

## Temperature Dependence of Viscosities and Potentiometric Titration Behavior of Poly(*N*-vinylimidazole) in Aqueous Salt Solutions

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**ABSTRACT:** The potentiometric titration behavior has been studied for the aqueous solutions of poly(*N*-vinylimidazole) (PVI) in the presence of various supporting electrolytes, NaCl, NaBr, NaNO<sub>3</sub>, NaI, NaSCN, and NaClO<sub>4</sub> at 5, 25, and 45°C. At low degree of neutralization  $\alpha'$ , an inflection on the titration curve and turbidity of solution have been observed for the systems containing NaNO<sub>3</sub>, NaI, NaSCN, or NaClO<sub>4</sub> with appropriate concentration. The viscosities of aqueous NaBr solutions of PVI have been measured at 5, 25, and 45°C as a function of  $\alpha'$ . The solution viscosities increase with temperature throughout the whole range of  $\alpha'$ . The intrinsic viscosity- $\alpha'$  curves pass through a minimum followed by normal increase with the increase in neutralization. The initial contraction of the polymer chain may be attributed to the formation of intramolecular chelate-like bridge between protonated and unprotonated imidazole rings.

**KEY WORDS** Viscosity / Potentiometric Titration / Poly(*N*-vinylimidazole)  
/ Aqueous Solution / Conformational Change /

Previously we reported the viscosities and potentiometric titrations for aqueous poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) as a function of temperature.<sup>1</sup> From these results pH-induced conformational transition observed for the PMA solution has been discussed in connection with hydrophobic interactions, hydrogen bonding, and local geometry of the polymer chain. At present, however, the exact nature of such a conformational transition is still poorly understood. It is interesting that a similar conformational change has been observed for poly(*N*-vinylimidazole) (PVI) in some solvent systems. Liu and Gregor<sup>2</sup> reported that the reduced viscosity of PVI in aqueous NaCl increases with the degree of neutralization in a manner similar to the normal polyacids like PAA, while in the

presence of NaBr or NaNO<sub>3</sub> it decreases to a minimum during the initial stage of neutralization and then increases normally. They have attributed this anomalous viscosity behavior as being due to intramolecular association with hydrogen bond or triple-ion ( $-\text{N}^+-\text{Br}^--\text{N}^+-$ ) formations. In the studies of potentiometric titration, viscosity, and NMR, IR, and Raman spectroscopies, Tan and co-workers<sup>3,4</sup> have found the conformational transition of PVI in methanol/acetonitrile mixed solvent and in some aqueous salt solutions, but not found if the ionic strength is very low. They have accounted for the transition by considering the competition between electrostatic repulsion force and hydrogen bonding attraction between protonated and unprotonated imidazole rings.

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In order to clarify the conformational transition of some synthetic polyelectrolytes in water, we have studied the effects of temperature and added neutral salts on the viscosity and potentiometric titration behavior of aqueous poly(*N*-vinylimidazole) solutions.

## EXPERIMENTAL

### Materials

Purified *N*-vinylimidazole was dissolved in benzene and polymerized under nitrogen atmosphere with azobis(isobutyronitrile) as an initiator. The white solid polymer precipitated from the reaction solution was washed with benzene. The polymer sample was purified by dissolving in methanol, precipitation with diethyl ether, and then dried. The sample used in this study was further purified by dialysis of the aqueous solution and then freeze-dried. The molecular weight was estimated to be about  $3 \times 10^5$  from the viscosity measurement in methanol solution at 25°C.<sup>5</sup> All other chemicals were guaranteed reagent grade and used without further purification.

### Potentiometric Titrations

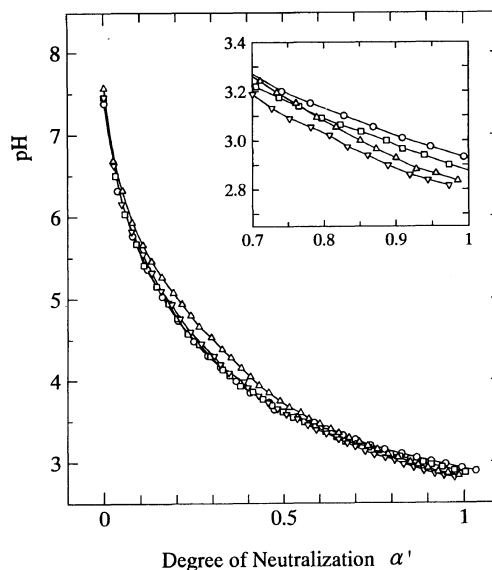
The pH measurements were made using an Orion Model 801A ion meter equipped with a Denkikagaku MG511 glass electrode and a Horiba 2535A calomel electrode connected by a saturated KNO<sub>3</sub>-agar salt bridge. The titrations of PVI were carried out with 0.15 M HCl, HBr, and HNO<sub>3</sub> in the presence of 0.2 M NaCl, NaBr, and NaNO<sub>3</sub> as a supporting electrolyte, respectively, under nitrogen atmosphere at 5, 25, and 45°C. The titrations were also carried out with 0.15 M HCl for the systems containing NaClO<sub>4</sub>, NaSCN, and NaI at 25°C. In most cases a constant pH value could be attained within 5 min after the titrant was added. For some systems, however, the reproducibility of pH reading was invariably poor in a certain neutralization range where the turbidity of solution was observed.

### Viscosity Measurements

By adding a calculated amount of 0.5 M HCl solution to the stock solution, we obtained solutions of PVI with various degrees of neutralization;  $\alpha' = 0, 0.1, 0.2, 0.3, 0.5, 0.8,$  and 1.0. The viscosities of these polymer solutions containing 0.2 M NaBr were measured by using a Ubbelohde-type dilution viscometer at 5, 25, and 45°C. Flow time of water in the viscometer used was about 300 s at 25°C and a kinetic energy correction could be neglected. The temperature of the thermostat bath was maintained within 0.02°C using a thermister temperature controller constructed in our laboratory.

## RESULTS AND DISCUSSION

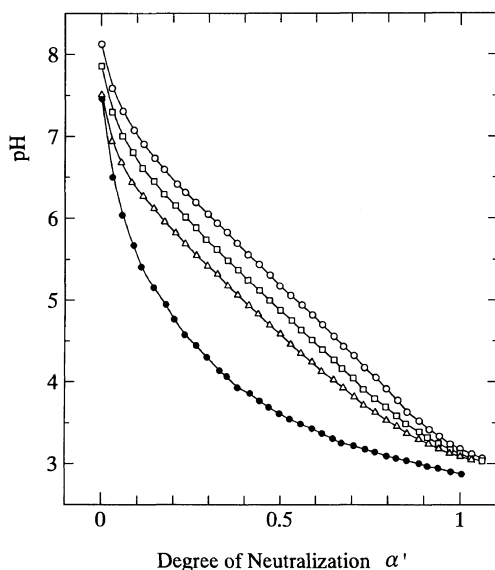
In Figure 1 are shown the potentiometric titration curves for PVI in water with 4 titrants, 0.15 M HCl, HBr, HI, and HNO<sub>3</sub> solutions, at 25°C. Because of weak basicity of PVI, the pH values of neutralized PVI are lowered and thus the end point inflection can never be observed.



**Figure 1.** Potentiometric titration curves for poly(*N*-vinylimidazole) in the absence of supporting electrolyte at 25°C with various 0.15 M titrants: ○, HCl; □, HBr; △, HNO<sub>3</sub>; ▽, HI. The polymer concentrations are 4.08, 4.67, 5.95, and  $6.29 \times 10^{-3}$  monomol dm<sup>-3</sup>, respectively.

It is obvious that the pH values titrated with HCl, HBr, and HI fall virtually on the same smooth curve at low neutralizations. By contrast, as is evident from the high-neutralization inserts, the pH values decrease in the order of  $\text{HCl} > \text{HBr} > \text{HI}$ . This order coincides with the acid strength of these titrants,<sup>6</sup> and hence the small difference in the titration behavior at higher  $\alpha'$  regions may be resulted from the difference in the degree of hydrolysis of PVI salts. As has been pointed out by Tan *et al.*,<sup>3</sup> in salt-free PVI solutions, the potentiometric titration curves do not have any transition point like PMA or other polyelectrolytes exhibiting conformational transition.<sup>1</sup>

Figure 2 shows the titrations with HBr in the presence of 0.2 M NaBr at 5, 25, and 45°C, along with the results for salt-free solution at 25°C. The presence of supporting electrolyte causes the screening effect due to the counterion within the polymer coil, which then increases the base strength of partially neutralized PVI. It is evident that the basicity of PVI decreases with the increase in temperature. This is in



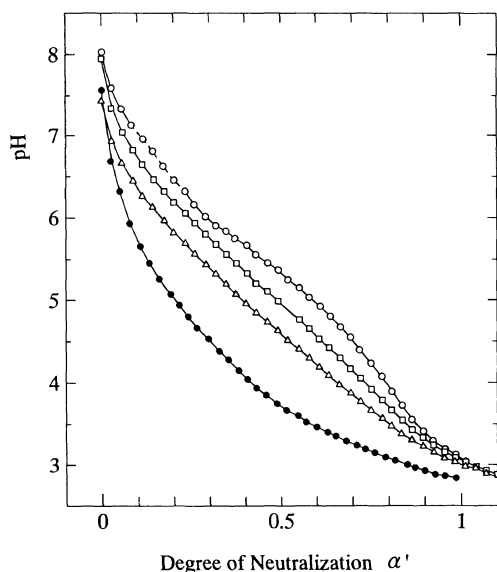
**Figure 2.** Potentiometric titration curves for PVI with 0.15 M HBr in the presence of 0.2 M NaBr at  $\circ$ , 5°C;  $\square$ , 25°C;  $\triangle$ , 45°C; and  $\bullet$ , in salt-free solution at 25°C. The polymer concentration is  $4.67 \times 10^{-3}$  monomol  $\text{dm}^{-3}$ .

marked contrast to the study of polycarboxylic acids such as poly(acrylic acid), of which the acid strength is almost independent of the temperature over the entire neutralization range.<sup>1</sup>

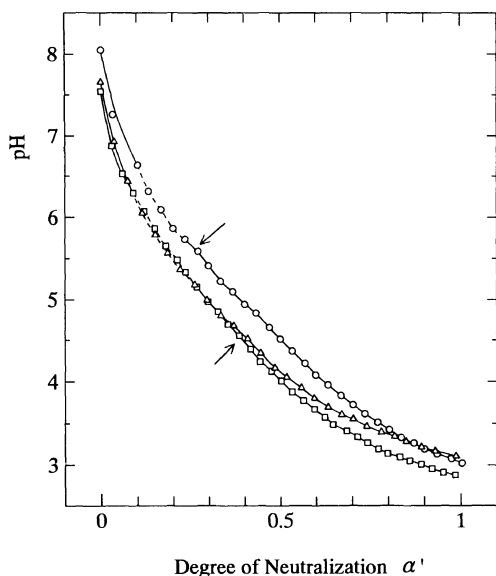
A very similar behavior was observed for the pH titration of PVI with HCl in NaCl solution at various temperatures. The presence of large amount of anions  $\text{Cl}^-$  or  $\text{Br}^-$  influences the base strength of protonated PVI in a manner similar to each other and gives a smooth sigmoidal titration curves. These solutions were clear throughout the whole range of  $\alpha'$  if the concentration of supporting electrolyte is less than 1 M. Although pH-induced conformational transition can be suggested for the system of PVI+0.2 M NaBr from viscosity behavior as will be shown later, no clear-cut transition in titration curve was found. This fact is in contrast to the case of aqueous PMA solution, which exhibits marked transition in both viscosity and pH-titration curve.

In general, the pH-titration results have been represented in terms of modified titration curve, that is, the plot of dissociation constant *vz.* degree of dissociation. As will be described below, however, the titration of PVI in salt solutions, except for NaCl or NaBr, are accompanied by more or less precipitation of PVI, and hence the degree of protonation or equilibrium constant can not be estimated exactly. In the present analysis, therefore, we used normal plot of pH vs. degree of neutralization rather than modified plot.

On the other hand, the addition of the other anions brings about somewhat different titration behavior. In Figure 3 are shown the titration curves of PVI with  $\text{HNO}_3$  in 0.2 M  $\text{NaNO}_3$  aqueous solution. The curves obtained at 25 and 45°C are analogous to those described in Figure 2. At 5°C, however, turbidity was observed in the  $\alpha'$  range from 0.1 to 0.2 and an unusual inflection point was detected at nearly  $\alpha' = 0.4$ . Figure 4 represents the pH titrations with HCl in the presence of 0.05 M NaI, 0.01 M NaSCN, and 0.006 M  $\text{NaClO}_4$  at



**Figure 3.** Potentiometric titration curves for PVI with 0.15 M  $\text{HNO}_3$  in the presence of 0.2 M  $\text{NaNO}_3$  at  $\circ$ , 5°C;  $\square$ , 25°C;  $\triangle$ , 45°C; and  $\bullet$ , in salt-free solution at 25°C. The polymer concentration is  $5.95 \times 10^{-3}$  monomol  $\text{dm}^{-3}$ . The dotted line represents the turbid solution (see the text).



**Figure 4.** Potentiometric titration curves for PVI with 0.15 M  $\text{HCl}$  in the presence of  $\circ$ , 0.05 M  $\text{NaI}$ ;  $\square$ , 0.01 M  $\text{NaSCN}$ ;  $\triangle$ , 0.006 M  $\text{NaClO}_4$  at 25°C. The polymer concentrations are 5.04, 5.67, and  $4.53 \times 10^{-3}$  monomol  $\text{dm}^{-3}$ , respectively. The dotted lines represent the turbid solutions (see the text).

25°C. The higher concentrations of these supporting electrolytes bring about precipitation of unneutralized PVI. In these systems turbidity of solution was observed in the  $\alpha'$  range from 0.1 to 0.2 or 0.3 as represented by dotted lines, and subsequent small inflection was found at low degree of neutralization designated by arrows in Figure 4. With the further increase in  $\alpha'$ , the turbid solutions redissolve and are completely clarified again prior to half neutralization.

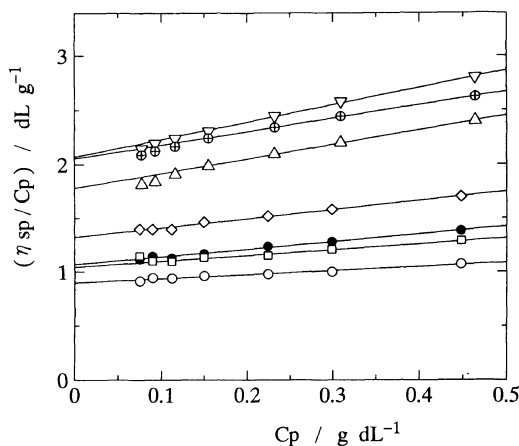
Thus, the appearance of inflection point in the titration curve of PVI depends on the nature and concentration of counterions and on temperature. It is to be noted that titrations having such an inflection are accompanied more or less with turbidity of solution for all systems studied here. It appears that the trend of precipitation of PVI by the addition of anions increases in the order  $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{SCN}^- < \text{ClO}_4^-$ , based on the minimum concentration of these ions required for the observation of turbidity of the solutions. No obvious explanation for the salting-out (or salting-in) effects have been offered at the present time since a very complex feature has often been reported according to various polymer-salt systems or salt concentrations. It is to be noted, however, that the above order is just reverse of the well-known salting-out Hofmeister series, which is usually interpreted in terms of the variation of hydration of added salts.<sup>7</sup> Therefore, the decrease in solubility of partially protonated PVI may be attributed to the direct interactions between ions and polar groups in the polymer chain, but not to the change of interactions between nonpolar groups of PVI and solvent due to, for instance, the alteration of water structure by the introduction of the ions.<sup>8</sup>

Tan and coworkers<sup>3</sup> have found a similar unusual pH titration behavior for PVI in some organic solvents and in some electrolyte solutions. They have also studied by means of viscometry and NMR spectroscopy and concluded that the conformational change of

PVI is resulted from competition between an intramolecular hydrogen bonding between protonated and unprotonated imidazole rings and charge repulsion. The pH-induced conformational change for PVI, however, seems to be less definitive in the pH titration where only faint inflection can be observed. This is in clear contrast to the well-known conformational transition of poly(methacrylic acid).<sup>1</sup> In our opinion, the inflection found in the pH titration curves at low  $\alpha'$  may be attributed to the change of the concentration of imidazole moiety to be neutralized because of the precipitation and subsequent redissolution of PVI during titration process, but not to the conformational change of polymer chain.

Liu and Gregor<sup>2</sup> have reported that the viscosity of PVI increases normally with neutralization in the absence of neutral salt or in the presence of NaCl, whereas it decreases to a minimum and then increases normally with increasing  $\alpha'$  in the presence of NaBr or NaNO<sub>3</sub>. They have explained this anomalous viscosity behavior by considering the significant intramolecular association such as  $-N^+-Br^- - N^+$  bond, which contracts the polymer chain.<sup>9</sup>

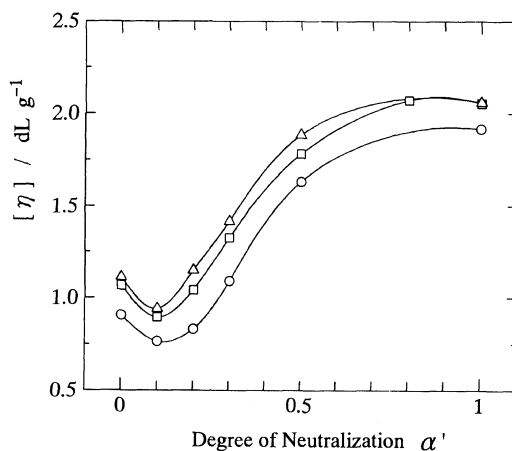
Among the neutral salts used in this study,



**Figure 5.** Reduced viscosities of PVI with various degrees of neutralization  $\alpha'$  in 0.2 M NaBr solutions at 25°C. The  $\alpha'$  values are ●, 0; ○, 0.1; □, 0.2; ◇, 0.3; △, 0.5; ▽, 0.8; ⊕, 1.0.

the addition of NaCl and NaBr do not bring about any precipitation of PVI throughout the whole range of neutralization at all temperatures and salt concentrations examined. Therefore, we measured viscosities of only NaBr solutions of PVI at various temperatures. Figure 5 represents the reduced viscosities,  $\eta_{sp}/C_p$ , of PVI having various degrees of neutralization in the presence of 0.2 M NaBr at 25°C. In the concentration range studied, the reduced viscosity can be generally represented by the well-known relation:  $\eta_{sp}/C_p = [\eta] + k'[\eta]^2 C_p$ , where  $[\eta]$  is intrinsic viscosity,  $k'$  is Huggins constant and  $C_p$  is polymer concentration. It should be noted that the reduced viscosities of higher  $\alpha'$  samples deviate slightly below from the linear relation at low concentrations. This may be resulted from the increase in hydrolysis of protonated imidazole moiety with the decrease in polymer concentration. In this case, the values of  $[\eta]$  were estimated by a linear extrapolation from the data at higher concentrations.

In Figure 6 are shown the plots of  $[\eta]$  vs.  $\alpha'$  at 5, 25, and 45°C. It might be expected that the viscosity increases monotonously with increasing neutralization owing to the increase in the electrostatic repulsion between charged groups on the polymer chain. At initial stage of

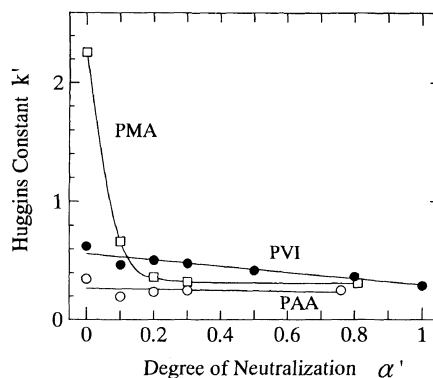


**Figure 6.** The intrinsic viscosities  $[\eta]$  of PVI with various degrees of neutralization  $\alpha'$  in 0.2 M NaBr solutions at ○, 5°C; □, 25°C; △, 45°C.

neutralization, however, the intrinsic viscosities decrease and pass through a minimum at about  $\alpha' = 0.1$ . Further neutralization brings about the normal increase in viscosity as observed for most polyacids, although the magnitude of its increase is considerably less than that for the PAA or PMA solutions with similar molecular weight and ionic strength<sup>1</sup> owing probably to the hydrolysis of fully protonated imidazole ring.

Our previous study<sup>1</sup> reported that a similar unusual viscosity behavior has been observed in the poly(methacrylic acid) solution at lower temperatures. In PMA solution, however, the feature is somewhat different from the PVI system. That is, the viscosities of the PVI solutions increase with increasing temperature throughout the whole range of  $\alpha'$ , whereas the negative temperature dependence has been observed for the viscosity of non-ionized or slightly ionized PMA. Furthermore, the viscosity minimum disappears at higher temperatures than 25°C for the PMA solution whereas it is almost independent of temperature for the PVI solution as displayed in Figure 6. It is also to be noted that the titration of PMA is not accompanied with any turbidity or precipitation of the polymer. We have interpreted the viscosity minimum observed for the PMA solutions in terms of hydrogen-bond formation which is considered to be very sensitive to temperature. The temperature-insensitive minimum observed for PVI solution, therefore, should be explained by the intramolecular interactions other than hydrogen bonding, as claimed by Tan and coworkers.<sup>3,4</sup>

At present it is difficult to account for such a strong attraction force since no detailed studies have been made of any of the origin of above phenomenon. Considering the low solubility of partially neutralized PVI in some salt solutions, however, the promising explanation seems to be that the formation of chelate-like bridge such as  $-N^+-Br^- - N-$  bond between protonated and unprotonated imidazole residues through counterions reduces the effective



**Figure 7.** Huggins constants  $k'$  of poly(*N*-vinylimidazole) (PVI), poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) solutions as a function of degree of neutralization  $\alpha'$  at 25°C. The ionic strength is 0.2 (NaBr) for PVI and 0.25 (NaCl) for PAA and PMA solutions.

charge on the polymer chain and hence initial contraction occurs. This attractive interaction may be more enhanced for the anions such as  $I^-$ ,  $SCN^-$ , or  $ClO_4^-$  when considered with the strong precipitating ability of these anions. Further increase in neutralization may increase the normal electrostatic repulsion force, which brings about the destruction of the bridge and the redissolution of the moderately protonated PVI, and hence the solution viscosity is increased.

There are again significant difference in the viscosity behavior of PVI and PMA solutions. Figure 7 shows the  $\alpha'$  dependence of the Huggins constants  $k'$  at 25°C, along with the values obtained for PAA and PMA in 0.25 M NaCl solutions<sup>1</sup>; the ionic strength is similar to the present study. As has been reported previously,<sup>1</sup> the viscosity behavior for the compact form of slightly ionized PMA is characterized by extraordinarily large value of  $k'$ . After the conformational transition with further increasing neutralization, the  $k'$  values are almost identical to those for PAA, and are consistent with the value expected for good solvent systems;  $k' = 0.2-0.3$ . On the other hand, the  $k'$  values obtained for PVI in 0.2 M NaBr solutions decrease linearly from  $k' = 0.6$  at  $\alpha' = 0$  to  $k' = 0.3$  at  $\alpha' = 1$ . That is, the

PVI solutions varies continuously from poor solvent, possibly  $\theta$ -condition, to good solvent system,<sup>10</sup> according to the increase in protonation.

In conclusion, the compact-to-extended coil change of poly(*N*-vinylimidazole) in aqueous salt solutions is induced rather continuously by pH variation. This phenomenon is apparently in contrast to the abrupt conformational transition observed for poly(methacrylic acid). The intramolecular attraction resulting in the compact coil form of partially protonated PVI is largely dependent on the nature of anions of supporting electrolytes but not temperature. Although we cannot definitely conclude the origin of such an attraction forces, it seems likely to be attributed to the formation of chelate-like bridge between protonated and unprotonated imidazole rings.

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