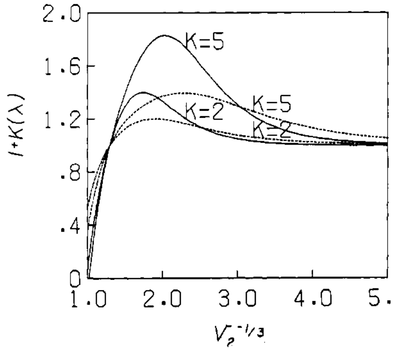

**Figure 4.** Calculations of 1 + $K(\lambda)$ vs. the linear dilation ratio $v_2^{-1/3}$ for networks formed at a volume fraction 0.457. For the solid curves $p = 4$, and for the dashed curves $p = 3$; values of $\kappa$ are given with each curve.

prominent, and second, as $\kappa$ is decreased ($p$ constant), the maximum occurs at smaller dilutions.

While a quantitative correspondence between Figures 3 and 4 cannot be made, the striking qualitative similarity between the experimental and theoretical curves cannot be denied. As Flory[4] has shown, the theoretical elastic equation of state reflects a transition between two extremes of behavior. At small strains the entanglement constraints predominate and the junction displacements approach affine behavior. At higher strains the entanglement constraints become less severe, and the behavior deduced by James and Guth[16] for phantom networks is approached.

## Conclusions

This work verifies that the elastic contribution to the chemical potential of the diluent in a solution-cured network is encompassed, qualitatively at least, by Flory's [4,15] recent theory of rubber elasticity. The separation of mixing and elastic contributions to the free energy of swollen elastomers now seems to be less questionable than it was in the earlier work. Further swelling measurements to test the implications of the theory are currently being undertaken.

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# Effect of Polyelectrolyte Charge Density on Calcium Ion Activity Coefficients and Additivity in Aqueous Solutions of Calcium Acrylamide–Acrylic Acid Copolymers

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ABSTRACT: Calcium ion activity coefficients have been determined in aqueous solutions of fully neutralized calcium poly(acrylamide–acrylic acid) copolymers whose charge spacing ranged from 3.9 to 25 Å. Measurements were made at 25 °C in both the absence and the presence of added simple electrolyte, $CaCl_2$. In the absence of $CaCl_2$, the activity coefficients are shown to decrease linearly with the square root of the polyelectrolyte charge density and are shown to obey an empirical expression relating the measured activity coefficients to the counterion charge and polyelectrolyte charge density. In the presence of $CaCl_2$, the measured activity coefficients are in excellent agreement with those predicted by an additivity of contributions from the simple salt and polyelectrolyte.

## Introduction

There are few systematic investigations in which the charge density of the polyelectrolyte is varied while the chemical nature of the backbone is kept constant.[1-8] Such studies aimed at understanding the interactions of monovalent and multivalent counterions with polyelectrolytes are of paramount importance. Recently, it was reported that in salt-free solutions of fully neutralized sodium acrylamide–acrylic acid copolymers a linear relationship between the measured counterion activity coefficients $\gamma_{\mathrm{Na}^+}$ and the polyion charge density was observed[5]

$$\gamma_{\mathrm{Na}^+} = I - S\xi^{1/2} \qquad (1)$$

where $\xi$ is the dimensionless charge density parameter commonly used to characterize polyelectrolytes

$$\xi = e^2/DkTb \qquad (2)$$

with $e$ being the protonic charge, $D$ the bulk dielectric constant, $k$ the Boltzmann constant, $T$ the absolute temperature, and $b$ the average spacing of ionic groups along

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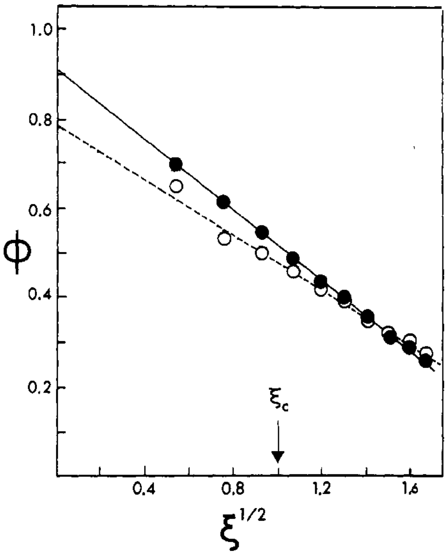

**Figure 1.** Dependence of osmotic coefficients $\phi$ on polyelectrolyte charge density parameter $\xi$ for the chloride salts of partially neutralized poly(vinylamine) (○) and the sodium salts of partially neutralized poly(acrylic acid) (●). Data from ref 9.

the contour length of the polyelectrolyte chain; $S$ and $I$ were respectively interpreted to be measures of the electrostatic and specific interactions between the counterions and polyions, with respective values of 0.42 and 0.96. The linear relationship for $\gamma_{Na^+}$ given by eq 1 was also found to be obeyed in partially neutralized sodium polymethacrylate solutions,[5] with $S = 0.35$ and $I = 0.85$.

When the osmotic coefficients $\phi$ reported by van Treslong and Moonen[9] for salt-free solutions of the sodium salts of partially neutralized poly(acrylic acid) (PAA) and chloride salts of partially neutralized poly(vinylamine) (PVA) are plotted, the same functionality with $\xi$ is observed; i.e., the osmotic coefficient is linearly related to $\xi^{1/2}$. This is demonstrated in Figure 1, where the slope is 0.39 for PAA and 0.31 for PVA.

With these findings, it seemed worthwhile to determine if a similar functionality exists for divalent counterions. Thus the same series of acrylamide–acrylic acid copolymers, ranging in charge density $\xi$ from 0.29 to 1.85, previously studied as their sodium salts,[5] were presently fully neutralized with $Ca(OH)_2$, and $Ca^{2+}$ ion activity coefficients were determined in aqueous solution.

Sodium bromide solutions containing sodium acrylamide–acrylic acid copolymers closely obey the additivity rule[5]

$$\left(\frac{\gamma_{Na^+}}{\gamma_{Na^+}{}^{\circ}}\right)_X = \frac{X}{X+1}(\gamma_{Na^+})_{\infty} + \frac{1}{X+1} \qquad (3)$$

where $X$ is a dimensionless concentration parameter, defined as the ratio of polyelectrolyte to simple salt, both in equivalents, $(\gamma_{Na^+})_{\infty}$ is the counterion activity coefficient in salt-free polyelectrolyte solution, and $(\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ})_X$ is the ratio, at a given value of $X$, of the counterion activity coefficient in the salt-containing polyelectrolyte solution to that in the polyelectrolyte-free salt solution. When expressed in this form, i.e., by correcting for small ion–small ion interactions[10] by $\gamma_{Na^+}{}^{\circ}$, the ionic strength dependence observed with other forms of the additivity rule was eliminated. Equation 3 was shown to be obeyed over the entire range of polyelectrolyte charge densities, polyelectrolyte concentrations, and simple salt concentrations investigated. It would be important to note if eq 3 also holds for calcium ions since no test of additivity of activity coefficients with divalent counterions has been reported in the literature. Thus calcium ion activity coefficients have been determined for calcium acrylamide–acrylic acid copolymers with and without $CaCl_2$, and the results have been compared with additivity eq 3.

Table I
Properties of Calcium Acrylamide–Acrylic Acid Copolymers Employed in This Study

| acrylic acid, mol % | $b$,[a] Å | $\xi$[b] |
|---|---|---|
| 10 | 25 | 0.29 |
| 14 | 18 | 0.40 |
| 22 | 11.3 | 0.63 |
| 30 | 8.3 | 0.86 |
| 42 | 6.0 | 1.20 |
| 57 | 4.4 | 1.62 |
| 65 | 3.9 | 1.85 |

[a] Based on a spacing of 2.5 Å for vinyl groups. [b] Calculated from eq 2.

## Experimental Section

Acrylamide–acrylic acid copolymers were prepared by alkaline hydrolysis of polyacrylamide (PAM). Details of the hydrolysis, purification, and characterization procedures have been reported previously.[5] The purified polyacids were converted to their calcium salts by complete neutralization with $Ca(OH)_2$. Polymer samples were labeled as CaPAM-*y*, where *y* denotes the degree of hydrolysis (as mole percent acrylic acid content of the copolymer). Poly(acrylic acid) (i.e., CaPAM-100) was insoluble as the calcium salt and could not be included in this series of measurements.

Analytical grade $CaCl_2$ was used without further purification. All solutions were prepared by volumetric dilution of the stock $CaCl_2$ and appropriate calcium polyelectrolyte solution.

A solid matrix ion exchange membrane calcium ion selective electrode purchased from HNU Systems, Inc., was used in conjunction with an Orion double-junction reference electrode (with 4 M KCl filling solution) for the measurement of activity coefficients. All measurements were carried out in stirred solutions thermostated at 25 ± 0.05 °C. Calibration curves were determined before and after every series of measurements on the polyelectrolyte solutions. Electrode slopes were Nernstian and were never found to differ by more than 0.5 mV/decade between the two calibrations. Activity coefficients of the standardizing $CaCl_2$ solutions were calculated by the extended Debye–Hückel equation.

## Results and Discussion

Calcium ion activity coefficients $\gamma_{Ca^{2+}}$ have been measured at 25 °C in aqueous solutions of the calcium polyelectrolytes listed in Table I. The polyelectrolyte concentrations were kept constant at 0.010 N for all measurements. For each polyelectrolyte, activity coefficients were measured in salt-free solution and in the presence of three different concentrations of $CaCl_2$, 0.020, 0.010, and 0.0020 N, i.e., excess $CaCl_2$ ($X = 0.5$), equal concentrations of polyelectrolyte and simple salt ($X = 1$), and excess polyelectrolyte ($X = 5$), respectively.

The dependence of the measured activity coefficients $\gamma_{Ca^{2+}}$ on $\xi$ in salt-free solution is shown in Figure 2, where $\gamma_{Ca^{2+}}$ is seen to decrease linearly with $\xi^{1/2}$, according to eq 1, with $I = 0.43$ and $S = 0.26$, which should be compared with the values $I = 0.96$ and $S = 0.42$ previously reported[5] for sodium counterions with the same series of polyelectrolytes. To further substantiate the linear relationship between divalent counterion activity coefficients and $\xi^{1/2}$, included in Figure 2 are $\gamma_{Ca^{2+}}$ values reported in the literature by various researchers for a number of salt-free solutions of calcium polyelectrolytes (primarily ionic polysaccharides) of different charge densities and different primary structures. Focusing first on the results of Rinaudo et al.[3] for a series of (carboxymethyl)cellulose (CMC)

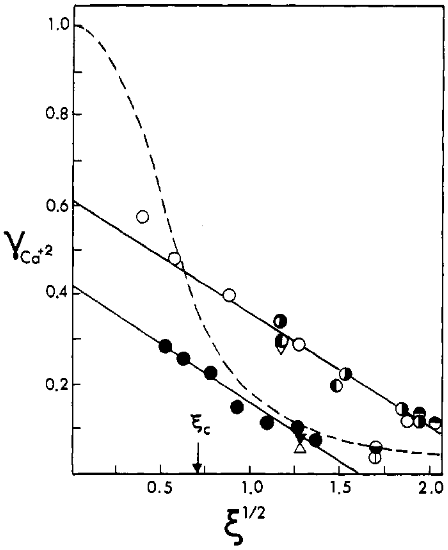

**Figure 2.** Dependence of calcium ion activity coefficients $\gamma_{Ca^{2+}}$ on $\xi$ at 25 °C in salt-free aqueous solutions of CaPAM-*y* (●) and the calcium salts of CMC (◑, ref 3), CMA (◒, ref 3), $\kappa$- and $\lambda$-CARR (◐, ref 12), PEC (○, ref 1), PCT (△, ref 11), GUL (▼, ref 11), MAN (▽, ref 11), DES (○, ref 14), and PMA (⊖, ref 11). The upper and lower solid lines are, respectively, least-squares fits of the experimentally determined activity coefficients for CaCMC and CaPAM-*y*. The broken line is theoretically predicted from the Manning theory.

polyelectrolytes, ranging in values of $\xi$ from 1.3 to 3.9, one can see that at any given charge density the values of $\gamma_{Ca^{2+}}$ are consistently higher than for the corresponding CaPAM polyelectrolytes. However, they *do* vary linearly with $\xi^{1/2}$, with a slope of 0.25, which is identical with that of the CaPAM series. The data of Kohn and Furda[1] for a series of calcium pectinates (PEC) covering a large range of charge densities, $0.16 < \xi < 3.4$, also vary linearly with $\xi^{1/2}$ and essentially coincide with the CaCMC results. Thus it appears that the slope is primarily determined by electrostatic interactions, while the intercept is strongly affected by the specific structure of the polyelectrolyte. The data of Kohn and Larsen[11] particularly substantiate the role of specific, short-range interactions on the degree of counterion–polyion interaction; while $\gamma_{Ca^{2+}}$ for calcium pectate[11] (PCT) and calcium polyguluronate[11] (GUL) fall experimentally with the CaPAM results, $\gamma_{Ca^{2+}}$ for calcium polymannuronate[11] (MAN), which is epimer of GUL, falls with the CMC data. Other data included in Figure 2 are for calcium (carboxymethyl)amylose[3] (CMA) and calcium $\kappa$- and $\lambda$-carrageenans[12] (CARR), which fall with the CMC results, and calcium polymethacrylate[11] (PMA) and calcium dextran sulfate[14] (DES), which fall intermediately between the CaPAM and CMC curves.

The demonstrated linearity of $\gamma_{Ca^{2+}}$ with $\xi^{1/2}$ for CaPAM and PEC polyelectrolytes is particularly interesting in that it extends over both sides of the Manning critical charge density, $\xi_c$, which for divalent counterions corresponds to $\xi = 0.5$. According to the Manning theory[14-16] different modes of interaction are predicted on both sides of the critical value, i.e., only Debye–Hückel type interactions between the counterions and polyion below $\xi_c$ and a combination of condensation of counterions onto the polyion *and* Debye–Hückel interaction above the critical charge density. Thus a different dependence on $\xi$ is predicted on either side of $\xi_c$. The experimentally determined $\gamma_{Ca^{2+}}$ values are compared with the theoretical ones in Figure 2. Above $\xi_c$ the experimental values of $\gamma_{Ca^{2+}}$ for the CaPAM series are in reasonable agreement with theory, substantiating the condensation concept; below $\xi_c$, calcium ion–polyion interaction is significantly greater than predicted, suggesting that condensation of counterions may occur below $\xi_c$ as well as above. The calcium activity coefficients obtained for the more complex polysaccharide structures above $\xi_c$ are seen to be generally significantly higher than the theoretical values; as discussed above, the discrepancy may be due to specific structural features and not due to electrostatic effects.

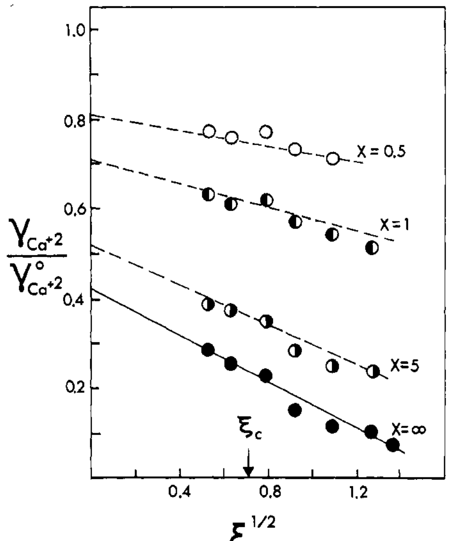

**Figure 3.** Dependence of the measured activity coefficient ratio $\gamma_{Ca^{2+}}/\gamma_{Ca^{2+}}{}^{\circ}$ on $\xi$ determined at 25 °C in aqueous solutions of 0.01 N CaPAM-*y* in the absence of simple electrolyte (●) and in the presence of 0.002 (◑), 0.01 (◐), and 0.02 N (○) $CaCl_2$. The solid line is the least-squares fit of the salt-free experimental data; the broken lines are predicted from additivity eq 5.

From a comparison of the measured calcium and sodium ion activity coefficients, it appears that for salt-free solutions eq 1 may be rewritten to give a more general empirical expression

$$\gamma_1 = |Z_1|^{-1} - 0.7\xi^{1/2}\exp(-0.5|Z_1|) \qquad (4)$$

where the subscript 1 indicates counterions. The second term in eq 4 is interpreted to be a measure of the reduction in the counterion activity coefficient due to electrostatic interaction with the polyion, and $|Z_1|^{-1}$ to be a measure of short-range interactions, which may include condensation. From eq 4 it should be noted that as $\xi$ approaches zero, $\gamma_1$ approaches $|Z_1|^{-1}$. Thus when the charges on a hypothetical chain are infinitely separated, $\gamma_{Na^+} = 1$ and $\gamma_{Ca^{2+}} = 0.5$. The values of $S$ or $0.7\exp(-0.5|Z_1|)$ for monovalent and divalent counterions are predicted by eq 4 to be 0.42 and 0.26, respectively. Experimentally, these were found to be 0.42 for sodium ions and 0.26 for calcium ions with the PAM-*y* polyelectrolytes and 0.25 for calcium ions with the CMC and PEC polyelectrolytes! Thus structural differences do not appear to affect electrostatic interactions. The intercept in eq 4 is predicted to be unity for monovalent counterions and 0.5 for divalent counterions. Experimentally, the intercepts were found to be 0.96 and 0.43 for sodium and calcium counterions, respectively, with PAM-*y* and 0.61 for calcium in CMC and PEC solutions. The differences between these experimentally observed intercepts and $|Z_1|^{-1}$ can probably be attributed to differences in specific interactions of the sodium and calcium ions with the different polyions.

In the presence of $CaCl_2$, the relationship between measured calcium ion activity coefficients and $\xi$ is shown in Figure 3, where the measured activity coefficients $\gamma_{Ca^{2+}}$ are corrected for small ion–small ion interactions by $\gamma_{Ca^{2+}}{}^{\circ}$, 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 $\xi$ 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.

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# 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 $1.5 \times 10^6$, 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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