from the critical value of s_c; this is shown for a particular value of σ in Figure 7 (the behavior would be the same for all values of σ). Thus in the restricted renormalization group transformation (σ and c held fixed) the s_c line is a line of fixed points, the system moving away from the line under the renormalization group transformation. In the more general renormalization group transformation, where all of the a_n are allowed to vary (as in section 4), the renormalization group transformation moves the system parallel to the $s_c(\sigma)$ critical line toward the trivial fixed point ($s^*=1,\sigma_n^*=0$).

Appendix. Comparison of the 1-D Ising Ferromagnet with the Zimm-Bragg Model

In the one-dimensional Ising model for the ferromagnet the magnetic moment can exist in one of two orientations (states): with (+) or against (-) the external field. Nearest-neighbor-like spins (++ or --) are assigned a Boltzmann factor $\exp(K)$ while nearest-neighbor-unlike spins (+- or -+) are assigned a Boltzmann factor $\exp(-K)$; K is the coupling constant, $K = J/RT$. Another Boltzmann factor reflects the interaction of a spin with the external magnetic field: $\exp(L)$ for alignment with the external field and $\exp(-L)$ for alignment against the external field ($L = H/RT$, H being the magnetic field). The transfer matrix for this model is

$$\mathbf{W} = \begin{matrix} \\ + \\ - \end{matrix}\begin{matrix} \begin{matrix} + & \quad - \end{matrix} \\ \begin{bmatrix} e^{K}e^{L} & e^{-K} \\ e^{-K} & e^{K}e^{-L} \end{bmatrix} \end{matrix}$$

$$= e^{K}e^{-L}\begin{bmatrix} e^{2L} & e^{-2K}e^{L} \\ e^{-2K}e^{L} & 1 \end{bmatrix} \qquad \text{(A1)}$$

Comparing eq A1 with eq 20, one finds the following correspondence for the matrix elements:

$$s = e^{2L} \qquad \sigma = e^{-4K} \qquad \text{(A2)}$$

At zero external magnetic field ($L = 0$, the analogue of $s = 1$), the eigenvalues are

$$\lambda_{1,2} = e^{K} \pm e^{-K} \qquad \text{(A3)}$$

or

$$\lambda_1 = 2\cosh K \qquad \lambda_2 = 2\sinh K \qquad \text{(A4)}$$

Using the analogue of eq 32, one finds the renormalization group transformation $K \rightarrow K'$

$$\tanh K' = \tanh^2 K \qquad \text{(A5)}$$

where the flow is toward $K = 0$. If one lets $x = \exp(2K)$, then eq A5 can be written

$$x' = \tfrac{1}{2}(x + (1/x)) \qquad \text{(A6)}$$

which is to be compared with eq 28.

Registry No. Polyethylene, 9002-88-4.

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Potentiometric Titration of Poly(vinylpyridines) and Hydrophobic Interaction in the Counterion Binding

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ABSTRACT: Potentiometric titrations of poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) were performed in the presence of 0.1 M NaCl or 0.1 M sodium benzenesulfonate (NaBS) in aqueous and 45 wt % aqueous ethanol solutions. It was found that pK_a values for P2VP titrated with benzenesulfonic acid (HBS) are higher at 40 and 25 °C and lower at 10 °C than those titrated with HCl at corresponding temperatures. The ΔH values for the protonation with HBS, which were estimated from the temperature dependence of the pK_a values of P2VP, become more endothermic at higher degrees of the polymer charge densities (α). In the case of P4VP, no significant difference was observed between HBS and HCl titrations. These results were discussed in terms of hydrophobic interactions between the polycations and BS^- ions.

Introduction

Counterion bindings in aqueous polyelectrolyte solutions are largely influenced by the hydrations of relevant ions. Since most synthetic polyelectrolytes have hydrophobic main chains, hydration sheaths of the polyions are composed of ionic (and hydrogen bonding) hydrations around the charged (and polar) groups and of hydrophobic hydrations around the nonpolar moieties. When hydrophilic hydrations are predominant around the polyion, simple inorganic counterions such as alkali cations and halogen

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anions which are surrounded by ionic hydration will be attracted by the polyions essentially through electrostatic interaction. Some theories for such counterion binding have been developed.[1-4] On the other hand, when hydrations of a polyion and the counterions are both hydrophobic, an additional attractive force referred to as "hydrophobic interaction"[5] becomes effective between the polyion and the electrostatically attracted counterions, because the driving force for the interaction is the reduction of the hydrophobic hydrations of the relevant ions due to the overlap of the hydration sheathes. Many studies have been reported on such a hydrophobic effect for ionic solutes. For example, tetraalkylammonium cations have been reported to be bound on polycarboxylates such as poly(L-glutamate),[6] poly(methacrylate),[7] and a copolymer of isobutyl vinyl ether and maleic acid[8] through hydrophobic interaction. This hydrophobic attractive force concerts with the electrostatic one. On the other hand, when the polyion is differently hydrated from the counterions, e.g., one hydration is ionic and the other hydrophobic, the counterion binding force will be reduced because particules with unlike hydrations are apt to repell each other due to the incompatibility of the hydrations.[9] Therefore, the binding strength of hydrophobic counterions is to depend more or less on the prevalent nature of hydrations around the charged groups of polyion. However, few studies from such a point of view have been reported.[10]

Poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) are hydrophobic polymers which are insoluble to water until more than ca. 35% of the pyridine groups is charged, e.g., by protonation. P4VP and P2VP have the same chemical constitution, except for the position of nitrogen; the charged site of P2VP is closer to the hydrophobic main chain than that of P4VP. This may lead to a significant alteration of the hydration structures of charged P4VP and P2VP. Then, the bindings of hydrophobic counterions to the charged sites of these two polymers should suffer from the very local natures in the hydration of the charged sites, which should result in the difference in the binding strength and hence in the binding degree.

In the present study, the different behaviors in the counterion binding of benzenesulfonate ion, a hydrophobic counterion, to P4VP and P2VP are examined by means of pH titration for the aqueous and aqueous ethanol solutions of the polymers. The apparent dissociation constant, pK_a, which is a sensitive function of the electrostatic surface potential[6,11,12] of the protonated polymers, is estimated with changing the degree of protonation, α, and the corresponding pH value. The pK_a values and the temperature dependence observed for P4VP, P2VP/benzenesulfonate ion (BS^-) systems are compared with those for a system containing a reference counterion, Cl^-, to see the discriminative counterion binding operative on these polycations.

Experimental Section

Poly(4-vinylpyridine) was purchased from Kouei Kagaku Co. Ltd. Poly(2-vinylpyridine) was prepared by radical polymerization of 2-vinylpyridine in a water/2-propanol mixture. Both polymer samples were purified by twice-repeated precipitation from ethanol into diethyl ether and dried in vacuo at room temperature. The molecular weights of P4VP and P2VP were estimated by viscometry as 2.3×10^5 and 1.3×10^5, respectively. 4-Ethylpyridine (4EP), 2-ethylpyridine (2EP), benzenesulfonic acid (HBS), and sodium benzenesulfonate (NaBS) of analytical grade were purchased from Tokyo Kasei Co. Ltd.

pH titrations for P4VP, P2VP, 4EP, and 2EP in aqueous and aqueous ethanol (45 wt %) solutions of 0.1 M NaCl or 0.1 M NaBS were performed with a pH meter F8AT (Hitachi-Horiba) and a pH electrode 6327-10c (Horiba, ±0.001 pH) under nitrogen atmosphere. Since NaBS completely dissociates into Na^+ and BS^- as NaCl, the titrations were carried out under the same ionic strength for the two salts. The concentrations of the polymers and the monomer analogues were 0.01 mol/L; 100 mL of the solutions was titrated by 2 N HCl or 2 N HBS. The aqueous solutions were prepared by partial protonation (35%) of the polymer solutes with HCl or HBS. In the case of the P4VP/HBS system, the polymer was insoluble to the aqueous salt solution until protonated more than 55%. The pH values in 45 wt % ethanol were expediently corrected by subtracting 0.245 from the measured values according to Gelsema's method.[13] The apparent dissociation constant, pK_a, of the protonated pyridinium ions is estimated by

$$pK_a = pH + \log (\alpha/1 - \alpha)$$

where α is the degree of protonation. An α value at a certain pH was obtained as the difference of the amount of H^+ added and that in a blank experiment. This procedure is justified when the effect of polymer on the activity coefficient of H^+ ions can be neglected under such an excess of added salt as in the present study. In the calculations of α, corrections were made for volume changes due to the titration and due to the solvent evaporation during the experiment. The volume corrections for aqueous and aqueous ethanol solutions were particularly important to obtain reliable titration curves at a low pH ($\leq$2.0)/high α ($\geq$ 0.8) region; without the corrections, pK_a values higher by 0.1–0.2 pK unit than the corrected values were estimated. By the solvent evaporation, the alcohol content decreased to ca. 43 wt % at the end of the titration runs. The effect on pK_a, however, was within the experimental error (~0.05 pK unit).

Table I
pK_0 Values of the Polymers and Monomers at 25 °C

monomer, polymer	H_2O	45 wt % EtOH
4EP	6.14 ± 0.05,[a] 6.1[b]	4.92 ± 0.05,[a] 5.02[c]
2EP	6.04 ± 0.05,[a] 6.12[b]	4.84 ± 0.05,[a] 5.00[c]
P4VP	5.0 ± 0.3[a,d]	3.8 ± 0.1,[a,d] 3.95[c]
P2VP	5.1 ± 0.5[a,d]	4.1 ± 0.2,[a,d] 3.95[c]

[a] In the presence of 0.1 M NaCl. [b] Reference 15, 0 M NaCl. [c] Reference 15, 0.05 M NaCl. [d] Obtained by the extrapolation to α = 0.

Results and Discussion

Potentiometric titrations of poly(vinylpyridine)s have been carried out by Fuoss and Strauss[14] for P4VP in aqueous solutions and by Kirsh et al.[15] for P4VP and P2VP in aqueous ethanol solutions. The latter reported the pK_0 values for the polymers and the monomers (4EP and 2EP). However, no reliable pK_0 values are available for P4VP and P2VP in aqueous solutions. In Table I, pK_0 values, which were obtained by linear extrapolation to α = 0 of the pK_a vs α plots in Figures 1 and 6, are compared with the literature values. Although the pK_0 values obtained by long extrapolation, as exemplified in Figure 1a, contain somewhat large uncertainty, good agreements are found for the pK values obtained in the present study and in the literature.

It is also seen from the table that pK values of the monomer analogues are higher by ca. 1 pK unit than those of the polymers. As Kirsh et al. pointed out, these results may be ascribed to the lower dielectric constants of the surroundings of the pyridine residues of the polymers. The difference between pK_0 values in the aqueous and aqueous ethanol solutions can be rationalized in the same way.

Parts a and b of Figure 1 show the dependences of pK_a on α for the aqueous solutions of P4VP and P2VP titrated with HCl. Although P2VP has almost the same pK_0 value as P4VP, pK_a values of the former become lower than those of the latter with the increase in α. The same trend

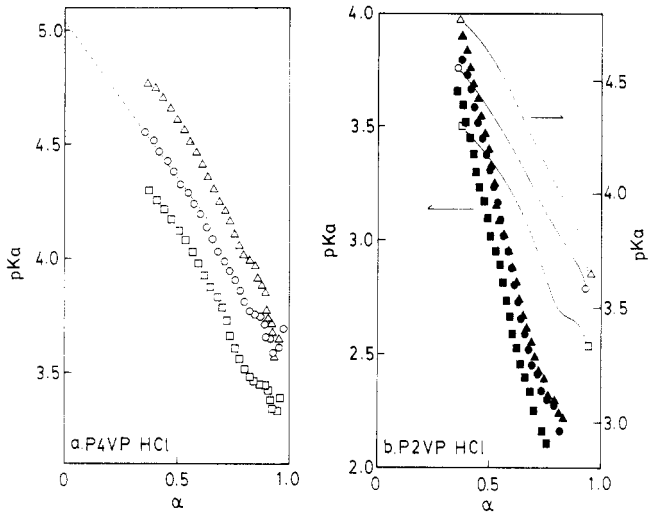

Figure 1. Dependence of pK_a on α for HCl titration in aqueous solutions. (a) P4VP: (△) 10 °C; (○) 25 °C; (□) 40 °C. Dashed line is the linear extrapolation to pK_0. (b) P2VP: (▲) 10 °C; (●) 25 °C; (■) 40 °C. Solid curves represent the pK_a values of P4VP.

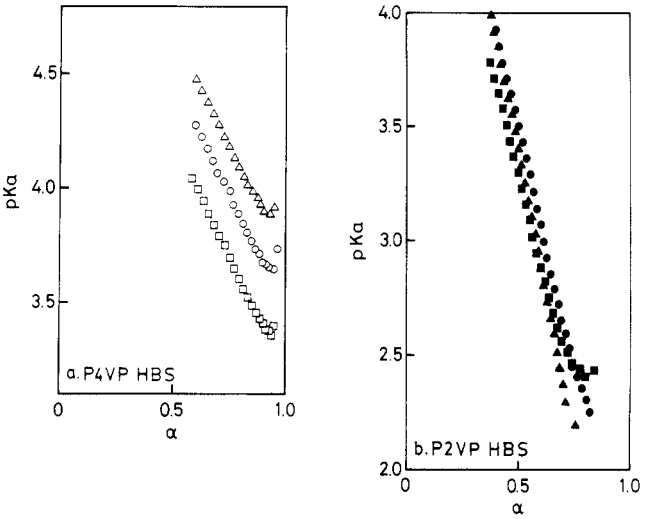

Figure 2. Dependence of pK_a on α for HBS titration in aqueous solutions. (a) P4VP; (b) P2VP. Symbols are the same as in Figure 1.

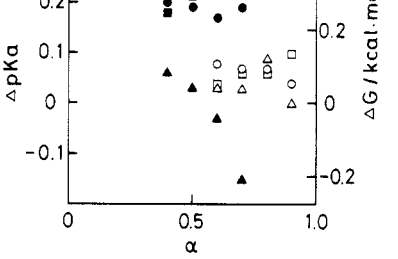

Figure 3. Dependence of ΔpK_a on α in aqueous solutions. Open symbols, P4VP; closed symbols, P2VP: (△, ▲) 10 °C; (○, ●) 25 °C; (□, ■) 40 °C.

can be seen for the aqueous ethanol systems (Figure 6). Kirsh et al. interpreted that the higher pK_a of P4VP is caused by a hydrogen bond formation of Cl^- counterion with the pyridinium proton. However, such charge screening by Cl^- has also been supposed for P2VP by Pierrola et al.[16] The latter authors studied pH dependence of P2VP emission in 50 wt % aqueous ethanol. They attributed the quenching at high α to a charge-transfer complex between the protonated ring and the Cl^- ion. The present authors attribute the higher pK_a values of P4VP to the longer spacing of the charges on P4VP than on P2VP. According to an NMR study on a protonated pyridine,[17] most of the positive charges (>0.7) are delocalized in the proton, α carbons, and α protons. Since the charged sites on the adjacent pyridine groups are closer on P2VP than on P4VP, the electrostatic interaction between the charged groups of P2VP should be stronger than that of P4VP. This accounts for the lowering of the pK_a values for P2VP. As a matter of fact, preliminary viscosity measurements support the above supposition; the specific viscosities of P2VP are higher than those of P4VP at around $\alpha = 0.5$ for both solvents in spite of the lower molecular weight of the former.[18] This fact suggests that P2VP has a more extended conformation under the present titration conditions than P4VP, probably due to the higher electrostatic repulsion between the charged groups. Contrary to the present study and that of Kirsh et al., a transition from a compact conformation to a more expanded one at $\alpha \sim 0.4$ has been reported for P2VP in aqueous and aqueous ethanol solutions.[19,20] If P2VP takes a compact conformation in such a way that the pyridine groups are held close together, the effective charge spacing becomes shorter than that of P4VP. This may partly contribute to the lowering of pK_a values at the α region.

In parts a and b of Figure 2, pK_a values are plotted against α for the titrations with HBS. The scrutiny of Figures 1 and 2 tells us that pK_a values at higher α for P2VP/HBS systems are higher at 25 and 40 °C and lower at 10 °C than those for HCl titration, while for P4VP no appreciable differences are found. For a detailed comparison, ΔpK_a values (relative to those of HCl titrations) are plotted against α in Figure 3.

The negative values for ΔpK_a at 10 °C suggest that the benzenesulfonate ion is less accessible to the polymer charged sites and less effective in screening the polymer charges than Cl^- at the lowest temperature studied here. The higher ΔpK_a values for P2VP at higher temperatures and at higher α suggest that the hydrophobic interaction is in cooperation with the electrostatic one for the counterion binding because the former is enhanced at higher temperatures (<60 °C) and the latter at higher charge densities (α).

The influences of the hydrophobic interaction upon the counterion binding of BS ions may also be seen from the comparison of temperature dependences of pK_a values for P4VP/HCl and HBS (Figure 4a,b) and P2VP/HCl and HBS (Figure 5a,b) systems. As shown in parts a and b of Figure 4, the temperature dependences of pK_a for P4VP are similar for the titrations with HCl and HBS; both the enthalpy changes due to the protonation, estimated by the slopes of the plots, are ca. −2.7 kcal/mol, independent of α. In the case of the P2VP/HCl system (Figure 5a), the corresponding ΔH values are ca. −1.8 kcal/mol. Since the ΔH values for the ionic and the hydrophobic hydrations are both negative, the less negative ΔH value for the P2VP/HCl system may suggest that the local averaged hydration structure is less ordered for the protonated site of P2VP than that of P4VP. On the other hand, Figure 5b shows that the temperature dependences of pK_a of P2VP/HBS systems except for P2VP with $\alpha = 0.8$ exhibit a maximum of pK_a at 25 °C. The decreasing trend of pK_a at 10 °C relative to that at 25 °C becomes remarkable with increasing α, and the inverse is observed for pK_a values measured at 40 °C. The negative slope at $\alpha = 0.8$, which means positive enthalpy change for the protonation, is consistent with the hydrophobic binding formation between the protonated polymer and BS^- ions. Thus, these

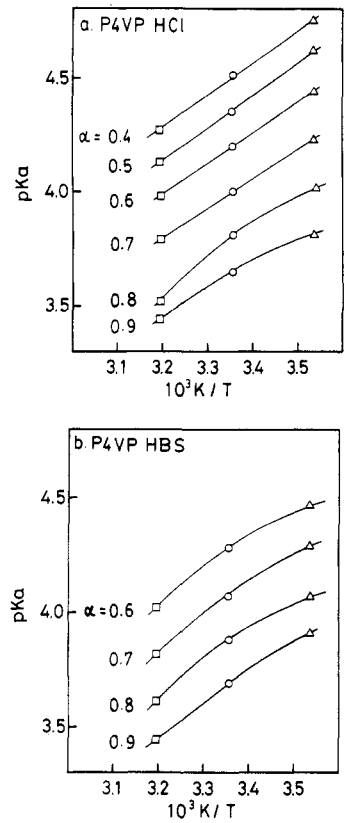

Figure 4. Arrhenius plots of pK_a values for P4VP in aqueous solutions. (a) HCl; (b) HBS: (△) 10 °C; (○) 25 °C; (□) 40 °C.

results, as well as those for ΔpK_a, suggest the participation of the hydrophobic interaction in the counterion binding of P2VP/BS^- system.

Returning to Figure 3, the largest difference of ΔpK_a for P2VP, ca. 0.4 pK unit, is observed between 10 and 40 °C at α = 0.7. If the entire difference is to be attributed to the contribution of the hydrophobic counterion binding, the excess interaction energy relative to the electrostatic one, which we assume here for the case of HCl titration, can be estimated with a counterion condensation theory proposed by the present authors.[4,12] The application of the theory reveals that the pK_a difference can be explained with the excess interaction energies, ~ −0.45 kcal/mol at 40 °C and +0.15 kcal/mol at 10 °C. Such small excess interaction energies may seem to be insignificant in the selectivity of the counterion binding. However, according to the counterion condensation theory, sizable selectivity is to be observed between the relevant counterions. For example, if equal amounts of BS^- ion and Cl^- ion coexist in the relevant system, the theory predicts that the degree of the counterion binding of BS^- is lower by 30% at 10 °C and higher by 80% at 40 °C, respectively, than Cl^-. Studies on the competitive counterion binding are now being undertaken.

In the results mentioned so far, only P2VP shows titration behavior indicative of the hydrophobic interaction between BS^- ion and the polymer. In the case of P4VP, the observed slightly positive ΔpK_a values hardly depend on the temperature and α. Since the charged sites of the latter polymer are relatively apart from the hydrophobic main chain, the positive charges introduced by the protonation are in a relatively hydrophilic atmosphere. Therefore, the hydrophobic interaction between the polymer and BS^- ions may be less important for the counterion binding than that for P2VP.

These results remind us of the study by Turro and Pierola,[10] who investigated the associative interactions of

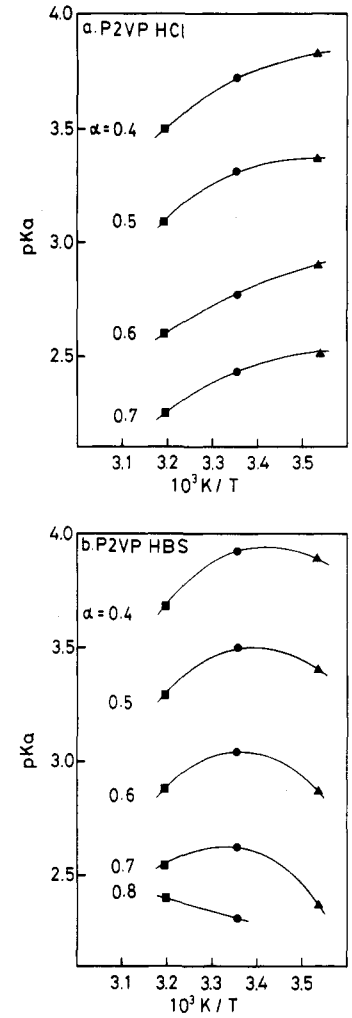

Figure 5. Arrhenius plots of pK_a values for P2VP in aqueous solutions. (a) HCl; (b) HBS: (▲) 10 °C; (●) 25 °C; (■) 40 °C.

arylmethylammonium cations with polyelectrolytes having a sulfonic acid group by fluorescence spectroscopy. In their study, two schemes were proposed for the counterion binding; in Scheme I, where hydrophobic interaction is predominant in the binding, a hydrophobic interior core composed of a polymer main chain and the bound cations is covered by a hydrophilic skin of the charged groups and the electrostrictional hydrations. In Scheme II, where electrostatic interactions predominate over the hydrophobic one, the counterions, remaining "outside" the polymer chain, interact with the hydrophilic portions of the polyelectrolyte. Scheme I seems to apply to the binding mode of benzenesulfonate ion to P2VP and Scheme II to P4VP. Thus, the counterion binding mode seems to vary with the hydration around the polymer and the counterions, particularly when different types of hydrations coexist.

By addition of 45 wt % ethyl alcohol to the relevant systems, it is expected that the hydrophobic interaction becomes inoperative. In parts a and b of Figure 6, pK_a values are plotted against α for P4VP/HCl, HBS and P2VP/HCl, HBS systems, respectively. As expected, both polymer systems show a similar interrelation for the pK_a values obtained by HCl and HBS titrations; namely, at $\alpha \leq 0.5$, PVP/HBS systems have higher pK_a values, and at $\alpha \geq 0.5$, the inverse trend is observed. The differences of pK_a values between HCl and HBS titrations observed at the whole α region may be attributed the accessibility of each counterion to the solvated polymers and the charged sites. Since poly(vinylpyridines) are hydrophobic when

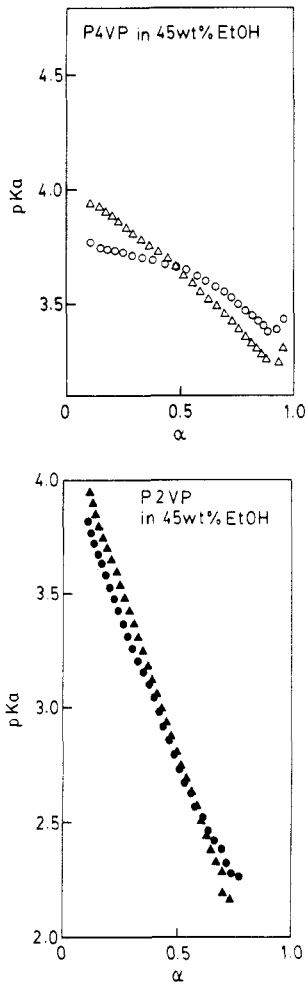

Figure 6. Comparison of α dependences of pK_a values for HCl and HBS titrations in 45 wt % ethanol solutions. (a) P4VP: (○) HCl; (△) HBS; 25 °C. (b) P2VP: (●) HCl; (▲) HBS; 25 °C.

the degrees of protonation are low, the polymers may be preferentially solvated by ethyl alcohol. Therefore, the hydrophobic counterions, BS^-, will be more accessible to the solvated polymers than Cl^- ions. With the increase in α, however, the hydrophilicity of the polymers increases, and the effect of the preferential solvation on pK_a will diminish. At the same time, a more specific interaction between counterions and polymer charges may emerge, as reported by Pielora et al.;[16] a charge-transfer complex between the protonated pyridine rings and Cl^- ions is formed at high α values in the aqueous ethanol solutions. The ability of bulky and soft BS^- ions for such a site binding, in the absence of hydrophobic interactions, seems to be much less than Cl^- ions.

Conclusion

The protonation of poly(vinylpyridines) is largely affected by the chemical structure as well as the solvation of the polymers. The differential behaviors of pK_a values observed for the P2VP/HBS system, dependences of pK_a and ΔpK_a on temperature and α, were explained in terms of the cooperation of the hydrophobic interaction and the electrostatic one in the counterion binding. As found between P4VP and P2VP in the present study, a slight difference in the position of the charged site seems to produce a significant effect on the counterion binding (mode) through the different local hydrations of the charged sites.

Registry No. 4EP, 536-75-4; 2EP, 100-71-0; HBS, 98-11-3; P4VP, 25232-41-1; P2VP, 25014-15-7; HCl, 7647-01-0.

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