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Counterion binding of poly(allylamine) hydrochloride in aqueous alcohols

Shintaro Miura, Mitsuru Satoh* and Jiro Komiyama
Department of Polymer Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
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Counterion binding has been investigated for poly(allylamine) hydrochloride (PAlAmHCl) in aqueous alcohols (methanol, ethanol, and 2-propanol). The activity of Cl^- was estimated as an apparent value by using an ion-specific electrode and compared with the theoretical prediction obtained from a counterion condensation theory. Marked deviations or overestimations of the counterion activity obtained by the theoretical method were observed for the higher-concentration regions of the respective alcohols. This has been attributed to a specific counterion binding which should be more favourable in a medium with a lower dielectric constant and of a lower solvation energy. Similar deviations were also observed for the molar conductivities of the polymer in the same solvent systems. These latter deviations could be remarkably reduced by introducing the extra interaction energy term, i.e., ΔE_{ex}, for the specific counterion binding that was used to correct the observed deviations for the counterion activities. By utilizing the ΔE_{ex} values as a measure of this specific counterion binding, the dependence on the alcohol species has been discussed in terms of the dielectric constant, preferential solvation and the Gutman–Mayer acceptor number. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyelectrolyte; counterion binding; solvent effect)

INTRODUCTION

Theoretical studies of the counterion binding of polyelectrolytes in solution systems have become extensively advanced during the last three decades. This development has been largely helped by the counterion condensation concept that was proposed by Oosawa[1] and Manning[2] and also through criticisms to the condensation model proposed by the Poisson–Boltzmann group[3], particularly for the condensation 'phase'. Although the condensation theory may not be appropriate for modelling the counterion distribution around a polymer chain, it has been widely and successfully applied in a variety of other fields[4–9]. The major merit of the theory seems to be in its simplicity. According to the Oosawa–Manning theory, the degree of counterion condensation, θ, for a univalent counterion, is given by the following equation:

$$\theta = 1 - \xi^{-1} \tag{1}$$

where

$$\xi = e^2/DkTb \tag{2}$$

with e being the unit charge, D the bulk dielectric constant, k the Boltzmann constant, T the temperature (K), and b represents the axial charge spacing.

A great deal of research has been carried out in order to test equation (1), in most cases by using polyelectrolytes with different charge densities or b values[10–12]. However, another key parameter appearing in ξ, namely D, the dielectric constant of the bulk phase, has been almost completely neglected in experimental studies of counterion binding[13]: most of these studies deal only with aqueous solution systems. Thus the validity of using D to estimate electrostatic interactions in the condensation theories should be confirmed by experiments on mixed solvent systems, e.g. aqueous alcohols with different D values.

One of the reasons that mixed solvent systems have not been employed in counterion binding studies seems to be that a specific counterion binding with substantial desolvation, which is outside the scope of equation (1), will be favoured in media with low dielectric constants. In fact, some of the present authors have shown that alkali metal salts of poly(L-glutamic acid) assume an α-helix conformation in aqueous alcohols with a marked dependence on the counterion species, and ascribed the counterion specificity to contact ion-pair formation between smaller counterions and polymer charges[1–4]. Thus, one may obtain two kinds of information through a study of counterion binding in mixed solvent systems, namely, validity of equation (1), e.g. through activity measurement, and specific counterion binding and its dependence on solvent properties. The former may be judged from measurements made for the low-concentration regions of organic cosolvents.

In this present study, we have investigated the counterion binding of poly(allylamine)hydrochloride (PAlAmHCl) in aqueous alcohols (methanol (MeOH), ethanol (EtOH) and 2-propanol (2PrOH)) through

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* To whom correspondence should be addressed

activity measurements with a Cl^--selective electrode, and conductivity and viscosity measurements. In an earlier study[15], we have shown that the counterion activity of PAlAmHCl in aqueous solution is quantitatively predicted by the condensation theory, i.e. the 'Intermediate Model' (IMM)[16], that we have previously proposed. Thus we expect that the IMM approach will also give a quantitative estimation of the Cl^- activity for the low-alcohol-content region. Furthermore, through studies on coil–helix transition of poly(L-glutamic acid) and poly(L-lysine)[17] we have shown that the dependence of specific counterion binding on solvent species may be controlled by the dielectric constant (D), the Gutman–Mayer acceptor number (AN)[18] and the water activity (a_w). Thus, in this present study we also employ the D, a_w and AN values of mixed solvents and alcohols as key parameters in the discussion on specific counterion binding that will be observed for the higher-alcohol-content region, when considering the deviations of the experimental activity and conductivity data from the theoretical estimations based on the condensation model.

EXPERIMENTAL

Materials

Poly(allylamine) hydrochloride (PAlAmHCl) ($M_w = 6.0 \times 10^4$) was purchased from Nittobo Co. Ltd. The polymer sample was purified by filtration through an Ultrafilter UP-20 (Toyo Roshi Co. Ltd) and collected by using a freeze-drying technique.

The alcohols used (MeOH, EtOH, and 2PrOH) were of analytical grade and obtained from Nacalai Tesque, Inc. Tetraphenylphosphonium chloride (TPPCl) (Tokyo Kasei Co. Ltd, analytical grade) was used as a standard reference material for calibrating the counterion activity measurements because it is well known that an ion-pair is less likely to be formed for a cation having a largely different hydration with the counter anion and vice versa[19]. The TPP cation is a strong structure maker, while Cl^- is a weak structure breaker. Thus, it is expected that the ion-pair formation of TPPCl may have the least effect on the estimation of the Cl^- activity in the mixed solvents.

Activity measurements

The apparent activities of Cl^- in PAlAmHCl solutions were obtained by a calibration method with TPPCl used as the standard. As mentioned above, any ion-pair formation of TPPCl may be neglected in aqueous solution. However, it may occur to some extent in mixed solvents with high alcohol contents. Thus, the activities estimated in this present study should be considered as being only apparent ones, obtained by assuming that the TPP cation and Cl^- interact with each other via a Debye–Hückel potential only, without any ion-pair formation. This means that these present experiments may overestimate the Cl^- activity to some extent and thus the resultant activity should be considered as representing an upper limit to its value.

The calibration was performed twice, i.e. before and after each measurement. The linearity of the calibration curves plotted as electromotive force (e.m.f.) vs Cl^- activity in TPPCl solutions (10^{-3} to 10^{-2} M), estimated by the extended Debye–Hückel equation[20], was satisfactory and the reproducibility of the respective e.m.f. values was confirmed as being within ±5%.

E.m.f. was measured with an Orion 901 Ion-Analyser by using a Cl^--specific electrode (Orion 94178B) and double junction reference electrode (Orion 90-02); the polymer concentration was fixed at 1.0×10^{-2} base-mol l^{-1} and the alcohol concentrations in mixed solvents were adjusted to 0–75 vol% (0–90 vol% for MeOH). All of the measurements were performed at 25 ± 0.05°C.

Conductivity measurements

The conductivities of PAlAmHCl and HCl solutions were measured with a CM-5B conductivity meter and a CG-201PL electrode (Toa Denpa Co. Ltd) at 25 ± 0.05°C. The polymer sample solutions were prepared both in the absence and in the presence of 1×10^{-3} N HCl by using the same mixed solvents as in the activity measurements. The HCl was added in order to estimate the conductivities corresponding to fully protonated PAlAm, because the polymer dissociates to a certain extent in the absence of added acid. (It is safely assumed that PAlAmHCl is fully protonated at pH 3.)[21] Thus, by assuming additivity, the conductivity, κ'_p, of PAlAmHCl in the absence of 1×10^{-3} N HCl is expressed as follows:

$$\begin{aligned}\kappa'_p &= \kappa_p(\mathrm{HCl}) + \kappa_p(1-\alpha)\\ &= \kappa_p(\mathrm{HCl}) + (\kappa_{p+\mathrm{HCl}} - \kappa_{\mathrm{HCl}})(1-\alpha) \qquad (3)\end{aligned}$$

where α is the degree of dissociation, $\kappa_p(\mathrm{HCl})$ represents a contribution to κ'_p from the HCl dissociated from the polymer, κ_p is the conductivity of fully protonated PAlAm, $\kappa_{p+\mathrm{HCl}}$ is the conductivity of a polymer solution in the presence of 10^{-3} N HCl, and κ_{HCl} is the conductivity of 10^{-3} N HCl.

We estimated the α values using equation (3) in the following way. First, κ'_p, $\kappa_{p+\mathrm{HCl}}$, and κ_{HCl} are obtained as experimental data. Then, since $\kappa_p(\mathrm{HCl})$ is estimated as the κ of HCl whose concentration is $\alpha \times C_p$ (if one uses an arbitrary α value), one may obtain another α value from equation (3). Thus the 'true' α value is obtained by iterating the calculation until the former value of α coincides with the latter α value.

RESULTS AND DISCUSSION

Estimation of α

In *Table 1*, the α values estimated as above are shown. The values are almost constant at 0.021 ± 0.006 except for the 70 and 75 vol% 2PrOH systems, where no definite tendency is found. This general constancy may suggest that enhancement of the electrostatic repulsion between charged groups due to an increase in alcohol content or a decrease in the dielectric constant is cancelled out by the concomitant increase in the counterion binding. Thus, in the following analysis of the activity of Cl^-, we assume a constant dissociation at $\alpha = 0.02$ for each solvent system.

Counterion activity (a')

Figure 1 shows plots of apparent activity (a'), of Cl^- vs. alcohol content (vol%). As seen in the figure, the a' values decrease with the alcohol content. The order for the higher-alcohol-content region is: MeOH > EtOH > 2PrOH. This qualitative tendency

Table 1 Degree of dissociation, α, of PAlAmHCl

Vol%	0	10	20	30	40	50	60	70	75	80	90
MeOH	0.021	0.021	0.022	0.022	0.027	0.020	0.023	0.016	–	0.020	0.021
EtOH	0.021	0.022	0.020	0.024	0.023	0.021	0.018	0.020	0.016	–	–
2PrOH	0.021	0.027	0.021	0.025	0.024	0.016	0.018	0.010	0.010	–	–

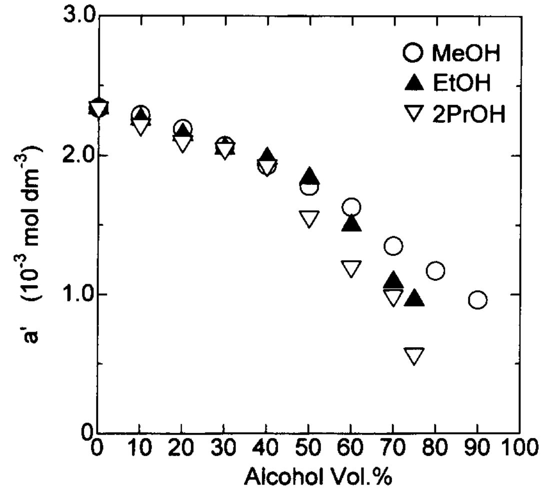

Figure 1 Dependence of the apparent activity (a') on the alcohol content of the various systems

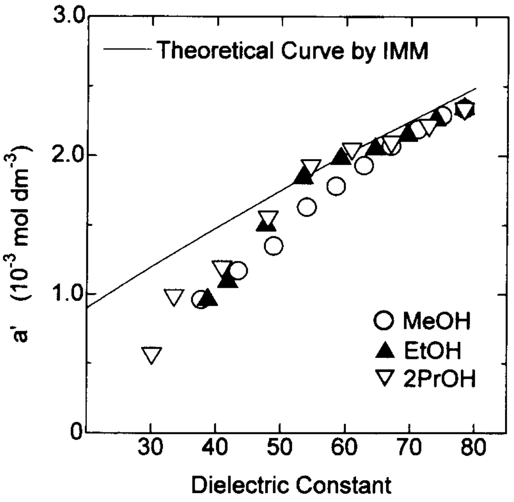

Figure 2 Dependence of a' on the dielectric constant (D) of the various aqueous alcohol systems

should be ascribed to counterion binding that depends on both the alcohol content and species. As stated in the Introduction, we will consider these solvent effects on the counterion binding in terms of D, AN and a_w, i.e. the lower the values of these parameters, then the higher will be the degree of counterion binding[14].

The effect of D may be easily understood by considering equations (1) and (2). For a_w, we consider this as a measure of the preferential hydration to the ions. Since the hydration energy of alcohols to ions[22] is higher than the corresponding solvation energy, specific counterion binding will be favoured for systems with lower desolvation energies, i.e. for ions with alcohol molecules that are solvated. Regarding AN, this effect may be rather more complex. Since AN is a measure of the solvation energy to the anions, specific counterion binding should be favourable for alcohols with lower AN values. However, too low an AN may promote preferential hydration to suppress the specific counterion binding. Thus consideration of the solvent effects through the AN values does not seem to be straightforward.

In order to compare the experimental a' values with the theoretical estimations based on the counterion condensation model, and to investigate the solvent effects by considering a_w and AN, we replotted a' against D of the mixed solvents (*Figure 2*). The theoretical curve was obtained by using the IMM. The agreement with the experimental data is qualitatively and quantitatively satisfactory for MeOH systems in the region from 0 to 30 vol% ($D = 78$ to 67)[23]. This result seems to give justification to the use of a bulk dielectric constant in the estimation of electrostatic interactions in polyelectrolyte solutions. However, the results for EtOH and 2PrOH are not necessary consistent with the theoretical curve; the decreasing rates of a' with decreases in D are smaller than the theoretical estimation over the alcohol content region from 30 to 50 vol% ($D = 64$–53) for EtOH and from 0 to 40 vol% ($D = 78$–55) for 2PrOH systems[23]. This discrepancy may be interpreted as a solvent effect through a_w. Since a_w in mixed solvents is in the order MeOH < EtOH < 2PrOH[24], polyions in the latter two solvent systems may be preferentially hydrated. In fact, according to Mori *et al.*[25], poly(L-lysine)hydrobromide is preferentially hydrated in aqueous 2PrOH systems with contents of 10–85 vol%. Thus, the local dielectric constant around the polyion can be higher than D in the bulk due to preferential hydration, resulting in lower degrees of counterion binding than those obtained from theoretical estimations. Therefore, this present comparison of the experimental a' values with the theoretical curve in *Figure 2* suggests that counterion binding in mixed solvent systems can appreciably deviate from estimations with the bulk D values used in equation (1) and in the IMM.

In the higher-alcohol-content region, remarkable downward deviations from the theoretical curve are found for the a' values of the respective alcohol systems. These deviations may not be attributed to any changes or decreases in the local dielectric constants as assumed above, since in this concentration region the polyion seems to be still preferentially hydrated, at least for the aqueous 2PrOH system. Thus, it appears reasonable to ascribe such deviations to the occurrence of specific counterion binding.

The dielectric constant values below which the experimental a' values start to show an appreciable downward deviation from the theoretical curve are ~59 (50 vol%) for MeOH, ~48 (60 vol%) for EtOH, and ~41 (60 vol%) for 2PrOH[23]. This order may again be interpreted in terms of a_w; in the aqueous MeOH system, which has the lowest a_w values of the three

Table 2 Values of $-\Delta E_{ex}$ (kcal mol^{-1}) estimated by using the IMM

Vol%	0	50	60	70	75	80	90
MeOH	0.4	0.9	1.2	2.1	–	2.5	3.2
EtOH	0.4	–	1.2	2.9	3.3	–	–
2PrOH	0.4	–	1.5	1.2	4.4	–	–

systems studied, the polyion is solvated by MeOH in a higher ratio than by any of the other alcohol species, a condition which is favourable for specific counterion binding. For EtOH and 2PrOH, a similar rationale may also be applicable.

In order to compare the deviations more quantitatively, we estimated the excess interaction free energy, ΔE_{ex} for counterion binding by fitting the theoretical estimation using the IMM to the respective experimental a' values[16]. The results are shown in *Table 2*. The value of -0.4 kcal mol^{-1} at 0 vol% alcohol, i.e. in aqueous solution, may be taken as an estimation error which is inherent in the IMM. Maximum values for the excess interaction (those specific between Cl^- and the polyion charged group) are obtained as -3.2 for 90 vol% MeOH, -3.3 for 75 vol% EtOH and -4.4 kcal mol^{-1} for 75 vol% 2PrOH. These values are close to that found for Ca^{2+} ions binding to sodium polyacrylate[26], i.e. $\Delta E_{ex} = -3.9$ kcal mol^{-1}. Although these present estimations may not be directly compared with results for other aqueous systems, since the former values were obtained by assuming an ideal behaviour for TPPCl, it may safely be said that the excess interaction in the present alcoholic systems is very strong for monovalent counterion binding. In other words, this comparison indicates how water as a solvent weakens the interactions between the ions.

Here it may be worthwhile considering the dependence of the largest excess interaction on the alcohol species. This value for the MeOH system is close to that found for EtOH, while the specific counterion binding seems to occur at a higher D value for MeOH than for EtOH. This is because the decreasing trend of a' with the decrease in D is smaller for aqueous MeOH, than for the other systems, particularly over the lower-D region. This behaviour may be explained by considering the highest AN value of MeOH, hence the highest desolvation energy among the alcohols used.

The strongest interaction estimated at 75 vol% 2PrOH does not always indicate that the aqueous 2PrOH system is inherently favourable for specific counterion binding such as contact ion-pair formation. Judging from the decreasing tendency of a' for the MeOH and EtOH systems, both of these might give a similar a' or ΔE_{ex} value at the D value of 75 vol% 2PrOH. The specific counterion binding with desolvation in aqueous 2PrOH systems, on the contrary, seem to be largely retarded by probably the highest preferential hydration of ions due to the highest a_w and the 'lowest' AN value of the relevant mixed solvent.

Equivalent conductivity of the polymer

Conductivity measurement is another useful experimental method for studying the counterion binding phenomena. According to Manning[6], who formulated the equivalent conductivity of a polyion, λ_p, in solution by incorporating the effects of counterion condensation and electrophoresis into the hydrodynamic interaction, this parameter is given by the following:

$$\lambda_p = (F/300)\xi^{-1}[e/(3\pi\eta b)]|\ln(\kappa_D b)| \tag{4}$$

where F is the Faraday constant, ξ is the polymer charge density (as defined by equation (2)), e is the electron charge, η is the solvent viscosity, b is the polymer charge spacing, and κ_D is the Debye parameter. Thus, the apparent equivalent conductivity of a polyelectrolyte, A_p, has been derived as follows:

$$A_p = 10^3\kappa_p/C_p = \xi^{-1}[(Bt_c + B')\lambda_s + B\lambda_p] \tag{5}$$

where $\kappa_p = \kappa - \kappa_s$. κ and κ_s are the conductivities of the polyelectrolyte solution in the presence of added salt and that of the corresponding salt solution, respectively. In this present study, κ_p is equivalent to $\kappa_{p+HCl} - \kappa_{HCl}$, as given in equation (3). The constants B and B' in equation (5) are 1 and $-1/6$, respectively, in this present work which employs HCl as the added salt, while t_c is the transference number of the counterion and λ_s is the equivalent conductivity of the relevant salt solution.

We can now modify equations (4) and (5) by using the degree of counterion binding, θ_{IMM}, as estimated by the IMM, instead of $1 - \xi^{-1}$, as follows:

$$\lambda_p = 8.19 \times 10^{-9}(1 - \theta_{IMM})S/\eta \tag{6}$$

$$A_p = (1 - \theta_{IMM})[(t_{Cl} - 1/6)\lambda_{HCl} + \lambda_p] \tag{7}$$

where S, the electrostatic interaction energy between the charged groups on the polyion (estimated from the IMM) is used instead of $|\ln(\kappa_D b)|$. η, with the values of t_{Cl} and λ_{HCl}, are available from the literature[27,28] (except for $t_{Cl}\lambda_{HCl}$ or λ_{Cl} in the MeOH and 2PrOH systems). These latter values were therefore roughly estimated by assuming that the respective values of the 'Walden' product, i.e. $\lambda\eta$, are equivalent to those in the EtOH systems.

In *Figures 3a–c*, the experimental A_p values and the theoretical curves derived by using equation (7) are shown as a function of the dielectric constant D of the respective mixed solvents[23]. As a general trend, the experimental A_p values monotonically decrease with the decrease in D. The theoretical curves reproduce the experimental data only for the higher-D region; for the lower $-D$ region, they predict a slower decrease in A_p, and even an increase for the MeOH system. If the relatively large deviations for the lower-D region result from the specific counterion binding or an underestimation of θ by the IMM, it now seems interesting to examine how the use of θ estimated from the IMM with the relevant ΔE_{ex} values may improve the prediction. The results obtained in this way are shown in *Figure 3* as dotted lines. The agreements are quite satisfactory when one considers the large number of assumptions that have been made. Therefore, it may be said that the deviations of the counterion activity and equivalent conductivity from the respective theoretical predictions obtained by using the IMM are well explained by considering the specific counterion binding that can be measured by a common value of ΔE_{ex}.

Viscosity of polymer solutions

We have measured the specific viscosity, η_{sp}/C_p, of

PAlAmHCl in the mixed solvents. Although polymer conformation should be discussed in terms of the limiting viscosity $[\eta]$, we employ here η_{sp}/C_p to observe the effects of solvent on the extension of a polymer chain through counterion binding and preferential solvation.

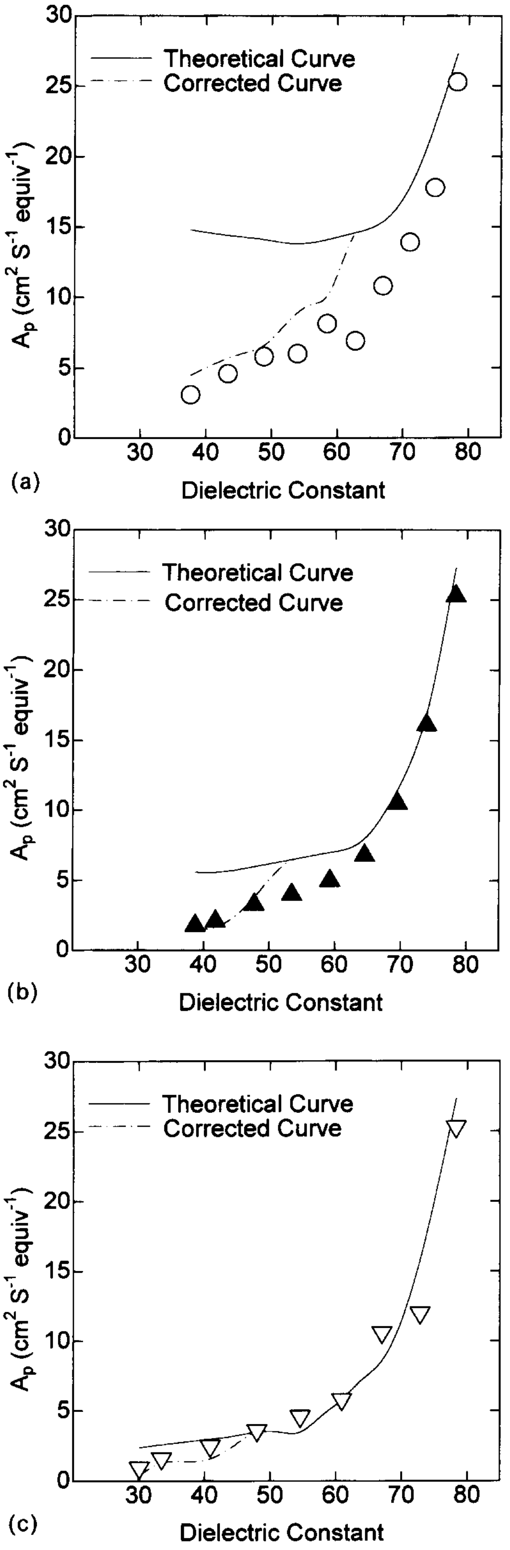

Figure 3 Dependence of A_p on the dielectric constant, D, for the various aqueous alcohol systems: (a) MeOH; (b) EtOH; (c) 2PrOH. The theoretical curves were derived by using equations (7) and (8), while the corrected curves were obtained by incorporating the θ values, corrected by values of ΔE_{ex}, into the equations

The use of this term may be rationalized by considering the low value of C_p, i.e. 1.0×10^{-2} basemol l^{-1} $= 9.4 \times 10^{-2}$ g dl^{-1}.

In *Figure 4*, η_{sp}/C_p is plotted against the respective alcohol content for the various systems. The decreasing trend is similar to that of a' in *Figure 1*. However, the dependence on D is essentially different from the case of a' and also of A_p, as shown in *Figure 5*, with no appreciable dependence on the alcohol species being found. (A similar dependence was also observed for otherwise similar systems in the presence of 1.0×10^{-3} N HCl, but these results are not shown here.) In other words, neither the differences in θ among the alcohols, nor the preferential solvation suggested from *Figure 2*, are observed in *Figure 5*. This may not be a puzzle, because the preferential hydration which should increase η_{sp}/C_p through the decrease in θ will also decrease η_{sp}/C_p through the lower microviscosity or local viscosity around the polyion when compared to the bulk. Moreover, the absence of an appreciable solvent dependence for the viscosity suggests that the observed solvent effects on a' and A_p are free from any contributions from the polymer conformation.

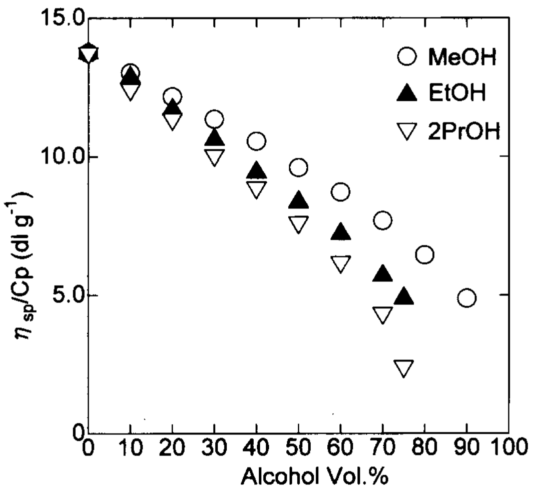

Figure 4 Dependence of η_{sp}/C_p on the alcohol content of the various systems

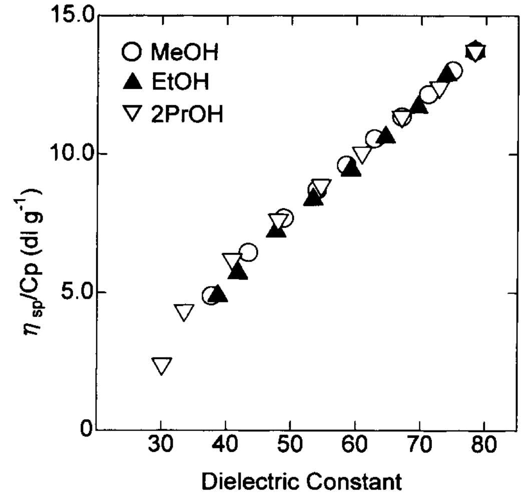

Figure 5 Dependence of η_{sp}/C_p on the dielectric constant, D, of the various aqueous alcohol systems

Here again we may say that the dependence of a' and A_p on the alcohol species and the deviations from the condensation theory are attributable to the specific counterion binding and the preferential solvation.

CONCLUSIONS

In this present study we have investigated the solvent effects on the counterion binding of polyelectrolytes through measurements of the counterion activity, polymer conductivity and viscosity of aqueous alcohol solutions of PAlAmHCl. There are two main findings: one is that certain counterion condensation theories such as the Manning two-phase model and the Intermediate Model are able to predict, at least semiquantitatively, the dependence on D of the degree of counterion condensation or apparent activity for mixed solvents for values of D near that of water. The other finding is that deviations between the experimental a' and A_p data and those from theoretical estimations can be consistently ascribed to a specific counterion binding, which can be essentially correlated with certain solvent parameters, e.g. D, a_w, and AN. In order to obtain a complete picture of the counterion binding in mixed solvent systems, however, we may need an experimental confirmation of a basic problem, i.e. whether the counterion condensation actually shows a critical dependence on D for its occurrence[13]. This study is currently being undertaken.

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