

Some Properties of Aqueous-Solutions of Poly(vinylamine chloride)

Zhiyong Hu, Shufen Zhang, Jinzong Yang, Yu Chen

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China

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ABSTRACT: In this study three types of poly(vinylamine chloride) (PVAmHCl) with different amination degrees were prepared from the Hofmann degradation of polyacrylamide. The behavior of dilute aqueous solutions of PVAmHCl was compared by viscosimetric, conductometric, and potentiometric measurements, and by consideration of the degree of amination. The results show that with increasing amination degree of polyvinylamine (PVAm) from 55 to 78%, the m value (a measure of electrostatic interactions of neighboring groups on the chains) increased from 3.65 to 5.14, and the reduced viscosity of PVAmHCl decreased

somewhat. With increasing ionic strength, the maximum of the reduced viscosity decreased. Moreover, the pK_a value of PVAmHCl decreased from 8.33 to 7.47 with increasing amination degree of PVAm from 55 to 78%. At the same time, the equivalent conductivity gradually decreased with increasing concentration of the polymer and was enhanced with increasing amination degree of PVAm. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3889–3893, 2003

Key words: polyelectrolytes; solution properties; viscosity

INTRODUCTION

Polyvinylamine (PVAm) is a kind of attractive polymer with a simple structure. It has an exceptional potential reactivity because of the presence of primary amino groups along the hydrocarbon main chain. It is widely used in catalysis,^{1,2} chelation,³ biomedical research,^{4,5} liquid chromatography,^{6,7} treatment of wastewater,⁸ paper making,⁹ and the recovery of oil¹⁰ and so on. Because it reacts with carbon dioxide, PVAm is not stable in the atmosphere. It is commonly used and stored in the form of polyvinylamine chloride (PVAmHCl) salt. PVAmHCl is a polyelectrolyte that is highly hygroscopic. It can be freely dissolved in water. Although there are a few articles on the solution properties of highly pure PVAmHCl samples an investigation on the properties of aqueous solutions of PVAmHCl prepared from the Hofmann degradation of polyacrylamide (PAM) has not been reported.

In this study, PVAm's with different amination degrees were prepared from the Hofmann degradation of PAM, and their aqueous solution properties, viscosity, pH, and conductivity, were compared.

EXPERIMENTAL

Materials

NaOCl was prepared before use, and other chemicals were analytical-grade reagents.

Preparation of PAM

The polymerization of acrylamide was carried out in a 40% aqueous solution with the use of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaHSO_3 initiator at 80°C for 5 h. The resulting polymer was purified by reprecipitation twice from water-ethanol. The nitrogen content of PAM was 18.92%. The intrinsic viscosity ($[\eta]$) was 0.27 (dL/g), which was determined at 25°C in aqueous solution with an Ubbelohde dilution-type viscometer (Beijing, China). The number-average molecular weight (M_n) was calculated from the following Mark-Houwink equation:¹¹
$$[\eta](\text{dL/g}) = 6.8 \times 10^{-4}/M_n^{0.66}$$

Hofmann degradation of PAM

PVAmHCl was prepared according to the method described by Achari.¹¹ We prepared an NaOCl aqueous solution by passing chlorine gas through a 30 wt % NaOH solution in an ice bath and titrating it by iodometry just before use. The mixture of 1M NaOCl and 15M NaOH aqueous solution were cooled to about -10°C. A 10 wt % solution of PAM in water was cooled to about 0°C and added into the mixture under vigorous stirring. After 1.5 h, a second amount of 11M NaOH cooled to about -10°C was added. The reactor was kept at -10°C for 0.5 h and then at 0°C for 17 h.

Correspondence to: S. Zhang (zhangsh@chem.dlut.edu.cn).

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TABLE 1
Data for the Copolymers of Vinylamine and Acrylamide

Polymer	$\text{---} \left[\text{CH}_2\text{---CH} \right]_a \text{---} \left[\text{CH}_2\text{---CH} \right]_b \text{---}$ <div style="display: flex; justify-content: space-around; width: 100%;"> <div style="text-align: center;"> CONH_2 </div> <div style="text-align: center;"> NH_2HCl </div> </div>			M (g/mol)
	Content of N ⁺ (%) ^a	Content of Cl (%)	Amination degree (%)	
PAA	18.92	—	—	71
PVAmHCl-55	17.96	46.88	55.65	75.73
PVAmHCl-69	18.01	46.15	69.64	76.92
PVAmHCl-78	17.89	45.72	78.11	77.64

M = average molecular mass of the constitutional repeating unit.

^a Determined by the Kjeldahl method.

We isolated the polymer by pouring the mixture into about a four-fold amount of methanol. The resulting precipitate was dissolved in water, and 6M HCl was added dropwise to this solution with stirring until the acidity was maintained at pH-2. Finally, the polymer was precipitated as a hydrochloride from a mixture of methanol and acetone. After washing, the polymer was dried in vacuum at 40°C.

Measurement of the amination degree

The amination degree was determined by the measurement of the chlorine content of the product. PVAmHCl (0.5g the accuracy was 0.001) was dissolved in 100/mL of water with stirring. Conductometric titration with 0.1N AgNO₃ was made, and the amination degree of PVAm was calculated from eq. (1):

$$C \times \frac{V}{1000} = \frac{mx\%}{79.5x\% + 71(1 - x\%)} \quad (1)$$

$$x\% = \frac{71CV}{1000m - 8.5CV} \times 100\% \quad (2)$$

where $x\%$ is the amination degree, C is the concentration of AgNO₃ solution (mol/L), V is the volume of AgNO₃ solution (mL), m is the mass of sample (g), and 79.5, and 71 are the average molecular masses of the PAM and PVAmHCl units, respectively (g/mol).

Viscosity measurements

Viscosity (η) measurements were made at 25°C with a Ubbelohde dilution-type viscometer with a flow time of 240.8 s for distilled water at 25°C.

Potentiometric titrations were performed at 25°C with a PHS-25 pH meter (Wei Ye Instrument Company, Shanghai, China).

The electrical conductivity of diluted aqueous solutions was determined at 25°C with a DDS-12A instru-

ment (Xiaoshan Analysis Instrument Company, Zhejiang, China).

RESULTS AND DISCUSSION

According to previous works^{11,12,13} although some side reactions such as hydrolysis of amido groups to form alkylacrylureas and alkylureas and the cleavage of the hydrocarbon main chain would take place during the Hofmann degradation of PAM, these reactions could be effectively prevented if the reaction temperature were low enough, when the molar ratio of NaOCl/CONH₂ were not more than 1, and when the average molecular weight of PAM were not too high. On the basis of these results, we prepared PVAmHCl assuming approximately the same average chain length but different amination degrees (Table I). With

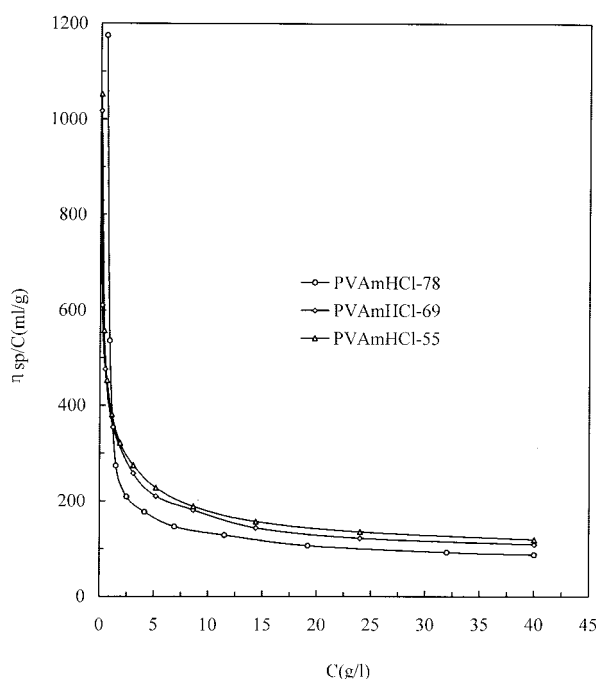


Figure 1 Reduced viscosity versus concentration.

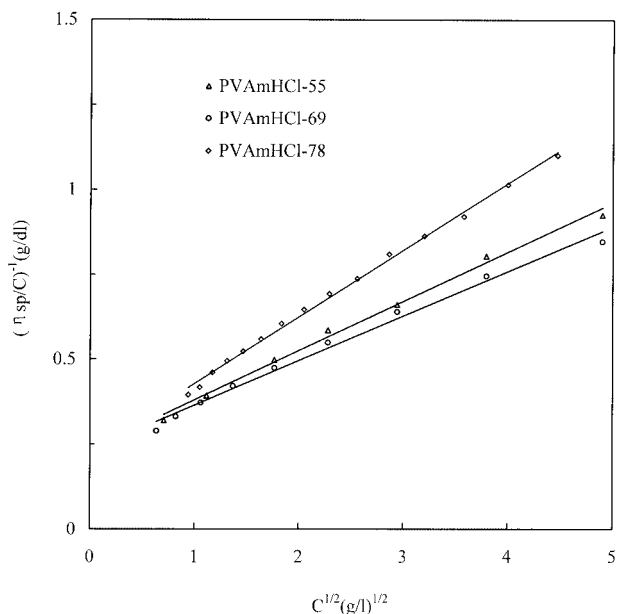


Figure 2 $(\eta_{sp}/C)^{-1}/-C^{1/2}$ relations for PVAmHCl with different amination degrees.

use of η and conductivity measurements and potentiometric titrations of diluted aqueous solutions of individual copolymers the behaviors of the PVAmHCl's were compared with regard to the degree of amination.

η measurements

Figure 1 present the relationship between the reduced viscosity and the concentration of PVAmHCl. All of the copolymers in the form of PVAmHCl showed the typical behavior of a polyelectrolyte—the increase in reduced viscosity (η_i/C) with decreasing concentration. When the concentration of the copolymer was lower than 5 g/L, the reduced viscosity increased dramatically with decreasing concentration, which was ascribed to the fact that PVAmHCl is a kind of polyelectrolyte with flexible chains. Thus, when the concentration was low, the shielding effect of counterion was weak. Due to the ionization groups on the molecular chains, the electrostatic repulsion between the neighboring groups became strong, which was good for the polymer stretch and enhanced the reduced viscosity greatly. Also, the higher the amination

TABLE II
 $[\eta]$ of PVAmHCl Calculated from Figure 2

PVAmHCl	$[\eta]$ (dL/g)	B	R ²
PVAmHCl-78	4.322	0.850	0.9971
PVAmHCl-69	4.296	0.565	0.9906
PVAmHCl-55	4.263	0.620	0.9948

R² = coefficient constant of equations.

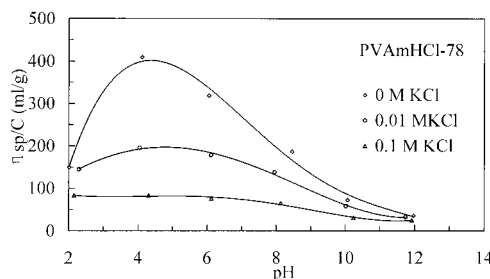


Figure 3 Reduced viscosity versus the pH of PVAmHCl-78.

degree was, the larger the increase was in reduced viscosity. This was caused by the charge repulsion, which resulted from the relatively high charge density of PVAmHCl with a high amination degree.

$[\eta]$ of polyelectrolytes can be calculated from eq. (2):

$$\left(\frac{\eta_{sp}}{C}\right) = \frac{[\eta]}{1 + B\sqrt{C}} \tag{2}$$

Figure 2 shows the relationship between the reduced viscosity and the square of the concentration of PVAmHCl. In Figure 2, the $[\eta]$ values of PVAmHCl with different amination degrees are shown, and they are also listed in Table II. $[\eta]$ of PVAmHCl was much higher than that of PAM; however, the effect of the amination degree of PVAmHCl on its $[\eta]$ was very slight.

Figures 3–5 illustrate the relationship between the reduced viscosity (η_i/C mL/g) and the pH of aqueous solutions of PVAm with different amination degrees under various ionic strengths (μs ; 0, $\mu s = 0.01$, and 0.1 mol/L of KCl). The η behaviors of the three samples were similar over the wide pH range 2–12. As the ionic strength decreased, a relatively steep peak appeared at about pH when $\mu = 0$ and 0.01 mol/L of KCl. In this pH region, the polymer structure was supposed to be the most stretched due to the electrostatic repulsion among neighboring ammonium groups. In the region pH > 4, the reduced viscosity decreased gradually because the electrostatic repulsion become relaxed, and the flexibility of the polymer chain was enhanced.

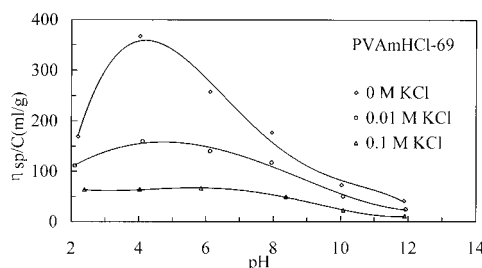


Figure 4 Reduced viscosity versus the pH of PVAmHCl-69.

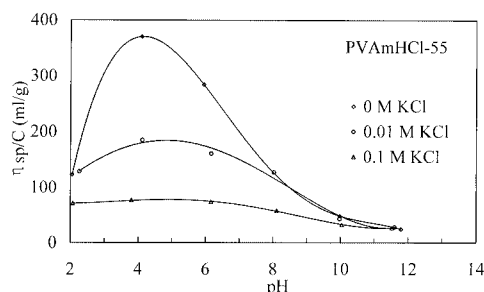


Figure 5 Reduced viscosity versus the pH of PVAmHCl-55.

However, η dramatically decreased with increasing pH in the region $\text{pH} < 4$, which was probably due to increasing the counterion (i.e., chloride anion) concentration. Moreover, it was clear that reduced viscosity decreased with increasing ionic strength. The reason is that as the concentration of counterions increased, the shielding effect produced by counterions on the charges of the main chain became strong, which led to a decrease in the number of groups with charges on the main chain and the electrostatic repulsion of PVAmHCl.

Potentiometric titrations

The potentiometric titration of a polyelectrolyte solution is closely related to the electrostatic interaction between a dissociating proton and an ionized group on the main chain of the polymer. Figure 6 shows the plot of pH versus the degree of neutralization of the copolymer (α) and presents the potentiometric titration curves of three PVAmHCl's with different amination degrees in a salt-free aqueous solution. As shown in the figure, the higher the amination degree of PVAmHCl was, the lower the initial pH value was. Also, it was apparent that PVAmHCl behaves as a monobasic acid. As the amination degree increased from 55.65 to 78.11%, the pH value of its aqueous solution rose from 2.87 to 3.96.

Figure 7 presents Henderson–Hasselbalch plots of

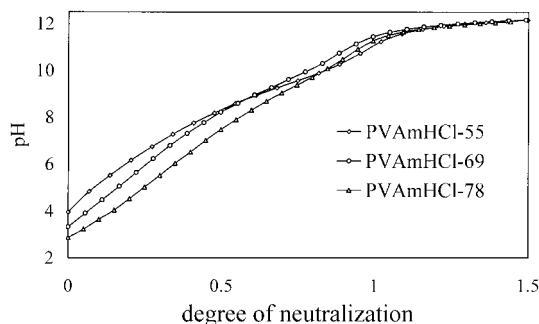


Figure 6 Potentiometric titration (pH vs. degree of neutralization).

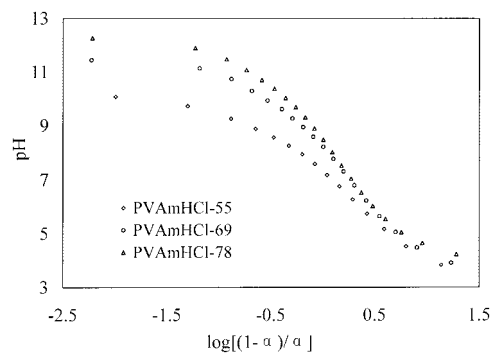


Figure 7 Henderson–Hasselbalch plots.

the simple neutralization of the curves in Figure 6. The Henderson–Hasselbalch equation is expressed as following:

$$\text{pH} = \text{p}K_a - m \log \frac{1 - \alpha}{\alpha} \quad (3)$$

where α is the degree of neutralization K_a is the average dissociation constant, and m is a constant that can be used to measure the electrostatic interactions of neighboring groups on the main chain of the polymer. The value of m can be obtained from the slope of plots at an α value range between 0.2 and 0.6 and $\text{p}K_a$ can be obtained from the intercept of the plot. The m and $\text{p}K_a$ values of PVAmHCl with different amination degrees are list in Table III. This table shows that with increasing amination degree of PVAm from 55 to 78%, the m value increased from 3.65 to 5.14 and the $\text{p}K_a$ decreased somewhat. This result reveals that the electrostatic interactions of neighboring groups on the main chain of the polymer were enhanced as the amination degree of the copolymer increased.

Conductivity measurements

The electrical conductivity of a polyelectrolyte solution can be used as a measurement of the ionization degree of the polyelectrolyte. The amount of free ions determines the conductivity of the aqueous solution. The amount of free ions contributing to the conductivity is dependent on the dimension and charge density of polyions. Figure 8 shows the dependence of equivalent conductivity (λ) on the molar concentration (C_p) for the dilute aqueous solutions of PVAmHCl

TABLE III
Data from the Simple Titration Curves for PVAm

Polymer	$x\%$	m	$\text{p}K_a$
PVAmHCl-55	55.65	3.65	8.33
PVAmHCl-69	69.64	4.68	8.23
PVAmHCl-78	78.11	5.14	7.47

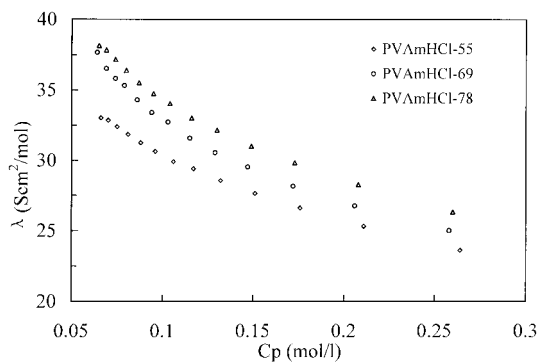


Figure 8 Equivalent conductivity versus the concentration for aqueous solutions of PVAmHCl.

with different amination degrees. For all of the three copolymers, the equivalent conductivity decreased with increasing concentration of PVAmHCl. Moreover, the higher the amination degree of PVAmHCl was, the higher the equivalent conductivity was. This was probably because the charge density of PVAmHCl with a higher amination degree was higher than that with lower amination degree.

CONCLUSIONS

The Hofmann degradation of PAM at -10 to about -15°C , $\text{NaOCl}/\text{CONH}_2 < 1$, and $M_n < 10,000$ did not

change the average chain length of the main chain, but the type and the character produced a marked change in physical properties. Dilute aqueous solutions of three types of PVAmHCl showed typical characteristics of polyelectrolytes. With increasing amination degree, the equivalent conductivity increased somewhat, and the electrostatic interactions of the neighboring groups on the main chain were enhanced. Also, with increasing ionic strength from 0 to 0.1 mol/L of KCl, the reduced viscosity of PVAmHCl decreased.

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