the calcium ion activity coefficient of the added $CaCl_2$ in the absence of polyelectrolyte. Values of $\gamma_{Ca^{2+}}{}^{\circ}$ were calculated from the extended Debye–Hückel equation. (For salt-free solutions, $X = \infty$ and $\gamma_{Ca^{2+}}{}^{\circ}$ is obviously unity.) At any given ratio of polyelectrolyte to simple salt, i.e., at constant X, a linear relationship with $\xi^{1/2}$ is observed, as in the salt-free case. However, with decreasing X, the intercepts are seen to increase and the slopes decrease. This behavior may be explained in terms of additivity; i.e., when $0.43 - 0.26\xi^{1/2}$ is substituted for $(\gamma_{Ca^{2+}})_{\infty}$ in eq 3, the variation of $(\gamma_{Ca^{2+}}/\gamma_{Ca^{2+}}{}^{\circ})_X$ with ξ at any value of X is given by

$$\left(\frac{\gamma_{Ca^{2+}}}{\gamma_{Ca^{2+}}{}^{\circ}}\right)_X = \frac{X}{X+1}(0.43 - 0.26\xi^{1/2}) + \frac{1}{X+1} \qquad (5)$$

The values of $(\gamma_{Ca^{2+}}/\gamma_{Ca^{2+}}{}^{\circ})_X$ for $X = 5$, 1, and 0.5 predicted by eq 5 as a function of charge density are represented in Figure 3 by the broken lines. These are in excellent agreement with the experimental results, thereby demonstrating that additivity eq 3 is obeyed not only in the presence of monovalent counterions but with divalent counterions as well.

References and Notes

(1) Kohn, R.; Furda, I. *Collect. Czech. Chem. Commun.* **1967**, *32*, 1925.
(2) Costantino, L.; Crescenzi, V.; Quadrifoglio, F.; Vitagliano, V. *J. Polym. Sci., Part A-2* **1967**, *5*, 771.
(3) Rinaudo, M.; Milas, M. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2073.
(4) Joshi, Y. M.; Kwak, J. *J. Phys. Chem.* **1979**, *83*, 1978.
(5) Kowblansky, M.; Zema, P. *Macromolecules* **1981**, *14*, 166.
(6) Ander, P.; Leung-Louie, L. "Polymeric Amines and Ammonium Salts"; Goethals, E. J., Ed.; Pergamon Press: New York, 1980; p 249.
(7) Ander, P.; Leung-Louie, L.; Sylvestri, F. *Macromolecules* **1979**, *12*, 1204.
(8) Vink, H. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1790.
(9) van Treslong, C.; Moonen, P. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 23.
(10) Wells, J. D. *Biopolymers* **1973**, *12*, 223.
(11) Kohn, R.; Larsen, B. *Acta Chem. Scand.* **1972**, *26*, 2455.
(12) Pass, G.; Phillips, G.; Wedlock, D. J. *Macromolecules* **1977**, *10*, 197.
(13) Satake, I.; Fukuda, M.; Ohta, T.; Nakamura, K.; Fujita, N.; Yamauchi, A.; Kimizuka, H. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 2343.
(14) Manning, G. *J. Chem. Phys.* **1969**, *51*, 924.
(15) Manning, G. "Polyelectrolytes"; Selegny, E., Ed.; Reidel Publishing Co.: Dordrecht, Holland, 1972; p 1.
(16) Manning, G. *Acc. Chem. Res.* **1979**, *12*, 442.

Effect of Charge Density and Ion Binding on Intrinsic Viscosity of Polyelectrolyte Solutions

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ABSTRACT: Intrinsic viscosities of the Na^+, K^+, and NH_4^+ salts of a series of acrylamide/acrylic acid copolymers of identical degree of polymerization but varying charge density have been determined at 25 °C in aqueous solutions containing NaBr, KBr, or NH_4Br. It is demonstrated that when counterion binding is taken into account, a linear relationship between intrinsic viscosity and polyelectrolyte charge density is obtained when the molecular weight and concentration of simple electrolyte are kept constant.

Introduction

It is well established that the introduction of ionic groups onto a polymer results in its expansion in aqueous solution due to electrostatic repulsions between the ionic groups, with a concomitant enhancement of the solution viscosity. The addition of a simple electrolyte to the solution results in shielding of the ionic groups with a reduction of the coil dimensions. A number of studies dealing with the effect of simple electrolytes and molecular weight on the expansion of polyelectrolytes have been reported and have been the subject of reviews.[1,2] However, systematic investigations of the effect of charge density on the viscosity of polyelectrolyte solutions are few.[3-5] Counterion–polyion interactions, particularly in the case of high charge density polyelectrolytes, have made interpretation of viscosity data problematic. Thus, comparisons with theory have generally been restricted to low charge density polyelectrolytes with the assumption that counterion binding is insignificant for these. However, recent studies[6,7] of counterion activity coefficients of low charge density polyelectrolytes have revealed that even at very low charge densities (comparable to 10% neutralized poly(acrylic acid)) approximately 20% of monovalent counterions are effectively bound to the polyion. Similar observations have been made with counterion self-diffusion coefficients with low charge density polyelectrolytes.[8]

To meaningfully study the relationship between charge density and viscosity of polyelectrolyte solutions, it is essential to keep the primary structure and degree of polymerization constant, while varying the degree of ionic character of the polyelectrolyte. A facile way of achieving this is to partially neutralize weak polybase or polyacid polymers, such as poly(vinylpyridine)[9] or poly(acrylic acid)[3,4] (PAA), to various extents. However, this approach can create difficulties, particularly at low degrees of neutralization, where self-ionization of the polyelectrolyte may occur and create ambiguities in interpretation of the resulting viscosity data. To overcome this difficulty in the present study, we determined intrinsic viscosities for acrylamide/acrylic acid copolymers fully neutralized with Na^+, K^+, or NH_4^+ ions, with the charge density being varied by the acrylic acid content of the copolymer. The spacing of charged groups in these polyelectrolytes ranged from 3.9 to 25 Å, which is comparable to PAA neutralized between 10 and 65%. The relationship between intrinsic viscosity and charge density, simple salt concentration, and counterion binding will be discussed.

Experimental Section

Acrylamide/acrylic acid copolymers of differing acrylic acid content but identical degree of polymerization were prepared by alkaline hydrolysis of polyacrylamide (PAM) purchased from Polysciences. The viscosity-average molecular weight of the nonionic PAM was determined to be 1.5×10^6, using the relationship of Klein and Conrad.[10] The hydrolysis was carried out in the presence of NaOH at 60 °C at the conditions described in Table I. Following hydrolysis, the solutions were acidified

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Table I
Conditions for Hydrolysis of PAM[a] and Several Properties of the Resulting Polyelectrolytes

sample	NaOH concn, N	hydrolysis time, min	mol % hydrolyzed	b,[b] Å	ξ
HPAM-0.6[c]			0.6	417	0.02
HPAM-11	0.1	15	11	23	0.31
HPAM-22	0.1	60	22	11	0.63
HPAM-39	1.0	15	39	6.4	1.11
HPAM-60	1.0	120	60	4.2	1.71
HPAM-65	1.0	300	65	3.8	1.85

[a] Hydrolysis temperature 60 ± 2 °C, PAM concentration 16.5 g/L. [b] Based on a spacing of 2.5 Å for vinyl groups. [c] Due to the very low charge density and the nonavailability of completely nonionic polyacrylamide, this polymer will be referred to as nonionic.

to a pH below 1 and then purified by exhaustive dialysis against doubly distilled water. Concentrations of the resulting polyacid stock solutions were determined by drying several aliquots of the stock to constant weight in a vacuum oven at 60 °C. Equivalent weights (degree of hydrolysis) of the purified samples were determined by potentiometric titration of the purified polyacids with NaOH. All polymer samples were labeled HPAM-*y*, where *y* denotes the degree of hydrolysis (i.e., mole percent acrylic acid content of the copolymer). The polyacids were converted to their Na^+, K^+, or NH_4^+ salts with their respective hydroxides.

Intrinsic viscosities $[\eta]$ of the polyelectrolyte salts were determined at 25 ± 0.05 °C in an Ubbelohde viscometer, using a minimum of five polyelectrolyte concentrations (0.1 g/dL and lower) for each intrinsic viscosity determination. Dilutions were made in the viscometer, keeping the concentration of simple salt constant. Plots of the reduced viscosity against polyelectrolyte concentration were linear, thereby enabling the usual extrapolation to obtain $[\eta]$. Although measurements were made on the Na^+, K^+, and NH_4^+ salts of the polyelectrolytes, the reported values of $[\eta]$ are calculated as dL/g of the *hydrogen form* of the copolymer. The use of these concentration units facilitated the comparison of viscosity data for the different ionic forms. Since the viscosities were determined in relatively high simple salt concentrations, shear corrections were not necessary.

Analytical grade NaBr, KBr, and NH_4Br were used without further purification. All solutions were prepared by volumetric dilution of the appropriate simple salt and polyelectrolyte stock solutions.

Results and Discussion

Intrinsic viscosities of the fully neutralized sodium poly(acrylate–acrylamide) polyelectrolytes listed in Table I were determined at 25 °C in 0.10, 0.25, 0.50, 0.75, and 1.50 N aqueous NaBr solutions. The results are plotted in Figure 1 as a function of the dimensionless charge density parameter, ξ, frequently used to characterize polyelectrolytes

$$\xi = e^2/DkTb \tag{1}$$

where e is the charge on a proton, D is the bulk dielectric constant, k is the Boltzmann constant, T is the absolute temperature, and b is the average stoichiometric spacing of charges along the contour length of the polyion. The importance of ξ and its influence on the properties of polyelectrolyte solutions has been propagated by Manning.[11-13] The values of b and ξ for each of the polyelectrolytes used in this study are given in Table I. At any given concentration of simple salt, $[\eta]$ is seen to increase with increasing charge density, with the largest increase being between $\xi = 0$ and $\xi = 1$, followed by a much smaller rate of increase with further increases in the charge density. This trend is most pronounced at the lower ionic strengths, while at the three highest salt concentrations, the intrinsic viscosity is nearly constant above $\xi = 1$. At any fixed charge density, $[\eta]$ is seen to decrease with increasing concentration of simple electrolyte. It is interesting, however, that $[\eta]$ for the "nonionic" polyacrylamide (which actually is 0.6% hydrolyzed but will be referred to as nonionic throughout this discussion) increases slightly with increasing NaBr concentration. Analogous results have been reported for nonionic polyacrylamide (0.3% hydrolyzed) in aqueous NaCl solutions.[14] This behavior may be due to site binding of sodium ions with the electron-rich polar amide groups on polyacrylamide, resulting in a pseudopolyelectrolyte.

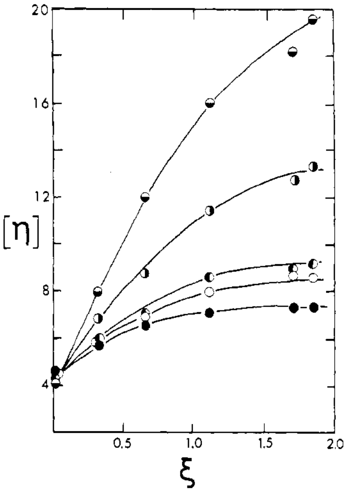

Figure 1. Dependence of the intrinsic viscosity of NaPAM-*y* polyelectrolytes on the charge density parameter ξ in aqueous solutions containing 0.1 (◒), 0.25 (◑), 0.5 (◐), 0.75 (○), and 1.5 (●) N NaBr at 25 °C. The units of $[\eta]$ are dL/g of the hydrogen form of the polyelectrolyte.

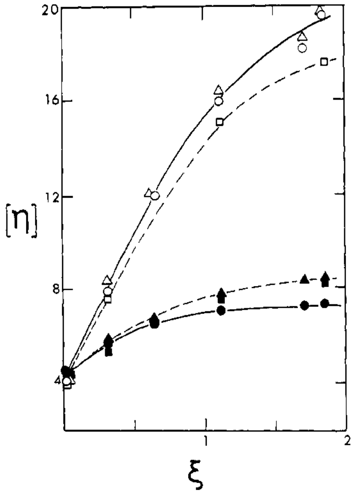

Figure 2. Intrinsic viscosities of Na^+, K^+, and NH_4^+ PAM-*y* polyelectrolytes at 25 °C in aqueous solutions of 0.1 (○) and 1.5 (●) N NaBr, 0.1 (△) and 1.5 (▲) N KBr, or 0.1 (□) and 1.5 (■) N NH_4Br. The units of $[\eta]$ are dL/g of the hydrogen form of the polyelectrolyte.

A comparison of the viscosities of the same series of PAM-*y* polyelectrolytes as their Na^+, K^+, and NH_4^+ salts, each respectively in 0.1 and 1.5 N aqueous Na^+, K^+, or NH_4^+ bromide solutions, is shown in Figure 2. For all three counterions the same general trends are observed, i.e., the large initial increase in $[\eta]$ with increasing charge density, with a gradual leveling off at higher charge densities. However, small specific effects are noted. In 0.1 N salts the viscosities obtained with Na^+ and K^+ counterions are identical, while the NH_4^+ salts give lower intrinsic viscosities. In 1.5 N salts, however, the K^+ and

NH_4^+ polyelectrolytes give identical viscosities, while the Na^+ viscosities are lower. For nonionic PAM, the same dependence of $[\eta]$ on salt concentration is observed for all three counterions, i.e., small increase in $[\eta]$ with increasing ionic strength.

Although a number of theoretical treatments for the expansion of a polyelectrolyte in the presence of simple electrolyte have been reported, the above results are most readily correlated with the relationship derived by Flory[15]

$$\alpha^5 - \alpha^3 = C' + 2C_I i^2 M^{1/2}/C_s \qquad (2)$$

where α, the linear expansion factor of the polyelectrolyte, is defined by

$$\alpha^3 = [\eta]/[\eta]_\Theta \qquad (3)$$

where $[\eta]$ and $[\eta]_\Theta$ are the respective intrinsic viscosities of the polyelectrolyte at the given conditions and under random flight conditions, i.e., in a Θ solvent, C' is the nonionic contribution to expansion, and the second term in eq 2 is the ionic contribution, which is dependent on the polyelectrolyte molecular weight M, the ionic strength of the added simple electrolyte C_s, the degree of ionization i of the polyelectrolyte, and the quantity C_I, given by

$$C_I = (3^3 \times 10^3/2^{9/2}\pi^{3/2})(\langle r_0^2\rangle/M)^{-3/2}N^{-1}M_0^{-2} \qquad (4)$$

where N is Avogadro's number, M_0 is the length of a monomer unit, and $(\langle r_0^2\rangle/M)^{1/2}$ is the characteristic ratio of the polymer, which is a measure of the backbone stiffness and has been found to be essentially independent of the nature of the solvent for several nonionic and ionic polymers.

Equation 3 takes into account ionic, as well as nonionic, contributions to the expansion of the polyelectrolyte over its random flight configuration. However, since the nonionic contribution is usually assumed to be small compared to the electrostatic contribution, $\alpha^5 - \alpha^3$ for ionic polymers is taken to be a measure of the electrostatic expansion of the polyelectrolyte.

For the present discussion a linear electrostatic expansion factor α_e is defined

$$\alpha_e^3 = [\eta]/[\eta]_0 \qquad (5)$$

where $[\eta]_0$ is the intrinsic viscosity of the nonionic "parent" polymer determined at the same experimental conditions as $[\eta]$, in this case the intrinsic viscosity of PAM measured at 25 °C and at the same simple salt concentration. Thus α_e should be a measure of *only* the electrostatic expansion of the polyelectrolyte, i.e., the expansion beyond its *nonionic* dimensions, and $\alpha_e^5 - \alpha_e^3$ should be expected to vary linearly with $1/C_s$, as was previously shown for $\alpha^5 - \alpha^3$ vs. $1/C_s$ with other polyelectrolytes.[2-4] As expected, for each of the polyelectrolytes presently under investigation, $\alpha_e^5 - \alpha_e^3$ does vary linearly with $1/C_s$, as shown in Figure 3, with the slopes increasing with increasing charge density of the polyelectrolyte and approaching zero as ξ approaches zero. According to eq 2, with a knowledge of i and M_0, the characteristic ratio $(\langle r_0^2\rangle/M)^{1/2}$ for each of the polyelectrolytes can be obtained from the slopes in Figure 3. Such a calculation was performed, with M_0 for NaPAM-*y* being the molecular weight of a polyion segment containing a single charge (i.e., M_0 decreases with increasing ξ), and thus the stoichiometric value of i is in all cases unity. However, it has been shown that experimentally determined slopes are significantly lower than predicted by eq 2, particularly for polyelectrolytes of high charge density.[3,4] This discrepancy between theory and experiment has been attributed to the fact that counterions bind to macroions, thereby lowering the degree of dissociation of the polyelectrolyte to a value much lower than its stoichiometric value of i. Thus it has been suggested that effective values of i be employed in eq 2, instead of stoichiometric values.[16,17] However, the nature of the correction to be applied to i has not yet been established.

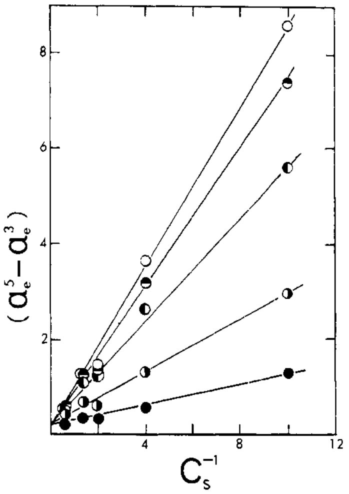

Figure 3. Dependence of $\alpha_e^5 - \alpha_e^3$ on C_s at 25 °C for NaPAM-*y* copolymers of different charge density: (●) $\xi = 0.31$; (◑) $\xi = 0.63$; (◐) $\xi = 1.11$; (◓) $\xi = 1.71$; (○) $\xi = 1.85$.

In a recent publication it was reported[6] that activity coefficients of monovalent sodium counterions γ_{Na^+} in salt-free solutions of sodium acrylate/acrylamide copolymers varied linearly with the polyelectrolyte charge density

$$\gamma_{Na^+} = 0.96 - 0.42\xi^{1/2} \qquad (6)$$

where 0.42 was interpreted to be a measure of the electrostatic interaction of the counterions with the polyion and the departure of 0.96 from unity was interpreted to be due to specific interactions of sodium ions with the polyelectrolyte. In the presence of simple electrolyte, even excess simple electrolyte, it was found that the contributions from the polyelectrolyte and added simple salt to the measured activity coefficients were additive; i.e., activity coefficients of the sodium ions originating from the polyelectrolyte were unaltered by the addition of simple electrolyte, and the activity coefficients of the counterions originating from the added simple electrolyte were the same as in the absence of polyelectrolyte. From this it would appear that the *effective* degree of dissociation of the polyelectrolyte (which may include both condensation and Debye–Hückel interaction) is not altered by the presence of simple electrolyte. Therefore, it would seem reasonable to employ *salt-free* values of γ_{Na^+} to correct i to its effective value. Using γ_{Na^+} values (calculated from eq 6) for i in eq 2, we calculated $(\langle r_0^2\rangle/M)^{1/2}$ values for each of the NaPAM-*y* copolymers of different charge density. These are listed in Table II. It is particularly interesting that the value of $(\langle r_0^2\rangle/M)^{1/2}$ is constant over all charge densities, with an average value of 2.48 ± 0.08 Å. However, the literature value[18] for the characteristic ratio of nonionic polyacrylamide is 1 Å. Since the expansion factor was calculated by eq 5, using the intrinsic viscosity of nonionic polyacrylamide at 25 °C and not of the polyelectrolyte in a Θ solvent, as called for in eq 2, the average calculated value of 2.48 Å for $(\langle r_0^2\rangle/M)^{1/2}$ must be interpreted to be that of nonionic PAM at 25 °C and not its random flight value.

The constancy of $(\langle r_0^2\rangle/M)^{1/2}$ for all charge densities suggests that the intrinsic viscosity of the polyelectrolyte solution should be a sum of the ionic and nonionic con-

Table II
Slopes of the Linear Plots Shown in Figure 3 and the Values of $(\langle r_0^2\rangle/M)^{1/2}$ Calculated from the Slopes

ξ	slope	$(\langle r_0^2\rangle/M)^{1/2}$,[a,b] Å
0.31	0.08	2.48
0.63	0.27	2.37
1.11	0.52	2.49
1.71	0.72	2.58
1.85	0.85	2.49
	av	2.48 ± 0.08

[a] Calculated from eq 2 and 5. [b] Does not refer to Θ conditions; see text.

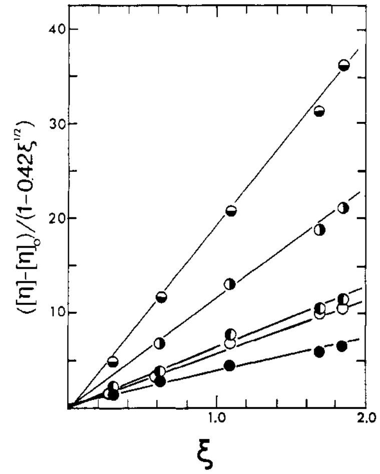

Figure 4. Dependence of $([\eta] - [\eta]_0)/(1 - 0.42\xi^{1/2})$ on ξ for NaPAM-y copolymers in 0.1 (⊖), 0.25 (◑), 0.5 (◐), 0.75 (○), and 1.5 (●) N NaBr.

tributions, with the ionic component being a function of the charge density and the effective degree of dissociation of the ionic groups and the nonionic component being independent of these variables. Thus it will be demonstrated that the intrinsic viscosity of a polyelectrolyte solution may be empirically expressed by

$$[\eta] = [\eta]_0 + [\eta]_e = [\eta]_0 + k\xi(1 - 0.42\xi^{1/2}) = [\eta]_0 + k\xi\gamma_1 \tag{7}$$

where $[\eta]$ is the intrinsic viscosity of the polyelectrolyte, $[\eta]_0$ is the viscosity of the nonionic parent polymer, $[\eta]_e$ is the electrostatic component of the intrinsic viscosity, the quantity $1 - 0.42\xi^{1/2}$ is the monovalent counterion activity coefficient γ_1 in a *salt-free* solution of the polyelectrolyte (as given by eq 6), which for the reasons discussed above is here considered to be a measure of the effective degree of dissociation, and k is a measure of polymer–solvent interactions. The term $k\xi$ can be viewed as the viscosity due to the hypothetical maximum electrostatic expansion of the polyion of charge density ξ in the absence of any counterion–polyion interactions, and $0.42k\xi^{3/2}$ as the reduction in $k\xi$ due to interaction of the polyion with its monovalent counterions. At any given concentration of simple salt, plots of $([\eta] - [\eta]_0)/(1 - 0.42\xi^{1/2})$ vs. ξ are linear and go through the origin, as shown in Figure 4 for the series of sodium polyelectrolytes presently under investigation. The values of k, determined as the slopes of these plots, are shown in Figure 5 to linearly increase with the inverse square root of the simple salt concentration. Further discussion of k will be deferred in order to test eq 7 with other polyelectrolyte systems.

Nagasawa et al.[4] measured intrinsic viscosities for aqueous NaBr solutions of different molecular weight samples of PAA neutralized with NaOH to various extents

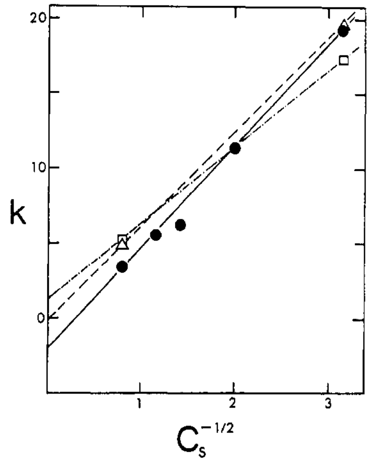

Figure 5. Dependence of interaction constant k on C_s for Na$^+$ (●), K$^+$ (△), and NH$_4^+$ (□) PAM-y copolymers, respectively, in NaBr, KBr, and NH$_4$Br.

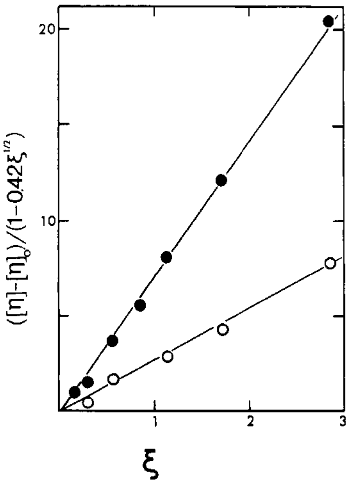

Figure 6. Dependence of $([\eta] - [\eta]_0)/(1 - 0.42\xi^{1/2})$ on ξ for sodium polyacrylates of molecular weight 1.2×10^5 (○) and 5.3×10^5 (●) in 0.1 N NaBr. Data from ref 4.

Table III
Values of the Interaction Constant k in Eq 7 for the Na$^+$, K$^+$, and NH$_4^+$ Polyelectrolytes of HPAM-y in Aqueous Solutions Containing NaBr, KBr, or NH$_4$Br

salt concn, N	k, dL/g		
	Na$^+$	K$^+$	NH$_4^+$
0.1	19.3	19.6	17.2
0.25	11.4		
0.5	6.2		
0.75	5.6		
1.5	3.4	4.9	5.2

(0–100%). For any given molecular weight and simple salt concentration, the variation of $[\eta]$ with ξ, which ranged between 0.3 and 2.8, was qualitatively similar to that shown in Figure 1. Since the charge density dependence of monovalent counterion activity coefficients given by eq 6 has been shown to hold for a number of polyelectrolytes[6,19] other than our NaPAM series, eq 7 should also be applicable to other polyelectrolytes. This indeed is so for the PAA data of Nagasawa et al., as shown in Figure 6, where plots of $([\eta] - [\eta]_0)/(1 - 0.42\xi^{1/2})$ for two molecular weight samples (1.2×10^5 and 5.3×10^5) in 0.01 N NaBr are linear and go through the origin, with the slope k being larger for the higher molecular weight polymer. In addition, for the K$^+$ and NH$_4^+$ copolymers, the values of $([\eta] - [\eta]_0)/(1 - 0.42\xi^{1/2})$, illustrated in Figure 7, follow the linearity with

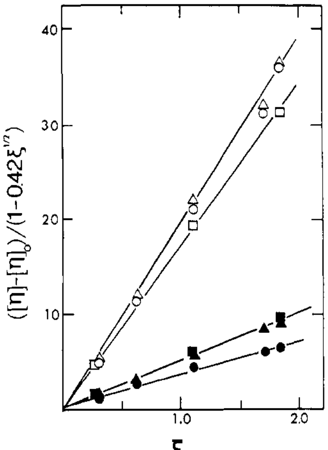

Figure 7. Dependence of $([\eta] - [\eta]_0)/(1 - 0.42\xi^{1/2})$ on ξ for Na^+, K^+, and NH_4^+ PAM copolymers in 0.1 (○) and 1.5 (●) N NaBr, 0.1 (△) and 1.5 (▲) N KBr, and 0.1 (□) and 1.5 (■) N NH_4Br, respectively.

ξ predicted by eq 7, with the values of k, given in Table III and Figure 5, closely approximating those obtained with the NaPAM polyelectrolytes. The intercepts in Figure 5 may reflect the incompatibility of the salt with the uncharged parent polymer, although suitable data for verifying this are not available.

An interesting aspect of the $([\eta] - [\eta]_0/(1 - 0.42\xi^{1/2})$ vs. ξ curves is that k, the slope of these curves, can be related to B in the Stockmayer–Fixman[20] equation

$$[\eta] = KM^{1/2} + 0.51\phi BM \qquad (8)$$

where ϕ is the Flory constant, K is a constant related to the unperturbed dimensions of the polymer, M is the molecular weight, and $KM^{1/2} = [\eta]_\Theta$. It has been demonstrated by Nagasawa et al.[4] that for polyelectrolytes, B can be considered as an apparent long-range interaction parameter, which may be determined from the slope of the linear plots of $[\eta]/M^{1/2}$ vs. $M^{1/2}$. These authors further showed that B varies linearly with the inverse of the square root of the simple salt concentration and may be expressed as a sum of nonelectrostatic, B_0, and electrostatic, B_e, interactions

$$B = B_0 + B_e = B_0 + B'f(\xi)/C_s^{1/2} \qquad (9)$$

where B' is a numerical constant, and $f(\xi)$ is an increasing function of charge density, although neither the form of this functionality nor the numerical values of B' were defined. B_0 was shown to be independent of ξ, and its value was small compared to B_e, which increased sharply at low charge densities, gradually leveling off at higher charge densities (qualitatively resembling the plots of $[\eta]$ vs. ξ in Figure 1).

Since the present study does not deal with Θ solvent measurements and operationally defines the expansion factor α_e as the expansion of a polyelectrolyte beyond its nonionic dimensions, it is convenient to empirically recast the theoretical expression given by eq 8 as

$$[\eta] = [\eta]_0 + 0.51\phi B_e M \qquad (10)$$

It should be recalled that $[\eta]_0$ does *not* refer to a Θ solvent. The second term in eq 10 and the second term in eq 7 should then be equal, and thus

$$B_e = k\xi(1 - 0.42\xi^{1/2})/0.51\phi M \qquad (11)$$

where for Na^+ counterions with our series of copolymers

$$k = -2.0 + 7.0/C_s^{1/2} \qquad (12)$$

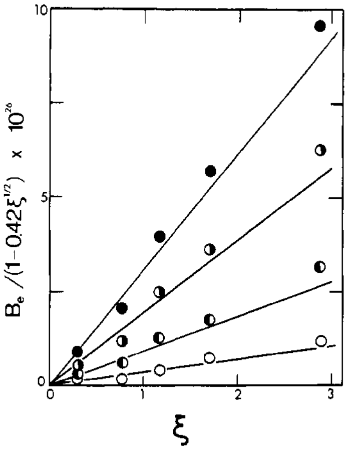

Figure 8. Comparison of the dependence of B_e on ξ for NaPAA and NaPAM-y. The lines are, from top to bottom, the values for NaPAM calculated by eq 11 and 12, for 0.01, 0.025, 0.1, and 0.5 N NaBr; the points are the values reported in ref 4 for NaPAA in 0.01 (●), 0.025 (◑), 0.1 (◐), and 0.5 (○) N NaBr.

With a value of 2.87×10^{21} for ϕ and 1.5×10^6 for the molecular weight, the charge density dependence of B_e for several concentrations of NaBr was calculated by eq 11 for our NaPAM polyelectrolytes. The resulting values of $B_e/(1 - 0.42\xi^{1/2})$ are represented as solid lines in Figure 8 and are shown to vary linearly with ξ. (Note that $B_e/(1 - 0.42\xi^{1/2})$ was also calculated for 0.01 and 0.025 N NaBr and extended to $\xi = 3$, although experiments were not performed at these concentrations of salt, and the highest charge density NaPAM investigated had a ξ value of 1.85.) The values of B_e thus calculated are compared in Figure 8 with the values of B_e reported by Nagasawa et al.[4] for partially neutralized sodium polyacrylates. The agreement between the values of B_e for the NaPAM and NaPA polyelectrolytes is good. This is particularly remarkable when it is considered that in the present study B_e was calculated from the variation of $[\eta]$ with charge density while the molecular weight was kept constant, whereas in the Nagasawa study B_e was calculated from the molecular weight dependence of $[\eta]$ while the charge density was kept constant.

The agreement in B_e for the two different series of polyelectrolytes appears to indicate that specific effects due to the nature of the polyelectrolyte play only a minor role in the electrostatic expansion of a polyelectrolyte. However, such generalization is premature and similar investigations employing polyelectrolytes with ionic groups other than carboxyl groups and stiffer backbone structures, such as ionic polysaccharides, should be undertaken.

References and Notes

(1) Crescenzi, V. *Adv. Polym. Sci.* **1968**, *5*, 358–86.
(2) Nagasawa, M. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 49*, 1.
(3) Flory, P.; Osterheld, J. *J. Am. Chem. Soc.* **1954**, *76*, 653.
(4) Noda, I.; Tsuge, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
(5) Dubin, P.; Strauss, U. P. In "Polyelectrolytes and Their Applications"; Rembaum, A., Selegny, E., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1975; p 3.
(6) Kowblansky, M.; Zema, P. *Macromolecules* **1981**, *14*, 166.
(7) Joshi, Y. M.; Kwak, J. C. T. *J. Phys. Chem.* **1979**, *83*, 1978.
(8) Ander, P., private communication.
(9) Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 246.
(10) Klein, J.; Conrad, K. *Makromol. Chem.* **1980**, *181*, 227.
(11) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 442.
(12) Manning, G. S. In "Polyelectrolytes"; Selegny, E., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1974; p 9.
(13) Manning, G. S. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
(14) Munk, P.; Aminabhavi, T. M.; Williams, P.; Hoffman, D.; Chmelir, M. *Macromolecules* **1980**, *13*, 871.
(15) Flory, P. *J. Chem. Phys.* **1953**, *21*, 162.

(16) Strauss, U. P.; Ander, P. *J. Phys. Chem.* **1962**, *66*, 2235.
(17) Strauss, U. P.; Wineman, P. L. *J. Am. Chem. Soc.* **1958**, *80*, 2366.
(18) Brandrup, J.; Immergut, E. H., Eds.; "Polymer Handbook"; Interscience: New York, 1966.
(19) Kowblansky, M.; Zema, P. *Macromolecules* **1981**, *14*, 1448.
(20) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.

Thermodynamic Characterization of Polystyrene–Poly(*n*-butyl methacrylate) Blends

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ABSTRACT: Inverse gas chromatography has been used to investigate the thermodynamic miscibility behavior of molten polystyrene–poly(*n*-butyl methacrylate) blends as a function of blend composition, temperature, and polystyrene molecular weight. A generally consistent and realistic measure of the polymer–polymer interaction has been obtained with this technique. The results suggest that there are no strong attractive forces between these two polymers. The combination of chromatographic and calorimetric data indicates that whereas blends of poly(*n*-butyl methacrylate) with high molecular weight polystyrene are immiscible, the corresponding blends with low molecular weight polystyrene are miscible over the whole range of composition. The resultant miscibility arises from more favorable entropic effects on lowering the molecular weight.

Introduction

Inverse gas chromatography (IGC) is generally recognized as a fast and reliable method for quantitative evaluation of polymer–solute interactions.[2,3] However, the technique can also be used to measure the interaction between two polymers in a mixed stationary phase. This is accomplished by analyzing the interaction between the volatile probe (1) and each of the two nonvolatile components (2 and 3), and then with a mixture of components 2 and 3.

In general, classical Flory–Huggins theory[4] can be used to interpret the results and to determine the χ_{23}' interaction parameter, which is a measure of the thermodynamic miscibility of the two polymers. Some mixtures that have been studied by IGC include poly(vinyl chloride) with di-*n*-octyl phthalate (DOP)[5] and poly(ϵ-caprolactone),[6] polystyrene with poly(vinyl methyl ether),[7] poly(dimethylsiloxane) with tetracosane and DOP,[8] and styrene–dimethylsiloxane block copolymers and blends.[9]

This report presents self-consistent polymer–solute and polymer–polymer interaction parameters for several polystyrene–poly(*n*-butyl methacrylate) blends.[10] These systems were investigated in the molten state by IGC as a function of temperature, blend composition, and polystyrene molecular weight. In addition, thin films of these blends were prepared and investigated by differential scanning calorimetry (DSC) in order to confirm the results. A previous publication describes the thermodynamic miscibility of the parent homopolymers as well as the behavior of some styrene–butyl methacrylate copolymers.[11]

Experimental Section

Materials. All solutes were chromatoquality or reagent grade and were used without further purification. The polystyrene samples ($\mathrm{PS_H}$: $\bar{M}_w = 110\,000$, $\bar{M}_w/\bar{M}_n < 1.06$; $\mathrm{PS_L}$: $\bar{M}_n = 1709$, $\bar{M}_w/\bar{M}_n < 1.06$) were obtained from Polysciences and Pressure Chemical Co., respectively. Poly(*n*-butyl methacrylate) (PnBMA: $\bar{M}_w = 320\,000$, $\bar{M}_n = 73\,500$) was obtained from Aldrich.

Table I
Stationary Phase and Column Parameters

polymer	loading, % w/w	wt of polymer, g	column length, cm
$\mathrm{PS_H}$	7.45	1.1778	152
$\mathrm{PS_L}$	10.72	1.3120	116
PnBMA	8.19	1.2656	152
$\mathrm{PS_H}$–PnBMA blends			
30 wt % $\mathrm{PS_H}$	9.47	1.1399	114
58 wt % $\mathrm{PS_H}$	9.80	1.1658	117
$\mathrm{PS_L}$–PnBMA blends			
15 wt % $\mathrm{PS_L}$	10.51	0.9908	91
27 wt % $\mathrm{PS_L}$	9.42	0.8090	91
30 wt % $\mathrm{PS_L}$	10.20	1.0404	91
35 wt % $\mathrm{PS_L}$	10.36	0.9813	91
40 wt % $\mathrm{PS_L}$	10.34	0.9985	91
58 wt % $\mathrm{PS_L}$	10.60	1.1893	107
80 wt % $\mathrm{PS_L}$	10.36	1.2432	107

Columns. The columns were prepared in the usual manner. The polymers were coated from a benzene solution onto Chromosorb G (AW-DMCS treated, 70/80 mesh). After drying in a vacuum oven for ca. 48 h at 60 °C, the coated support was resieved and then packed into 48-mm-i.d. copper columns. The total percent loading of polymer on the support was determined by calcination using a suitable blank correction. The relative concentration of polymers in the blends is assumed to be identical with that in the original solution prior to deposition on the inert support. Columns were conditioned under nitrogen for 3 h at 100 °C above their glass transition. A description of the columns is given in Table I.

Instrumentation. The gas chromatographic (IGC) measurements were carried out with a Hewlett-Packard 5830A gas chromatograph, which was equipped with a dual flame ionization detector. The experimental setup and procedure have been described in a previous publication.[11]

The calorimetric measurements (DSC) were carried out with a Du Pont 990 thermal analyzer (approximately 10 mg of sample) at a scan rate of 5 °C/min (second run). The glass transition temperature was taken as the onset of the transition.

Data Reduction. Specific retention volumes, $V_g°$ (cm^3/g), were computed in the usual manner[11,12]

$$V_g° = t_N F J / w_L \tag{1}$$

where t_N is the net retention time for the probe, F is the carrier gas flow rate at 0 °C and 1 atm (STP), J is a correction factor for gas compressibility, and w_L is the weight of polymer in the column.

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