ($<10^{-1}$ M) is not equal to the unperturbed dimension. Strictly speaking, the evaluation of the factors for a worm-like chain must be corrected for the value of $[\eta]$ by means of an expansion factor [28]. Unfortunately, it was not possible to evaluate the unperturbed dimension of P4VP from data in dilute solution of HCl ($<10^{-1}$ M). If the charge of P4VP was masked, the conformation of P4VP in the solvent is equal to a random conformation (as seen from the data in 1 M, 3 M and 6 M HCl). In this report, the evaluation of the parameters of a worm-like model was carried out assuming that the theory of Yamakawa–Fujii–Yoshizaki could be applied to the explanation of the conformation of P4VP in dilute HCl ($<10^{-1}$ M). In the evaluation of parameters of a worm-like model, the chain contour length (L) or the molar mass per unit contour length (M_L) must be evaluated. Yamakawa, Fujii and Yoshizaki [7, 8] proposed the expression for $[\eta]$ of a worm-like chain, which contains M_L, q and d. For $L/2q > 2.278$:

$$[\eta] = \Phi_0 M^{1/2}(M_L/2q)^{-3/2}[1 - (\Sigma C_i(L/2q))^{-i/2}]^{-1} \quad (7)$$

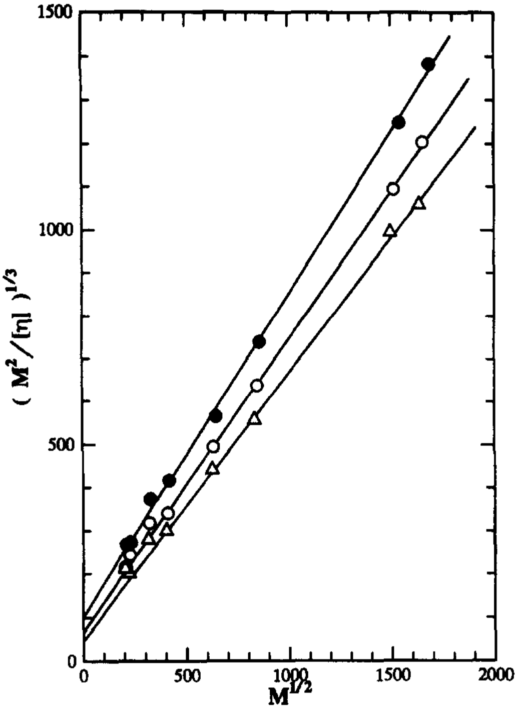

Fig. 6. Plots of $(M^2/[\eta])^{1/3}$ against $M^{1/2}$ for P4VP in different concentrations of HCl. The symbols are the same as those in Fig. 3.

where Φ_0 is the Flory universal constant for the unperturbed random coil, d is the cylinder diameter and C_i are coefficients depending on the values of d and q. In practice, it is difficult to evaluate M_L, q and d from equation (7) and the measured value of $[\eta]$. Recently, Bohdanecky proposed a simple procedure for evaluation of the worm-like chain parameter as follows [9]:

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2} \tag{8}$$

with

$$A_\eta = A_0 M_L \Phi_0^{-1/3}$$

$$B_\eta = B_0 \Phi_0^{-1/3} (M_L/2q)^{1/2}$$

A_0 and B_0 are functions of $d/(2q)$.

Plots of $(M_w^2/[\eta])^{1/3}$ vs $M_w^{1/2}$ of P4VP in acidic aqueous solution of several concentrations of HCl were presented in Fig. 6. A_η and B_η were evaluated from the intercept and the slope of the linear relationship, respectively. According to Bohdanecky [9], the value of d is insensitive to $[\eta]$, in comparison with M_L and q. Thus, the value of d was assumed to be 1.0 nm for this polymer. The values of q and M_L for $d = 1.0$ nm in these solvents are presented in Table 3.

Table 3. Worm-like chain parameters of P4VP for several concentrations of HCl

[HCl]	M_L (nm^{-1})	q (nm)
2×10^{-3}	387	13
4×10^{-3}	444	13
10^{-2}	580	13

The value of d was assumed to be 1.0 nm.

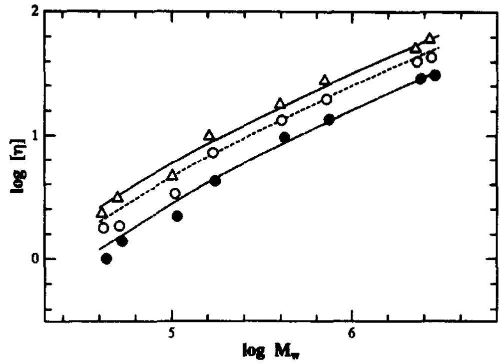

Fig. 7. Comparison between the value of $[\eta]$ from experimental data (symbols) and the value calculated from equation (7) (lines).

In Fig. 7, the value of $[\eta]$ calculated from equation (7) by employing these parameters is presented together with the measured value of $[\eta]$. The agreement is satisfactory for all the systems. If the precise value of d is evaluated in some way or other, more reasonable values of M_L and q can be obtained. However, qualitatively it seems that the value of q is almost constant, at least for the data which give an upward curvature in the double logarithmic plot of M_w and $[\eta]$. The value of M_L depends on the concentration of HCl in these systems ($<10^{-1}$ M HCl). In other words, the behavior of $[\eta]$ is attributed to M_L. The values of M_L and q of P2VP at the maximum of reduced viscosity in 2.3×10^{-3} M HCl–ethylene glycol at 25°C are 420 nm^{-1} and 5.1 nm, respectively [27]. The values of q and M_L for P4VP in this study may be acceptable, but the former is larger than that of P2VP in 2.3×10^{-3} M HCl–ethylene glycol. Judging from the value of q, P4VP in these solvents is much more flexible than the typical semi-flexible poly(hexyl isocyanate) ($q = 21$–42) [17]. P4VP in the dilute solution of HCl ($<10^{-1}$ M) is more rigid than poly(diisopropyl fumarate) ($q = 7.6$) [18].

In conclusion, the dependence of $[\eta]$ of P4VP on the concentration of HCl in the acidic aqueous solution was investigated. Except for the cases of 2×10^{-3}, 4×10^{-3} and 10^{-2} M HCl, the usual M–H–S equations were obtained. From the two parameter theory, the characteristic ratio, C_∞, depends on the molecular weight of the polymer whose repeating unit was protonated. On the other hand, the relationship between $[\eta]$ and M_w in the acidic aqueous solution at the lower concentration of HCl was explained by the worm-like model chain. Good agreement was obtained between the experimental values of $[\eta]$ and those evaluated from the Yamakawa–Fujii–Yoshizaki theory, assuming the value of d to be 1.0 nm.

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