Polymer Vol. 39 Nos. 6–7, pp. 1387–1392, 1998
PII: S0032-3861(97)00431-X
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

Counterion binding and ionomer-like behaviour of partially quaternized poly(4-vinyl pyridine) in aqueous alcohols

Daisuke Kawaguchi, Susumu Kawauchi, Mitsuru Satoh* and Jiro Komiyama
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Tokyo, Japan

(Received 11 February 1997; revised 21 April 1997)

Counterion binding of poly(4-vinyl pyridine) which was quaternized to different extents (10, 15, 20, 25, 30, 35 mol%) was investigated by measuring the apparent counterion activity and the reduced viscosity for the aqueous alcohol (methanol, ethanol and 2-propanol) solutions. Plots of the activity data against the dielectric constant of the solvent suggested that, at a charge density which was close to the critical one for the counterion condensation predicted by Manning theory, the counterions start to be bound to the polyion more strongly than expected by the non-specific condensation mode. At the same critical points, the reduced viscosity started to decrease in spite of an increase in the charge density of the polyion. The polymer concentration dependence of the reduced viscosity suggested that the polycation assumes an ionomer-like conformation in a higher concentration region. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyelectrolyte; counterion binding; ionomer)

INTRODUCTION

In recent years the coil–globule transition of weakly charged polymers has been theoretically and experimentally investigated by the group of Khokhlov and other researchers with remarkable results. Khokhlov[1] predicted that in a monomer concentration region, $c_e \ll c \ll c_b$ (c_e is the mean monomer concentration in the case of an extended coil, and c_b is the mean monomer concentration in a blob), the collapse of polyelectrolyte is closely connected with the 'avalanche-type' counterion condensation. According to Mandel *et al.* [2], sodium polyacrylate in methanol seems to show the coil–globule transition with an increasing degree of neutralization, being consistent with the prediction by Khokhlov[1]. As for polyion gels, the volume phase transition has been observed even for aqueous systems; Kudo *et al.*[3] and Khokhlov *et al.* [4] have found that polycations such as poly(N-n-butyl-4-vinylpyridinium bromide) and poly (diallyldimethylammonium chloride) show transitions to the collapse states in the presence of iodide counterion. All these findings indicate that the transition takes place in much polar medium and for polyions of much higher charge densities than expected for the traditional ionomer formation[5].

In a previous study[6], we examined the counterion binding of poly(allylamine)hydrochloride (PAlAm·HCl) in aqueous alcohols and found that a specific counterion binding such as a contact ion-pair formation becomes appreciable in a lower dielectric constant region below the dielectric constant (D)~*ca.* 50, although no sign for formation of the ionomer-like conformation was observed. The dependence of the counterion activity on D was interpreted by a counterion condensation model (Intermediate Model, IMM[7]) which we have proposed as an extension of the Manning theory. In the present study, we have measured the apparent activity of Cl^-, the counterion of partially quaternized poly(4-vinyl pyridine), and the reduced viscosity in aqueous alcohols. The initial aim was to investigate the effect of the dielectric constant on the counterion condensation around a charge density, $\xi = e^2/DkTb = 1$ (e is the electronic charge, and b is the charge spacing), which has been predicted as being critical for counterion binding by the Manning theory[8]. Since we had excluded the possibility of formation of the ionomer-like conformation in the relevant solvent systems of relatively high polarity, we had expected that similar behaviour to that in poly(allylamine) would be observed for the counterion activity as a function of D. However, as shown in the following, both of the experimental results on the activity and the viscosity strongly suggested that a conformational change occurs, which appears to be triggered by the counterion condensation. In this report, we discuss the correlation between the counterion condensation and the ionomer-like conformational change or ion cluster formation in comparison with the previous study on PAlAm·HCl.

EXPERIMENTAL

Preparation of polymers

Poly(4-vinyl pyridine)(P4VP), purchased from Koei Chemical Co. Ltd, was purified by reprecipitation in diethylether. The molecular weight was estimated as 2.3 $\times 10^5$ by viscometry[9]. P4VP thus prepared was quaternized by ethylbromide in different amounts (10, 15, 20, 25, 30, 35 mol%) in 5 wt.% nitromethane solution at 46°C for 5 days. The samples quaternized to 25, 30 and 35 mol% were collected as precipitates in an ice bath, and 10, 15,

---

* To whom correspondence should be addressed

20 mol% samples were collected by addition of dioxane. The degrees of quaternization were estimated by ^{1}H NMR peak area for α proton (for unquaternized N at 6.0 ppm and for quaternized N at 6.6 ppm) as 10.2%, 14.8%, 18.9%, 24.3%, 29.1% and 34.6%, respectively. Thus, we simply used 0.1, 0.15, 0.20, 0.25, 0.30 and 0.35 as the respective quaternization degrees or charge densities in the following discussion.

The counterion species of the polymer samples was exchanged to Cl$^-$ by ultrafiltration (ultrafilter UP-20 and UK-10, Toyo Roshi) in the presence of excess amounts of HCl. Afterwards the solution was neutralized by NaOH and then ultrafiltrated in distilled water five times. The samples were collected by freeze-drying. Since a precipitation was formed for P4VP of lower charge densities by the alkali addition, the precipitate was thoroughly washed by distilled water and then dried in a vacuum oven at 90°C for 24 h. The polymer samples having Cl$^-$ as the counterion, are abbreviated as, for example, P4VP·EtCl(0.35).

Counterion activity measurement

Apparent activity of Cl$^-$ in the relevant polymer solutions was measured with a Cl$^-$ selective electrode (Orion9417B) at 25 ± 0.1°C. The detailed description on the measurement and the estimation of the apparent activity is found in a previous paper[6].

The polymer concentration, C_p, for the measurement was adjusted to keep the counterion concentration at 2.0×10^{-3} M. The reason why we did not use a usual concentration scale such as g dm^{-3} or mol of pyridine residue dm^{-3}, is that a constant ionic strength seems to be more essential for the activity and the viscosity measurements in the absence of added salt. Thus the C_p values were 0.218, 0.155, 0.124, 0.099, 0.085 and 0.074 g dl^{-1}, respectively for 10–35% quaternization.

Alcohol species and the composition used for preparing the polymer solutions were as follows: methanol(MeOH), 20, 80 vol.%; ethanol(EtOH), 20, 40, 60, 80 vol.%; 2-propanol(2PrOH), 20, 80 vol.%

Viscosity measurement

The reduced viscosity was measured for the same polymer systems as the activity measurement with an Ubbelohde viscometer (Shibata 2613-0005) at 25 ± 0.1°C. For water and 80 vol.% EtOH systems, dependence of the reduced viscosity on C_p was also investigated for the C_p region 0.03–0.15 g dl^{-1}.

RESULTS AND DISCUSSION

Activity coefficient

Figure 1 shows the apparent activity coefficient, γ', of Cl$^-$ as a function of the degree of quaternization or the charge density for the respective solvent systems. For aqueous solution or 0 vol.% alcohol, the dependence of γ' on the charge density is slight, while it becomes much more marked with increasing alcohol concentration. This behaviour is qualitatively natural because any increase in the alcohol content is accompanied by a decrease in the dielectric constant and, hence, results in an increase in the counterion condensation degree. However, a crucial question here is whether the decrease in γ' is quantitatively or at least semi-quantitatively explained in the framework of the counterion condensation concept. This was examined by replotting the γ' data as a function of the dielectric constant (D) for the respective P4VP·EtCl of different degrees of quaternization in *Figure 2a–f*. The figures contain theoretical curves by the counterion condensation model (IMM) which has been proposed by us. As seen in *Figure 2a*, the prediction is satisfying for the polymer of the lowest charge density, 0.10. For the higher charge density polymers (0.15–0.35), however, the theoretical curves underestimate γ' in the higher D region and the decreasing tendency of γ' in the lower D region. The former disagreement may be ascribed to an inherent limit of the counterion condensation theory, which seems to overestimate the contribution of polyelectrolyte to the ionic strength in a dilute system ($C_p \ll 10^{-2}$ M) as suggested by a previous study[10]. However, it should be noted here that the decreasing tendency of γ' or the slope of the plot is almost correctly reproduced by the theory in the higher D region. Hence, the points where the experimental γ' values start to deviate from the theoretical decreasing tendency may be considered as showing where the counterion condensation mode fails. In *Table 1*, solvent properties at the 'critical' points are summarized . Note that the charge density parameters, ξ, estimated for the critical points are close to unity. This strongly suggests that an onset of counterion binding of the condensation mode triggered the subsequent significant decrease in γ', namely a stronger counterion binding. These experimental results remind us of the prediction by Khokhlov on the 'avalanche' type counterion binding, according to which counterion condensation is enhanced by contraction of the polymer chain through the concomitant decrease in the effective dielectric constant for the ion pair formation. As stated in the Introduction, some examples which seem to be consistent with the Khokhlov's theory have already been found and the characteristic behaviour is a sudden decrease in the viscosity[2] or collapse of the polymer volume with increasing polymer charge density[11]. Thus, we have measured the reduced viscosity of P4VP·EtCl under the same experimental conditions (same

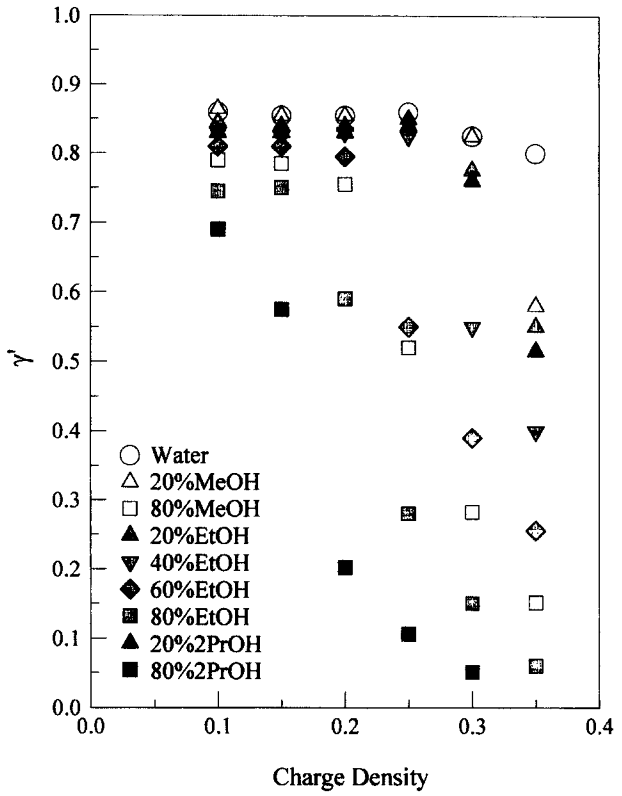

Figure 1 Dependence of the apparent activity coefficient (γ') of Cl$^-$ on the polymer charge density

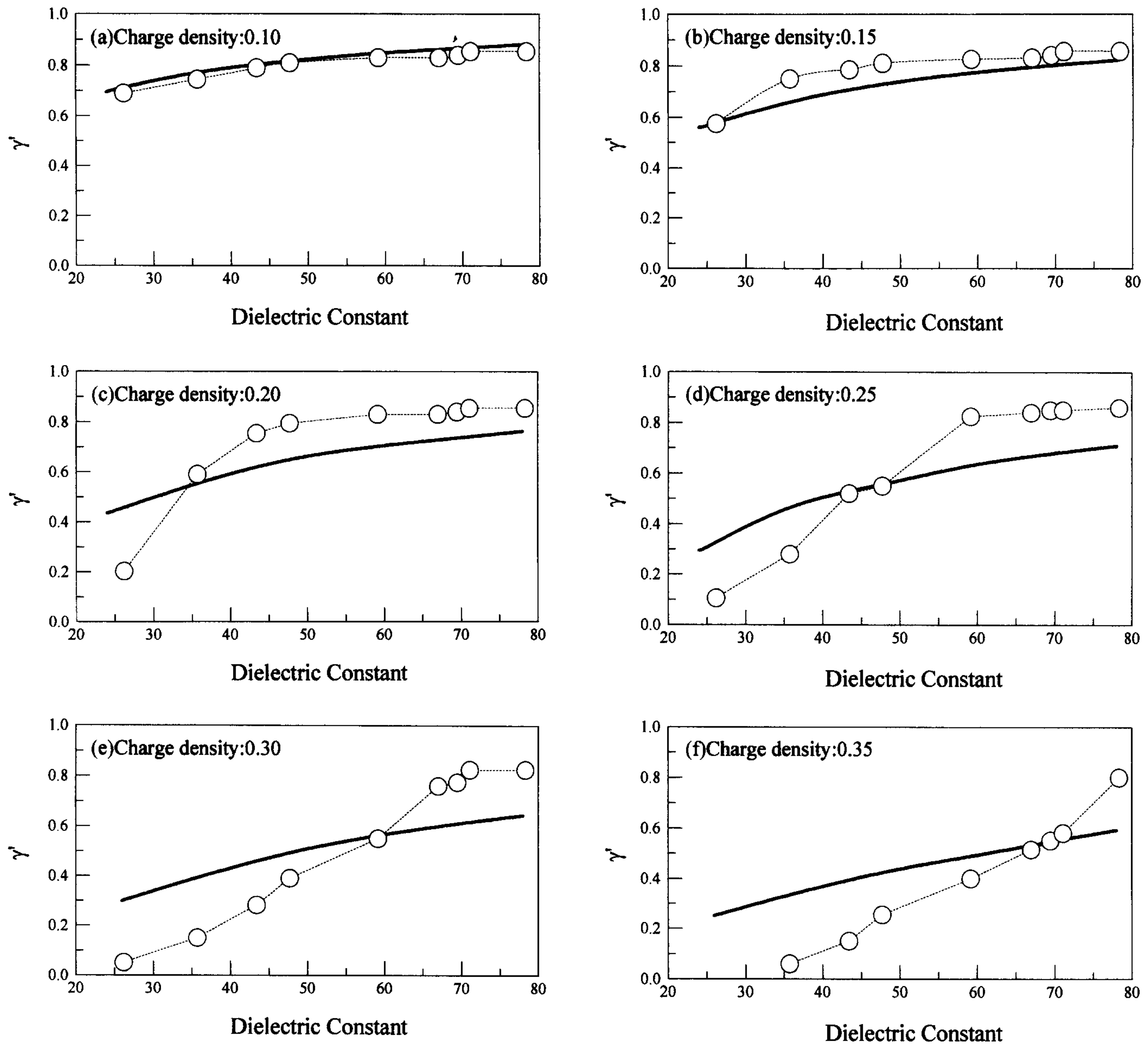

Figure 2 Dependence of γ' on the dielectric constant of the solvents. Polymer charge density: 0.10(a), 0.15(b), 0.20(c), 0.25(d), 0.30(e), 0.35(f)

polymer concentrations, same solvent compositions) as in the activity measurements to see whether the appreciable deviation in the counterion activity from the condensation mode is accompanied by any conformational change.

Reduced viscosity

In *Figure 3*, the reduced viscosities were plotted against the charge density for the respective solvent systems. A monotonical increase in the viscosity was observed only for the water system; for the other solvent systems which contain at least 20% of alcohol, the reduced viscosity decreased with increase in the charge density. Since the critical points where the viscosity starts to decrease (*Figure 3*) are almost consistent with those observed for the activity measurement (*Figures 1 and 2*), the origin for this characteristic decrease in the activity and viscosity with increasing polymer charge density seems to be the same. This type of non-polyelectrolyte behaviour is similar to the ionomer formation of slightly charged polymers in a non-polar medium. The conformational transition predicted by Khokhlov may be regarded as one type of ionomer formation. Since it has been known that reduced viscosity of ionomers in solution decreases with decreasing polymer concentration[5], which is a contrast to the usual polyelectrolytes, we examined the dependence of the reduced viscosity on the polymer concentration for water and 80 vol.% EtOH systems. *Figure 4a* shows that the reduced viscosity for P4VP·EtCl in the water system monotonically increases with decrease in the polymer concentration,

Table 1 Solvent properties and the charge densities at the critical points

Alcohol	Vol.%	D	Charge density	ξ
MeOH	20	71.1	0.3	0.94
	80	43.4	0.2	1.03
EtOH	20	69.5	0.3	0.96
	40	59.2	0.25	0.94
	60	47.7	0.20	0.93
	80	35.7	0.15	0.94
2PrOH	20	67.0	0.30	1.00
	80	26.8	0.10	0.83

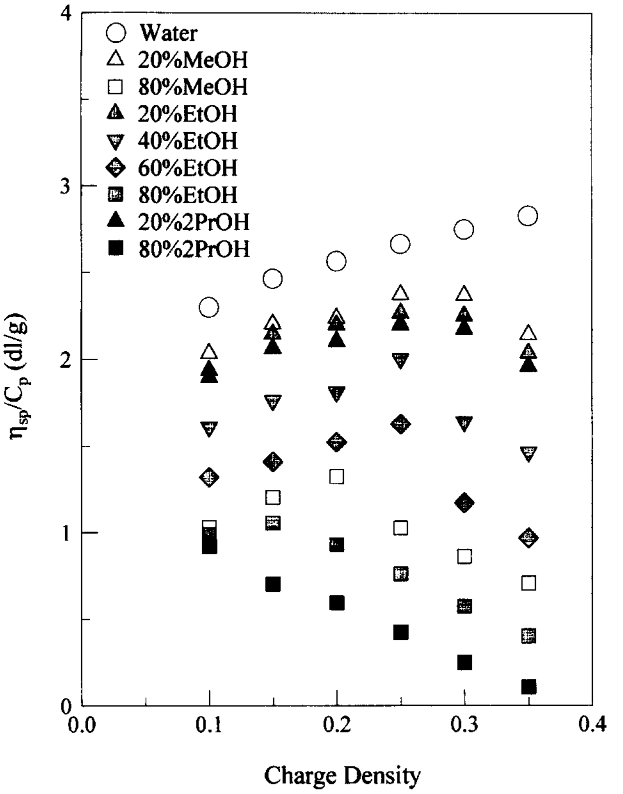

Figure 3 Dependence of the reduced viscosity (γ_{sp}/C_p) on the polymer charge density

typical behaviour of polyelectrolytes in the absence of added salts. On the other hand, in 80 vol.% EtOH (*Figure 4b*), the reduced viscosity once decreases and then increases with decrease in C_p, except for the lowest charge density polymer, for which no specific behaviours have been observed in the activity and viscosity measurements. This result suggests that the characteristic decrease in the counterion activity and the concomitant viscosity decrement with increasing polymer charge density accompany a transition to an ionomer-like conformation. This conformation seems to be much more loose and the stability of the ion cluster is much weaker than that supposed for the so-called collapse state of a polyelectrolyte chain, since the ionomer-like conformation seems to be untied just with a further decrease in C_p.

Comparison with other studies

As stated in the Introduction, we investigated the counterion binding of poly(allylamine) hydrochloride in aqueous alcohols by measuring the apparent activity of Cl^-, the apparent molar conductivity and the reduced viscosity. According to the study[6], dependence of the activity on D was satisfactorily reproduced by IMM in the higher D region, while the disagreement in the lower D region was adjusted by assuming an extra interaction energy[7], ΔE_{ex}, for each of the solvent systems. For example, we could reproduce the counterion activity at 80 vol.% MeOH by introducing $\Delta E_{ex} = -2.5$ kcal mol^{-1} to the free energy minimization calculation for the counterion binding system. This level of interaction energy for the counterion binding may be rationalized by assuming a contact ion-pair formation between the counterion and the polymer charge. However, one needs to assume much stronger interaction between Cl^- and the present polyion in order to explain the low γ' values as observed in the present study. For example, in the same solvent (80 vol.% MeOH), the present γ' value for P4VP·EtCl(0.35) is only reproduced by assuming $\Delta E_{ex} = -4.8$ kcal mol^{-1}. The actual difference of the two interaction energies might be much larger, since IMM inherently overestimates the interaction between counterion and polyion for the present low C_p system.

A direct comparison of the experimental and the theoretical γ' values also suggests that the present decrease in γ' is much more significant than that for PAlAm·HCl system. For example, the experimental γ' value of Cl^- for PAlAm·HCl in 75 vol.% 2PrOH ($D = 30$) was *ca.* half of the theoretical prediction by IMM, while that for P4VP·EtCl(0.35) in 80 vol.% EtOH ($D = 36$) is *ca.*

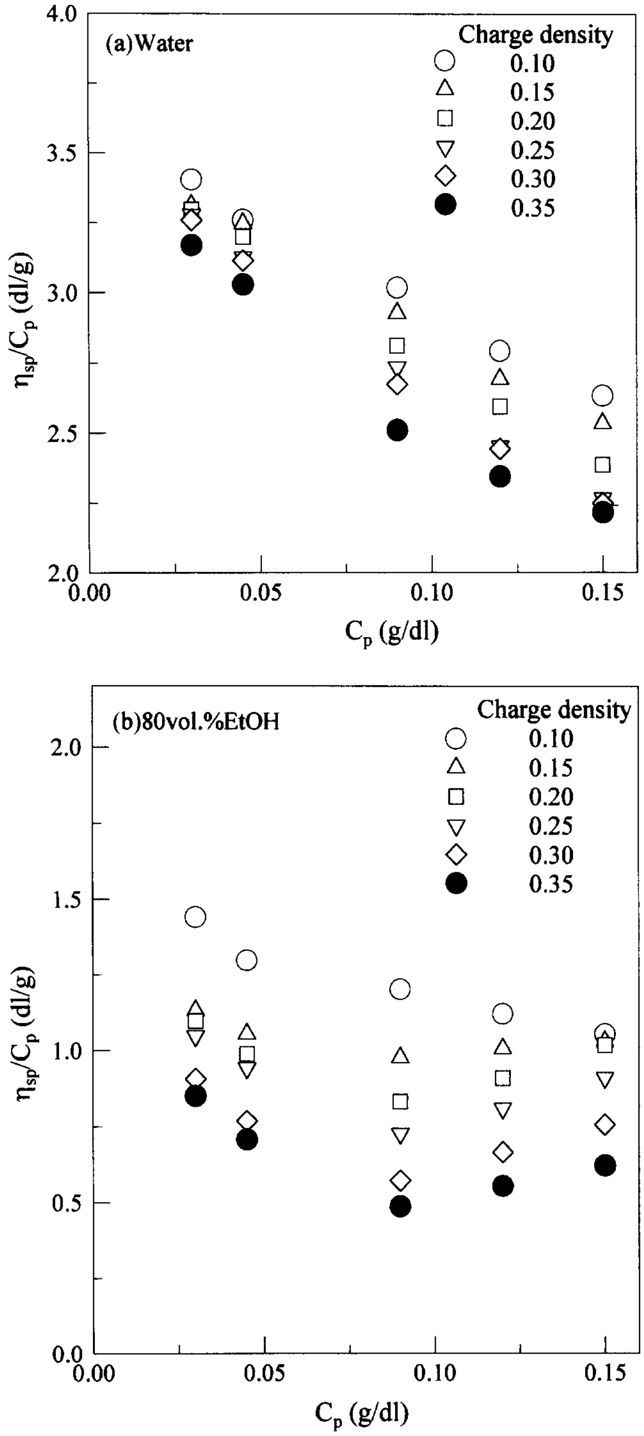

Figure 4 Dependence of η_{sp}/C_p on the polymer concentration (C_p). Solvent: water (a), 80 vol.% EtOH (b)

one-sixth as low as IMM's prediction, or it may be even one-tenth, if one takes the inherent underestimation of γ' by IMM into account.

The decrease in the reduced viscosity with decreasing D is also more significant for the present P4VP·EtCl than that observed for PAlAm·HCl; the ratio of the reduced viscosity to that of aqueous solution is *ca.* 1/7 for P4VP·EtCl(0.35) in 80 vol.% EtOH, while it was *ca.* 1/5.7 for the latter in 75 vol.% 2PrOH. This may appear only a slight difference. However, since the dimension of a polyion of a higher charge density, in this case PAlAm·HCl, should be more effectively reduced with a decrease in D or with a suppression of the electrostatic repulsion among the polymer charges due to the contact ion-pair formation, the apparent slight difference in the degrees of the polymer size reduction, in fact, suggests that the extent of the polymer chain contraction of P4VP·EtCl(0.35) is much larger than that of PAlAm·HCl.

All these comparisons on γ' and the reduced viscosity with those for PAlAm·HCl indicate that the specific counterion binding such as the contact ion-pair formation in the present polyion systems is more effectively stabilized than usual by some mechanism, which we suppose to be caused by an ionomer-like conformation. If this is the case, a question will arise as to why the ionomer-like conformation was not observed for PAlAm·HCl systems. Here we consider two factors as the reason: one is the difference in the selective solvation and the other is that of the molecular weight or chain length. The former will be determined by the charge density and the monomer's chemical property of the pertinent polyions. Since PAlAm·HCl is almost fully charged and the monomer residue has a relatively less hydrophobic moiety, it is expected to be preferentially hydrated in aqueous alcohols. As a matter of fact, an appreciable dependence of γ' on the alcohol species was observed for PAlAm·HCl, even when compared at the same dielectric constant, a result interpreted in terms of a difference in the preferential hydration degree. In the present study, as shown in *Figure 2*, the dependence of γ' on D seems to be expressed as a smooth line for the three kinds of aqueous alcohol systems. This means that P4VP·EtCl is not preferentially hydrated or preferentially solvated by the alcohols, and may be explained by the lower charge density and the hydrophobic monomer constitution compared with PAlAm·HCl. Thus, the medium around PAlAm·HCl should be more polar than PVP·EtCl, and it would be less favourable for the ionomer-like conformation.

The molecular weight is also largely different for the two polyions: 2.3×10^5 (DP = 2200) and 6.0×10^4 (DP = 640) for P4VP and PAlAm·HCl, respectively. According to the study on sodium poly(acrylate) in MeOH by Mandel *et al.*[12], the conformational transition to the collapsed state was observed only for higher molecular weight samples (DP > 800), which is qualitatively consistent with the theoretical prediction on the coil–globule transition by Khokhlov. Although the present results may not correspond to a typical coil–globule transition (see below), it seems natural to assume that an ionomer-like conformation modelled as a multiplet cluster of ion-pairs[13] would also be more stable for longer polyions. Thus, the relative shortness of the PAlAm·HCl chain can be a cause for showing only polyelectrolyte behaviour. It should be noted here, however, that the experiments on PAlAm·HCl were performed only for aqueous alcohols; a possibility that this polycation shows a transition to an ionomer-like conformation still remains in less polar systems such as pure alcohols.

As stated above, the conformational change observed here is not so critical as that of sodium poly(acrylate) (PAANa) in MeOH. The decrease in η_{sp}/C_p with increasing charge density of P4VP·EtCl (*Figure 3*) is far less remarkable compared with the results of PAANa, and the dependence of η_{sp}/C_p of P4VP·EtCl on C_p showed a minimum, not a typical behaviour in an ionomer polymer. These results suggest that the supposed ionomer-like conformation is less stable and more loose than the so-called collapsed state in the coil–globule transition, probably corresponding to an intermediate of the extended and collapsed states of PAANa in MeOH. The reason may be simply ascribed to the relatively polar medium, i.e. aqueous alcohol, used here instead of non-polar solvents. Although marked collapse has been observed for polycationic gels in aqueous solution[3,4], this has been ascribed partly to hydrophobic interaction and partly to strong ion-pair formation between the quaternary ammonium cation and counterion, especially iodide anion. In the present case, the former contribution is lacking and the latter, namely counterion binding of Cl^-, is also weaker than that of I^-. Therefore, use of large anions such as I^- and SCN^-, which have been known to be strongly bound to polycations[14], as a counterion of the present system may result in a more critical conformational transition, even in aqueous solution.

A relation of the conformational transition and the counterion condensation has been explicitly incorporated into Khokhlov's theory on the polyion collapse as the avalanche-type counterion condensation. This counterion condensation mode, assumed for the collapse state, seems to be somewhat different from the mechanism supposed in the present study that a transition to an ionomer-like conformation is triggered by the counterion condensation. In fact, a typical collapse found for Na poly(acrylate) in MeOH occurred at a lower charge density than that for $\xi = 1$; the peak of the reduced viscosity appeared at $\alpha = 0.1$ which corresponds to $\xi = 0.68$. It seems also difficult to interpret the behaviour of PAALi system, which shows a maximum of the reduced viscosity at $\xi \approx 1.4$, suggesting no direct correlation between the appreciable decrease in the viscosity with increasing polymer charge density and non-specific counterion condensation. Further data will be necessary to conclude the 'condensation-triggered' conformational transition supposed here.

In conclusion, in this paper we have demonstrated that an ionomer-like conformational transition occurs under a relatively unfavourable condition, namely aqueous alcohols as the solvents and Cl^- as the counterion. Further, we suggested that the transition is triggered by counterion condensation. Whether the transition which was observed in the solution system also occurs in the gel system or not, and its relation to the counterion condensation will be investigated in a subsequent paper.

REFERENCES

1. Khokhlov, A. R., *J. Phys. A.: Math. Gen.*, 1980, **13**, 979.
2. Klooster, N. Th. M., van der Touw, F. and Mandel, M., *Macromolecules*, 1984, **17**, 2070.
3. Kudo, S., Konno, M. and Saito, S., *Polymer*, 1993, **34**, 2370.
4. Starodoubtsev, S. G., Khokhlov, A. R., Sokolov, E. L. and Chu, B., *Macromolecules*, 1995, **28**, 3930.
5. Lantman, C. W., MacKnight, W. J., Peiffer, D. G., Sinha, S. K. and Lundberg, R. D., *Macromolecules*, 1987, **20**, 1096.
6. Miura, S., Satoh, M. and Komiyama, J., *Polymer*, 1996, **37**, 1641.
7. Satoh, M., Kawashima, T. and Komiyama, J., *Biophys. Chem.*, 1988, **31**, 209.

8. Manning, G. S., *J. Chem. Phys.*, 1969, **51**, 924.
9. Boyes, A. G. and Strauss, U. P., *J. Polym. Sci.*, 1956, **22**, 463.
10. Satoh, M., Kawashima, T., Komiyama, J. and Iijima, T., *Polym. J.*, 1987, **19**, 1191.
11. Khokhlov, A. R. and Kramarenko, E. Yu., *Macromolecules*, 1996, **29**, 681.
12. Klooster, N. Th. M., van der Touw, F. and Mandel, M., *Macromolecules*, 1984, **17**, 2078.
13. Eisenberg, A., Hird, B. and Moore, R. B., *Macromolecules*, 1990, **23**, 4098.
14. Makino, S. and Sugai, S., *J. Polym. Sci. Part-2*, 1967, **5**, 1013.