

An Approach for Assessment of the Hydrophobicity/Hydrophilicity of Charged Polymers

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Gibbs–Donnan-based logic, employed to examine counterion equilibria in charged polymer suspensions, has led to assessment of their water sorption properties. With such information made available, a number of factors which promote hydrophobicity in charged polyions have been identified. Examples of the effect that such enhancement of hydrophobicity can have on the chemical properties of the charged polymer phase have also been provided. The information gained from this study of hydrophobicity in charged polymers, while demonstrating how important this property can be, provides a sound introduction to the dimensions of this phenomenon.

Introduction

Gibbs–Donnan-based logic^{1–11} has led to the development of an approach which permits accurate assessment of counterion activity levels, e.g., $\{\bar{H}^+\}$ and $\{\bar{C}^+\}$, in the separate phase defined by suspensions of linear weak acid polyelectrolytes $(\overrightarrow{HA})_p$ and their cross-linked gel analogues $(\overrightarrow{HA})_r$ in the course of their dissociation in the presence of simple salt, CX, solutions. (The arrows and bar are placed above the various quantities introduced above to show their association with the separate phase defined by the linear polyelectrolyte, \rightarrow , and the cross-linked gel, $-$, and such identification of phase participation is provided throughout this presentation.) To reach this capability one only needs to obtain a valid assessment of \bar{K}_a^{int} , the intrinsic dissociation constant of the weak acid functionality repeated throughout the polyion domain for comparison with K_a , the dissociation constant measured. One approach that has been used for this purpose is presented in Figure 1.⁴ In this figure the dissociation of carboxymethyldextran, CmDx, suspensions in NaCl solutions, at concentration levels ranging from 0.020 to 1.0 mol dm⁻³, has been carefully monitored during neutralization with standard base. The separate pK_a versus α plots that the different salt concentration levels give rise to have been obtained with the well-known Henderson–Hasselbalch equation presented below:

$$pK_a = p\{H^+\} - \log \frac{\alpha}{1 - \alpha} \quad (1)$$

In this equation:

$$p\{H^+\} = p\{\bar{H}^+\} + p\{C^+\} - p\{\bar{C}^+\} + \frac{\pi(V_{C^+} - V_{H^+})}{2.3RT} \quad (2)$$

with π representing “swelling pressure” of the system and V_{C^+}

and V_{H^+} corresponding to the partial molar volumes of the counterions.^{3,4,7,8,11} When eq 2 is substituted for $p\{H^+\}$ in eq 1

$$\begin{aligned} pK_a &= p\{\bar{H}^+\} - \log \frac{\alpha}{1 - \alpha} + p\{C^+\} - \\ &\quad p\{\bar{C}^+\} + \frac{\pi(V_{C^+} - V_{H^+})}{2.3RT} \\ &= p\bar{K}_a^{\text{int}} + p\{C^+\} - p\{\bar{C}^+\} + \frac{\pi(V_{C^+} - V_{H^+})}{2.3RT} \end{aligned}$$

and

$$pK_a - p\bar{K}_a^{\text{int}} = p\{C^+\} - p\{\bar{C}^+\} + \frac{\pi(V_{C^+} - V_{H^+})}{2.3RT} \quad (3)$$

Since

$$p\{C^+\} - p\{\bar{C}^+\} = \log DP \quad (4)$$

with DP corresponding to the Donnan potential term determined by the difference in activity level of the C^+ ion in the two phases defined by the salt solution and the charged polymer suspension.^{3,4}

$$pK_a - p\bar{K}_a^{\text{int}} = \log DP + \frac{\pi(V_{C^+} - V_{H^+})}{2.3RT} \quad (5)$$

With NaX the ionic strength-defining constituent of the aqueous phase $V_{C^+} - V_{H^+} = 0.0012 \text{ dm}^3 \text{ mol}^{-1}$ and the pressure, volume term is small enough to neglect even when π reaches 300 atm, a value as high as one encounters with even the most highly cross-linked ion exchangers.¹¹ $[\pi(V_{Na^+} - V_{H^+})]/(\ln 10 RT) = [300 \text{ atm} (0.0012 \text{ dm}^3)(\text{mol})^{-1}]/[2.3(0.0821 \text{ dm}^3 \text{ atm deg}^{-1} \text{ mol}^{-1})(298^\circ)] = 0.0064$. Elimination of the “swelling pres-

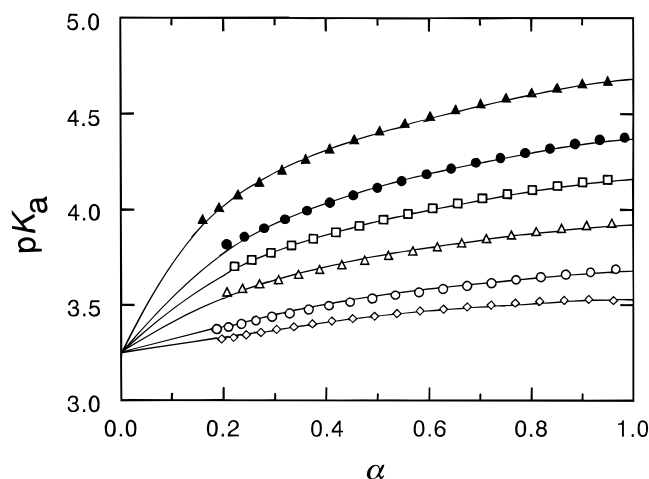


Figure 1. Effect of salt concentration level on the measurable dissociation properties of carboxymethyl dextran ($DS = 1.70$), the linear polyelectrolyte analogue of the Sephadex C-25 and C-50 gels, when Na^+ ion is the Donnan potential determining counterion: (\blacktriangle) $C_s = 0.02$; (\bullet) $C_s = 0.05$; (\square) $C_s = 0.10$; (\triangle) $C_s = 0.20$; (\circ) $C_s = 0.50$; (\diamond) $C_s = 1.00 \text{ mol dm}^{-3}$.

sure" term yields the following useful equation.

$$pK_{a,\alpha} - p\bar{K}_a^{\text{int}} = p\{C^+\} - p\{\bar{C}^+\}_\alpha = \log DP \quad (6)$$

Extrapolation of the curves to intercept the $p\bar{K}_a$ coordinate at $\alpha = 0$ leads to an assignment of 3.25 to the $p\bar{K}_a^{\text{int}}$ term, the DP term approaching unity as α approaches zero in each of the curves. The fact that the $p\bar{K}_a^{\text{int}}$ value essentially duplicates the pK_a value reported in the literature¹³ for methoxyacetic acid, the simple acid that resembles most closely the weak acid functionality repeated in the CmDx, is strongly supportive of the above assignment of $p\bar{K}_a^{\text{int}}$ since the weak acid functionality of the CmDx is repeated enough times to be statistically equivalent to the methoxyacetic acid it so closely resembles. With $p\bar{K}_a^{\text{int}}$ accessible in this way, its subtraction from any pK_a measurement made at a particular experimental situation, e.g., α and $p\{\text{Na}^+\}$, is equatable to $\log DP$, where, as noted above, DP corresponds to the Donnan potential term prevailing in the system at equilibrium.^{3,4}

Reasonably accurate assessment of water sorption by the separate phase defined by the linear, weak acid polyelectrolyte in the course of its dissociation at a particular CX concentration level has been readily accessible with this approach. By merely using eq 6 to resolve $p\{\bar{C}^+\}_\alpha$ at the experimental conditions employed, one obtains the counterion activity level over the dissociation range of study. For example, with the CmDx, 0.02 mol dm^{-3} NaCl system at a dissociation value of 0.95 application of eq 6 to this single point accessible with Figure 1

yields a $p\{\text{Na}^+\}_{\alpha=0.95}$ value of 0.31. This corresponds to a Na^+ activity level of $0.5 \text{ mol kg}^{-1} \text{H}_2\text{O}$, a Na^+ ion concentration level of $0.70 \text{ mol kg}^{-1} \text{H}_2\text{O}$, and a transfer of 1.43 kg of H_2O /mol of Na^+ ion into the polyion domain. To support this assessment of the above molality, it was only necessary to show that the $\bar{\gamma}_{\text{Na}^+}$ value estimated to prevail at that molality yielded a $\{\text{Na}^+\}$ ion activity value in agreement with the value made accessible with eq 6.

The assumptions that $\gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} = \gamma_{\pm\text{KCl}}$ at $[\text{Na}^+] = [\text{Na}^+]$ and that $\bar{\gamma}_{\text{Na}^+} = \gamma_{\text{Na}}$ when $[\text{Na}^+] = [\text{Na}^+]$ in these systems have been presumed to justify employment of eq 7, presented below, to reach the above objective. In this equation the

literature-based mean molal activity coefficient values for NaCl and KCl¹⁴ at $[\text{Na}^+]$ equal to $0.7 \text{ mol kg}^{-1} \text{H}_2\text{O}$ have been selected on this basis

$$\bar{\gamma}_{\text{Na}^+} = \frac{(\gamma_{\pm\text{NaCl}})^2}{(\gamma_{\pm\text{KCl}})} \text{ at } m_{\text{NaCl}} = 0.7 \text{ mol kg}^{-1} \text{H}_2\text{O} = \frac{(0.667)^2}{0.626} = 0.711 \quad (7)$$

The fact that the transport numbers of K^+ and Cl^- ions are essentially duplicated in KCl over a sizable concentration range¹⁵ is believed to indicate that these ions have the same shape and size. Their essentially identical charge density should, as a result, be expected to yield the equivalent nonideality presumed to prevail. Equating $\bar{\gamma}_{\text{Na}}$ to γ_{Na} when $[\text{Na}^+] = [\text{Na}^+]$ does not appear to be unreasonable as well.

When the molality selected is multiplied by the $\bar{\gamma}_{\text{Na}^+}$, so obtained, in eq 8

$$\{\text{Na}^+\} = \bar{\gamma}_{\text{Na}^+}[\text{Na}^+] = 0.711(0.7 \text{ mol kg}^{-1} \text{H}_2\text{O}) = 0.50 \text{ mol kg}^{-1} \text{H}_2\text{O} \quad (8)$$

$\{\text{Na}^+\}$ duplicates the value resolved with eq 6 to validate the $[\text{Na}^+]$ ion molality selection.

When the hydrophobicity phenomenon is encountered, however, activity levels estimated for the Donnan potential determining counterions with eq 6 reach levels considerably higher than those normally encountered. Accurate estimate of water sorption by the method described is no longer feasible. Despite this loss of the ability to assess water sorption tendencies of the charged polymers in a precise manner, the accessibility of counterion activities with eq 6 suffice. This information is believed to permit reaching the following objective, a valid assessment of change in the water sorption properties of charged polymers that is affected by modifying their structure or composition. With this capability the insight gained with respect to factors that lead to enhancement of hydrophobicity in charged polymers assures the successful incorporation of water sorption properties being sought for a particular charged polymer.

The results obtained with charged polymer, simple salt systems selected for examination in this manner, show how this approach has served the above objectives. It has been possible, by merely comparing the magnitude of DP that is associated with various polyions at the same salt concentration level and the same α value, to show (1) how the physical properties of different charged polymers affect water sorption properties, (2) how different Donnan potential determining counterions affect hydrophobic response, (3) how other factors influence hydrophobicity, and (4) how hydrophobicity influences the chemical properties of the charged polymers.

Employment of this approach to compare estimates of $p\{\bar{C}^+\}$ in the cross-linked gel analogues of these linear, weak acid polyelectrolytes with the $p\{\bar{C}^+\}$ values made accessible by direct measurement of the water sorbed by these gels in the course of their dissociation has proved useful as well. Contradictory results obtained with the flexible, Sephadex C-50 (CmDx)¹⁶ and the Amberlite IRC-50 (polymethacrylic acid, PMA) gels¹⁷ were assignable to their macroporosity^{18,19} which was presumed to function as an extension of the solution phase. The consequent

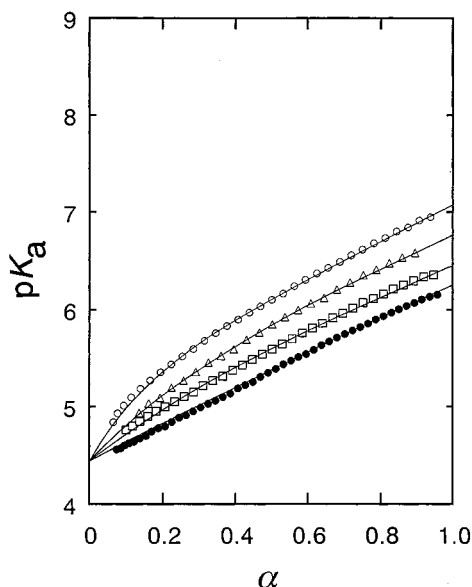


Figure 2. Effect of salt concentration level on the measurable dissociation properties of poly(acrylic acid) when Na^+ is the Donnan potential controlling counterion: (○) $C_s = 0.01$; (△) $C_s = 0.02$; (□) $C_s = 0.05$; (●) $C_s = 0.10 \text{ mol dm}^{-3}$.

overestimate of the water content of the gel phase led to variability and exaggeration of the $\text{p}K_{\text{a}}^{\text{int}}$ values resolved with eq 6.

How Physical Properties of Different Polyelectrolytes Affect Their Interaction with Water

The $\text{p}K_{\text{a},\alpha}$ value of 4.15 that is reached by CmDx at $\alpha = 0.95$ in the presence of 0.10 mol dm^{-3} NaCl by the third curve presented in Figure 1⁴ has been selected to show how this charged polymer's tendency to interact with water differs from the tendency of poly(acrylic acid), PAA, to interact with water at the same salt concentration level and the same α value. In the first step of this exercise the DP term for the CmDx, NaCl system is found to equal 7.9 with eq 6. In the second step the

value of $\{\text{Na}^+\}_{\alpha=0.95}$ is found to equal 0.622 by multiplying $\{\text{Na}^+\}$, equatable to $\gamma_{\text{Na}^+}[\text{Na}^+]$, by the DP term. The activity coefficient, γ_{Na^+} , estimated by equating it to $(\gamma_{\pm\text{NaCl}})^2/(\gamma_{\pm\text{KCl}})$ at $[\text{Na}^+] = 0.10 \text{ mol kg}^{-1}\text{H}_2\text{O}$ is equal to 0.787. With $\{\text{Na}^+\}_{\alpha=0.95}$ equal to 0.622, its molality is estimated to reach a value of approximately $0.87 \text{ mol kg}^{-1}\text{H}_2\text{O}$. Water sorption per mol of Na^+ ion amounts to 1.15 kg.

The dissociation properties of PAA measured in the presence of NaCl at concentration levels of 0.01, 0.02, 0.05, and 0.10 m during neutralization with standard base are presented as plots of $\text{p}K_{\text{a}}$ versus α in Figure 2.²⁰ In this instance extrapolation of the curves to intercept the $\text{p}K_{\text{a}}$ axis at $\alpha = 0$ leads to resolution of a $\text{p}K_{\text{a}}^{\text{int}}$ value of 4.45. The $\text{p}K_{\text{a},\alpha=0.95}$ value resolved at $\alpha = 0.95$ with NaCl at a concentration level of 0.10 m is found to equal 6.15. In this instance the DP term made available by subtracting $\text{p}K_{\text{a}}^{\text{int}}$ from $\text{p}K_{\text{a},\alpha=0.95}$ is equal to 50.1 and $\{\text{Na}^+\}_{\alpha=0.95}$ reaches a value of 3.94. The Na^+ ion molality of 3.8, found to be compatible with this Gibbs–Donnan-based assessment of $\{\text{Na}^+\}_{\alpha=0.95}$, is 4.5 times larger than the Na^+ ion molality of 0.87 that was determined to prevail in the CmDx domain exposed to exactly the same experimental conditions as the PAA domain.

The minimal resistance to water sorption that is signaled by the low DP values one observes with the CmDx, NaCl system

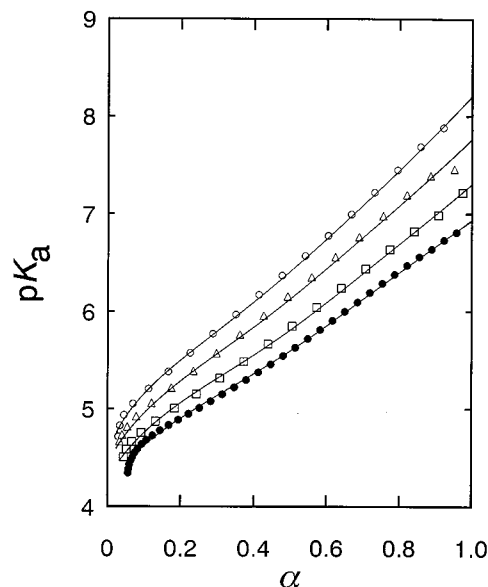


Figure 3. Effect of salt concentration level on the measurable dissociation properties of poly(acrylic acid) when tetramethylammonium ion, TMA^+ , is the Donnan potential controlling counterion: (○) $C_s = 0.01$; (△) $C_s = 0.02$; (□) $C_s = 0.05$; (●) $C_s = 0.10 \text{ mol dm}^{-3}$.

is characteristic of polysaccharides in general and is a consequence of the flexibility of their skeletal structure²¹ and the presence of OH groups. Because of these factors there is lowered resistance to water sorption by the solvent-permeable matrix. The lower sorption of water by the PAA domain is predictable on the basis of its more rigid structure.²¹

How Different Donnan Potential Determining Counterions Affect the Interaction of Charged Polymers with Water

*Effect of Substituting Tetraalkylammonium Ions for Na^+ Ion as the Donnan Potential Determining Counterion on the Measurable Dissociation Properties of Poly(acrylic acid).*²⁰ The dissociation properties of PAA, measured separately in the presence of tetramethylammonium chloride, TMACl, tetraethylammonium chloride, TEACl, and tetrabutylammonium chloride, TBACl, at concentration levels of 0.01, 0.02, 0.05, and 0.10 mol dm^{-3} , during neutralization with standard base, are presented as plots of $\text{p}K_{\text{a}}$ versus α in Figures 3–5. They show that the substitution of tetraalkylammonium, TAA^+ , ions for Na^+ ion leads to sizable gain in the rate of increase in the $\text{p}K_{\text{a}}$ values as α is increased. Activity levels reached by the TAA^+ ions in the solvent sheath of the polyion domain at the highest α values reached are much larger than the activity level reached by Na^+ ion in these parallel experiments. To facilitate this comparison representative $\text{p}K_{\text{a}}$ values measured for each of the counterions at a concentration level of 0.01 mol dm^{-3} are plotted versus α in Figure 6. The $\text{p}K_{\text{a}}$ values resolved for the three TAA^+ ions separate from the values obtained with the Na^+ ion, the extent of separation increasing as α is increased. Since the difference between the $\text{p}K_{\text{a}}$ values measured for the TBA^+ and Na^+ ions is larger than for the others (TEA^+ and Na^+ and TMA^+ and Na^+), confining analysis of this phenomenon to their difference in Figure 6 is felt to provide most effectively the example of system disturbance being examined. Examination of Figure 6 on this basis shows that at α values as low as 0.1 the replacement of Na^+ ion by the TBA^+ ion results in a noticeable increase in the magnitude of the Donnan potential term accessible by subtracting the intrinsic $\text{p}K_{\text{a}}^{\text{int}}$ value of ~ 4.45

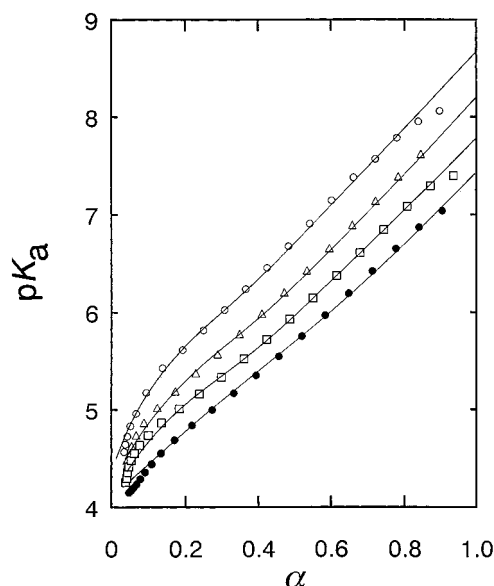


Figure 4. Effect of salt concentration level on the measurable dissociation properties of poly(acrylic acid) when tetraethylammonium ion, TEA^+ , is the Donnan potential controlling ion: (○) $C_s = 0.01$; (△) $C_s = 0.02$; (□) $C_s = 0.05$; (●) $C_s = 0.10 \text{ mol dm}^{-3}$.

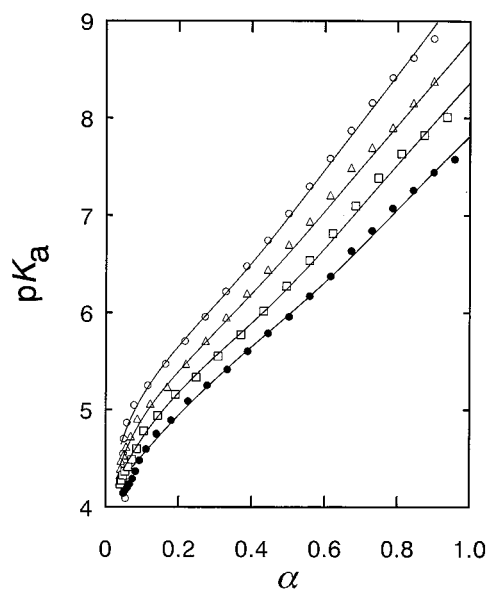


Figure 5. Effect of salt concentration level on the measurable dissociation properties of poly(acrylic acid) when tetrabutylammonium ion, TBA^+ , is the Donnan potential controlling counterion: (○) $C_s = 0.01$; (△) $C_s = 0.02$; (□) $C_s = 0.05$; (●) $C_s = 0.10 \text{ mol dm}^{-3}$.

assignable to the weak acid functionality repeated in the PAA macromolecule from the pK_a values measured. At $\alpha = 0.1$, the vertical displacement of pK_a from pK_a^{int} is larger by 0.2 log unit when TBA^+ replaces Na^+ ion as the Donnan potential determining counterion. When α reaches a value of 0.9, the vertical displacement of pK_a from pK_a^{int} , with TBA^+ the Donnan potential controlling counterion, appears to have reached a value approximately 2 log units larger than the value reached with the Na^+ ion. This gain in the Donnan term is promoted by the hydrophobicity introduced to the system by replacing the dipolar water-bound Na^+ ion with the bulky, water-repelling organic constituency of the TBA^+ ion. Forces repelling water in much the same way as surfactants do are apparently accompanied by strong interaction of the negatively charged sites to the TAA^+ ion to yield the water-depleted polymer phase one observes.

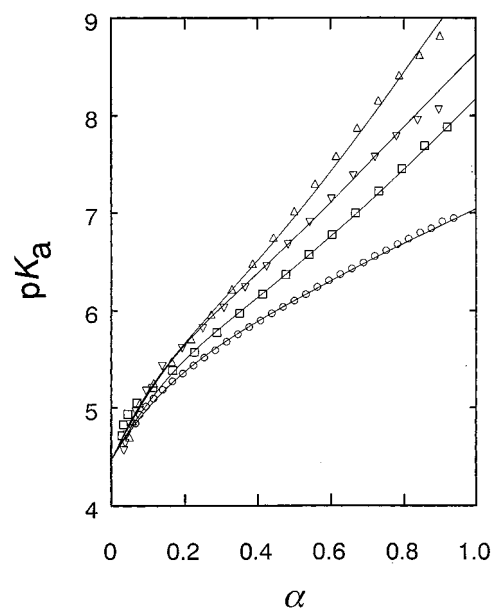


Figure 6. Comparison of the separate pK_a versus α plots obtained for PAA in the presence of the four different salts, NaCl , TMACl , TEACl , and TBACl , at the same concentration level, $0.010 \text{ mol dm}^{-3}$.

The magnitude of the gain in the DP term may be somewhat exaggerated by disturbance of this measurement by the swelling pressure term, V_{TBA^+} , being so much larger than V_{Na^+} . However, such disturbance of DP assessments cannot approach dimensions which could seriously affect the conclusions drawn above. The value of π used in the example examining the contribution that the $\pi(V_{\text{Na}^+} - V_{\text{H}^+})/2.3RT$ term might have is much larger than the π value expected to prevail in the PAA, NaCl system to justify this assessment of the situation. Insight with respect to this aspect is provided in the literature.²²

Hydrophobic Influence of Different Alkali Metal Ions in Their Function as Donnan Potential Controlling Counterions During Dissociation of the Bifunctional, Weak Acid Polyelectrolyte Poly(maleic acid). An excellent example of how the hydration tendencies of Donnan potential determining counterions can affect the hydrophobicity characteristics of charged polyion surfaces has been provided in research carried out by Minakata et al.²³ In their study of the dissociation properties of the bifunctional weak acid polyelectrolyte poly(maleic acid), PMA, during neutralization with standard base, the affect of the presence of four different alkali metal ions, Li^+ , Na^+ , K^+ , and Cs^+ , at a fixed chloride ion concentration level of 0.10 mol dm^{-3} was examined. These data are summarized in plots of pK_a versus α presented in Figure 7.

In the presentation of these data, the two separate carboxylic acid moieties repeated in the PMA macromolecule were treated as if they were identical and α values ranging from 0 to 1 were employed to evaluate the apparent pK_a associated with the dissociation of the bifunctional moiety. Since the dissociation pattern of the two weak acids of maleic acid is sufficiently different in magnitude²⁴ ($pK_{a1} = 2.00$ and $pK_{a2} = 6.26$), the weaker acid of the two can be expected to remain essentially undissociated until the stronger acid is completely dissociated. The result of substituting α for α_1 and α_2 is the two-step dissociation pattern that is projected.

In the first dissociation step three of the four curves are essentially superimposable. Only the curve obtained in the presence of Cs^+ ion deviates significantly from the others. The fact that all pK_a values are as low in value as they are informs one that counterion concentration levels in the polyion domain

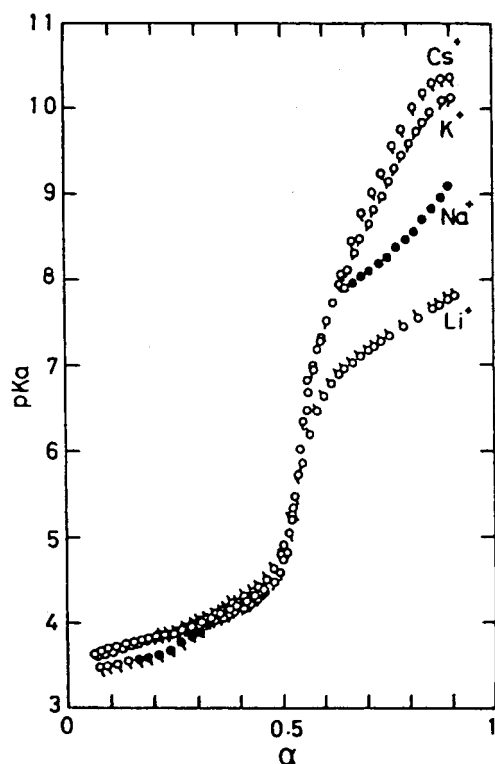


Figure 7. Effect of changing alkali metal counterion on the pK_a response of PMA to change in α : $C_s = 0.10 \text{ mol dm}^{-3}$; (○) Li^+ ; (●) Na^+ , $C_p = 0.045 \text{ monomol dm}^{-3}$; (○) K^+ , $C_p = 0.021 \text{ monomol dm}^{-3}$; (○) Cs^+ , $C_p = 0.033 \text{ monomol dm}^{-3}$.

are well within the normal range encountered with hydrophilic polyions and that counterion size and hydrophobicity factors are not contributors to the system pK_a response. With the second dissociation step entered, however, sizable separation of the curves is encountered as α increases to show (1) the increasing importance of the hydrophobicity factor and (2) the contribution of counterion size to the magnitude of this factor.

The larger the counterion, the smaller is the tendency for dipolar interaction of the water with it. The hydrophobicity introduced with the second dissociation step is enhanced by interaction with the solvent-freed counterion. With Cs^+ the largest counterion, the tendency for water removal from the polyion domain is greatest. With Li^+ , the smallest ion, the interaction of solvent is considerable and dipole interaction between counterion and solvent is at its highest level. The resultant enhancement of the solvent content of the polyion domain removes hydrophobicity from the system.

Other Factors Influencing Hydrophobicity in Linear Polyelectrolytes and Their Cross-Linked Gel Analogues

It has been observed that the substitution of TAA^+ ions for Na^+ ion as the counterion of the fully dissociated PAA leads to hydrophobicity in the separate phase generated. The positively charged N, C, and H ensemble introduced as counterion to the polyion domain by its interaction with the negatively charged sites repeated in the PAA macromolecule is obviously responsible for its water repellent properties. Since the arrangement of N, C, and H in the functionality repeated in linear, strong and weak base polyelectrolytes and their cross-linked gel analogues is similar to their arrangement in the PAA, TAA^+Cl^- systems, one can expect the strong and weak base polyelectrolytes to exhibit water repellent properties as well. Confirmation of this assessment has been sought by examining

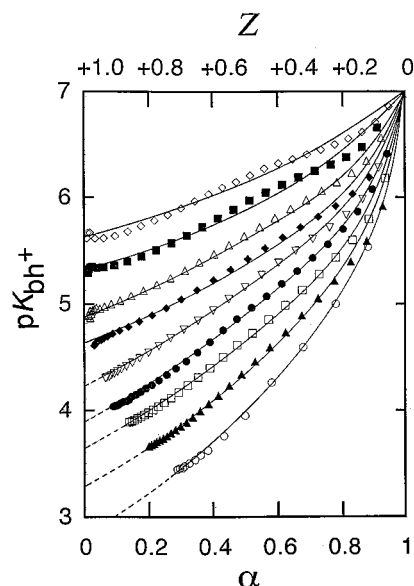


Figure 8. Dissociation properties of the conjugate acid of poly(vinylimidazole), PVImH^+ , at different salt concentration levels during its neutralization with standard base: (○) $C_s = 0.01$; (▲) $C_s = 0.02$; (□) $C_s = 0.05$; (●) $C_s = 0.10$; (▽) $C_s = 0.20$; (◆) $C_s = 0.50$; (△) $C_s = 1.0$; (■) $C_s = 2.0$; (◇) $C_s = 3.0 \text{ mol dm}^{-3}$ (NaCl).

the dissociation properties of the conjugate acids of poly(vinylimidazole), PVImH^+ , and poly(allylamine), PAAmH^+ , during their neutralization with standard base at different salt concentration levels. The details of this exercise are presented below.²⁵

Water Repellent Properties of Linear, Weak Base Polyelectrolytes. Suspensions of the conjugate acids of the linear, weak base polyelectrolytes PVImH^+ and PAAmH^+ in salt solutions at concentration levels ranging from 0.01 to 2 and 3 mol dm^{-3} were neutralized with standard base to permit assessment of the $pK_{bh^+,\alpha}$ versus α response to the change in the concentration level of the Donnan potential controlling counterion provided by the salt. (The NaCl molalities that correspond to the NaCl molarities of 2.0 and 3.0 mol dm^{-3} are 2.085 and 3.19 $\text{mol kg}^{-1}\text{H}_2\text{O}$.) Plots of the $pK_{bh^+,\alpha}$ versus α data that were obtained are presented in Figures 8 and 9. The more extensive data presentation for the PVImH^+ , NaCl system in Figure 8 is attributable to the lower pH range encountered with this system. In this lower pH range the glass electrode-based measurement program was less susceptible to error. The elevated pH values encountered with the PAAmH^+ , NaCl system limited the accessibility to accurate data and are responsible for the more restricted set of points reported in Figure 9.

When analyzing these results one needs to remember that the direct relationship that is observable between Z , the net charge of the weak acid functionality repeated in the CmDx and PAA simple salt systems, and α , the degree of dissociation, when similarly examined in Figures 1–6 is completely reversed with the PVImH^+ and PAAmH^+ simple salt systems. Instead of Z equaling α as it did earlier, it is now equatable to $1 - \alpha$. This complete reversal of the relationship between Z and α is noted by listing their respective values along the x coordinate at the top and bottom of Figures 8 and 9.

Since the charge of these conjugate acids of weak base polyions is positive instead of negative, the response of their $pK_{bh^+,\alpha}$ values to change in salt concentration level at fixed α values is the reverse of the response of $pK_{a,\alpha}$ values of the weak acid polyions to the same change in salt concentration level at these fixed α values. A consequence of this is that when

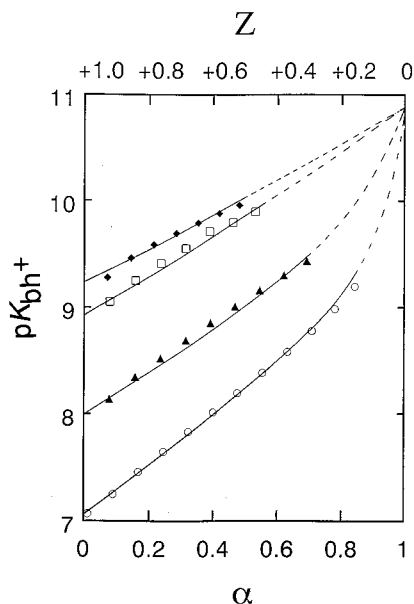


Figure 9. Dissociation properties of the conjugate acid of poly(allylamine), PAAMH⁺, at several different salt concentration levels during its neutralization with standard base: (○) $C_s = 0.01$; (▲) $C_s = 0.10$; (□) $C_s = 1.0$; (◆) $C_s = 2.0 \text{ mol dm}^{-3}$ (NaCl).

Gibbs–Donnan-based logic is employed to relate the $pK_{bh^+,\alpha}$ values measured to $p\bar{K}_{bh^+}^{\text{int}}$ one obtains the reciprocal of the Donnan potential, DP , term with eq 6. Because the H⁺ ion is repelled by the positively charged polyion domain, this equation must be modified as shown to obtain the value of the $(DP)_\alpha$ term applicable to Cl[−], the salt anion that determines its value.

$$p\bar{K}_{bh^+}^{\text{int}} - pK_{bh^+,\alpha} = \log DP \quad (9)$$

The $pK_{bh^+,\alpha}$ versus α plots, extended to intercept the $pK_{bh^+,\alpha}$ coordinate at $\alpha = 1$, converge to a common point identifiable with $p\bar{K}_{bh^+}^{\text{int}}$. As α approaches unity, Z approaches zero and DP , as a consequence, approaches unity to justify this assessment of the situation. The $p\bar{K}_{bh^+}^{\text{int}}$ value of 7.0 resolved in this manner for the PVImH⁺ is quite close in value to the pK value reported in the literature for imidazole, the weak base functionality repeated in the PVIm to once again support the statistically based rationalization of this result.

When the data compiled for the PVImH⁺, 3.0, 2.0, 1.0, 0.10, and 0.010 mol dm^{−3} (3.19, 2.085, 1.020, 0.10, and 0.010 mol kg^{−1}H₂O), NaCl systems are employed to project the Cl[−] ion activity, $\{\text{Cl}^-\}$, levels reached in the polyion domain as α approaches zero in these systems by equating $p\bar{K}_{bh^+}^{\text{int}} - pK_{bh^+,\alpha=0} + \log \{\text{Cl}^-\}$ to $\log \{\text{Cl}^-\}_{\alpha=0}$ the following results are obtained: $\{\text{Cl}^-\}$ activity levels of approximately 44, 56, 77, 97, and 113 mol kg^{−1}H₂O are projected to prevail in the solvent-sheathed polyion domain of the PVImH⁺ at the Cl[−] ion concentration levels of 3.19, 2.085, 1.020, 0.10, and 0.010 mol kg^{−1}H₂O (3.0, 2.0, 1.0, 0.1, and 0.01 mol dm^{−3}) employed. For the less accurately monitored PAAMH⁺, NaCl systems $\{\text{Cl}^-\}$ activity levels of ~56, ~51, ~58, and ~57 mol kg^{−1}H₂O are assignable to the polyion domain in the equilibria encountered with NaCl solutions at concentration levels equal to 2.085, 1.02, 0.10, and 0.010 mol kg^{−1}H₂O (2.0, 1.0, 0.10, and 0.010 mol dm^{−3}).

In order to facilitate use of eq 9 for estimate of $\{\text{Cl}^-\}_{\alpha=0}$ in the separate phase defined

$$pK_{bh^+}^{\text{int}} - pK_{bh^+,\alpha=0} + \log \{\text{Cl}^-\} = \log \{\text{Cl}^-\}_{\alpha=0} \quad (9)$$

by the PVImH⁺ and PAAMH⁺ suspensions at α equal to zero, the value of $\{\text{Cl}^-\}$ at the different salt concentration levels employed had to be accessed. To reach this goal literature-based $\gamma_{\pm\text{NaCl}}$ values at the experimental salt concentration levels encountered were assigned to γ_{Cl^-} . This path to the assessment of γ_{Cl^-} is consistent with the earlier approach to the estimate of γ_{Na^+} and $\bar{\gamma}_{\text{Na}^+}$ by equating its value to the literature-based¹⁴ $(\gamma_{\pm\text{NaCl}})^2/\gamma_{\pm\text{KCl}}$ term. In both instances γ_{K^+} is presumed to equal γ_{Cl^-} to justify the pattern of their employment.

The assessment of $\{\text{Cl}^-\}_{\alpha=0}$ values as large as those obtained for the two linear, weak base polyelectrolytes examined demonstrates quite clearly that they become strongly water repellant in their highly charged state. The factor leading to this hydrophobicity is identifiable with the pattern of positively charged N, C, and H ensembles repeated in the polymer domain. The discovery that this phenomenon is associated with the repetition of ensembles of N, C, and H in charged polymers was provided by the pioneering studies of the effect of substituting TMA⁺, TEA⁺, and TBA⁺ for Na⁺ ion as the Donnan potential counterion of PAA salt systems.²⁰

Halide Selectivity Pattern of Anion Exchangers. The quaternary ammonium ion repeated throughout the three-dimensional matrix of strongly basic anion exchangers leads to a configuration that strongly resembles the one assumed by PAA[−] in its TAA⁺ ion forms. One can, on this basis, expect them to exhibit hydrophobic properties as well. On this basis one expects I[−] ion, the largest and consequently least solvated halide ion, to be most strongly attracted to the positive charge of the anion exchanger. The bare F[−] ion is the smallest, on the other hand, and is as a consequence coordinated to the most water because of its higher charge density. This surplus of water is repelled by the polyion hydrophobicity so that interaction of the polyion domain with the F[−] ions is resisted. The tendency of the halide counterion to interact with the positively charged polyion is thus believed to be dictated by whether the water coordination tendencies of the halide counterion compliment or disturb the hydrophobicity of the polyion surface. The selectivity pattern predicted for the halide ions on this basis is I[−] > Br[−] > Cl[−] > F[−].

This selectivity order of the halide ions has been experimentally verified in studies carried out by Gregor, Belle, and Marcus^{11,26} with the Dowex 2-X8 anion exchanger. Their data provide further support for the concept projected by showing that attractive forces between I[−] ion and positive sites of Dowex 2-X8 anion exchanger are larger by at least a factor of 100 than the attractive forces between F[−] ion and oppositely charged anion-exchanger sites.

How Hydrophobicity Affects the Chemical Properties of Positively Charged Polymer Gels and Their Linear Polyelectrolyte Analogues

Examination of the Unique Pattern of Transition-Metal Ion Complexation in Positively Charged Polyion Domains.^{27–32} When an anion, e.g., Cl[−], of the supporting electrolytes, e.g., HCl, serves as both the counterion of the positively charged polymer and the complexing ligand of the transition-metal ion, e.g., Zn²⁺, its fully coordinated tetrahedral complex, e.g., $[\text{ZnCl}_4]^{2-}$, is usually the one complexed species that is present in the polyion domain. The few exceptions to this complexation pattern that have been reported involve the uranyl and silver ions; the number of Cl[−] ligands coordinated to them in the

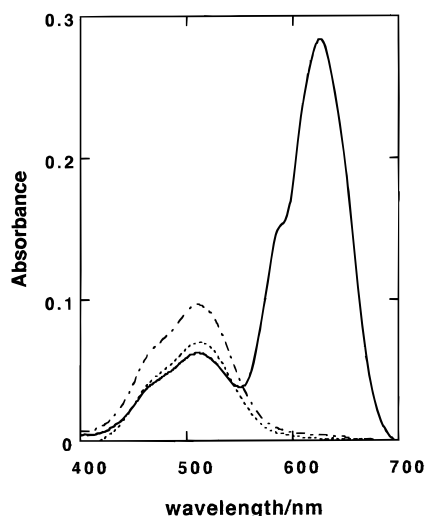
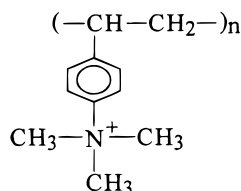


Figure 10. Shift and increase in intensity of the absorption peak due to a solution of 0.01 M CoCl_2 , 0.02 M NaSCN , and 1.0 M in NaCl when it is made 0.1 M PVBtMA^+ as well: (---) system 1; (···) system 2; (—) system 3.

dominant complex found to be associated with the anion exchanger was three instead of four.³³

In those instances where the four ligands are coordinated to the metal ion in the polyion domain, this species is not observable in the solution phase.^{11,27–31} One can rationalize this unusual complexation behavior by referring to the fact that (1) the ligand (counterion) concentration level of the charged polymer phase is very high because of the hydrophobicity of the charged polymer surface and (2) the hydrophobicity of the charged polymer surface rejects any coordinated species where water is substituted for the complexing ligand.

Another Example of How Hydrophobicity Affects the Chemical Properties of Positively Charged Polyions. Recently electronic spectroscopy has been employed to examine further those factors that either add to or subtract from the sizable role that hydrophobicity plays in the formation of transition-metal ion complexes in positively charged domains defined, for example, by polyelectrolytes such as poly(vinylbenzyltrimethylammonium ion), PVBtMA^+ .³⁴ In one series of experiments



selected for the examination of this phenomenon the absorption spectra of the following systems were obtained. System 1: 0.010 mol dm^{-3} CoCl_2 , 0.020 mol dm^{-3} NaSCN . System 2: 0.010 mol dm^{-3} CoCl_2 , 0.020 mol dm^{-3} NaSCN , 1.0 mol dm^{-3} NaCl . System 3: 0.010 mol dm^{-3} CoCl_2 , 0.020 mol dm^{-3} NaSCN , 1.0 mol dm^{-3} NaCl , 0.10 monomol dm^{-3} PVBtMA^+ . The spectra obtained with these three systems are presented in Figure 10 and show quite clearly that in the absence of the positively charged polyion only the absorption spectrum assignable to the octahedrally coordinated $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ species is observable at a wavelength of ~ 510 nm. With the addition of 1.0 mol dm^{-3} NaCl the absorption spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ remains essentially unaffected. A dramatic change in the absorption spectrum occurs only when PVBtMA^+ is added to the second system. There is a shift in the absorption peak from

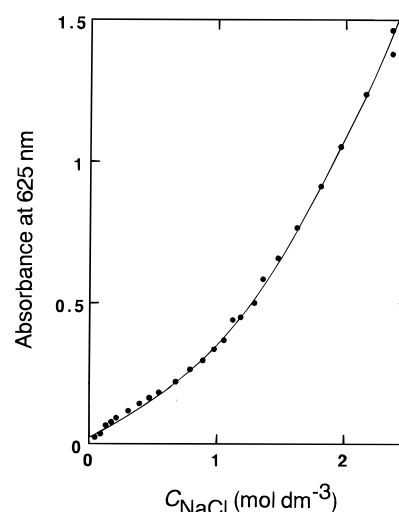


Figure 11. Effect of NaCl concentration level on the intensity of the shifted peak (625 nm). Concentrations of CoCl_2 , NaSCN , and PVBtMA^+ are the same as those indicated in Figure 10.

~ 510 to ~ 625 nm accompanied by an approximately 3-fold increase in the peak intensity. In affecting this shift the octahedrally coordinated $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion is apparently stripped of its water by repulsive forces exerted by the hydrophobic surface of the water-depleted domain defined by PVBtMA^+ . The coordination of the bare Co^{2+} ion by four SCN^- ions, whose presence as the tetrahedrally coordinated complex is fostered by the hydrophobicity of the charged polyion, duplicates the complexation response of the Zn^{2+} and Cl^- ions first discussed in an examination of a system paralleling this one.^{27–32}

The effect of increasing the NaCl concentration level of the aqueous phase on the intensity of the absorption peak due to the $[\text{Co}(\text{NCS})_4]^{2-}$ complex that prevails in the separate phase defined by the hydrophobic PVBtMA^+ has been examined and is shown in Figure 11. There is a steady increase in peak intensity as the NaCl concentration level of the solution phase is increased to 1.0 mol dm^{-3} ; the rate of increase is then approximately doubled by further increase in the concentration level of the NaCl . Since peak intensity is directly proportional to the concentration level of the $[\text{Co}(\text{NCS})_4]^{2-}$ complex in the polyion domain, such gain in intensity must be attributable to water removal from the polyion domain to the solution phase. Such enhancement of water transfer has to arise from gain in hydrophobic forces exercised by the charged polymer surface when the concentration level of NaCl is increased. More insight with respect to the above path to Donnan potential enhancement of the tetrahedrally coordinated $[\text{Co}(\text{NCS})_4]^{2-}$ complex in the hydrophobic PVBtMA domain has been provided by comparing the gain and loss in intensity of the $[\text{Co}(\text{NCS})_4]^{2-}$ absorption peak when NaI , NaBr , and NaF are substituted for NaCl . This comparison, presented in Figure 12, shows that within the range of its applicability the water repellant I^- ion promotes hydrophobicity most effectively; Br^- ion, while less effective, is more effective than the Cl^- ion. There is no noticeable hydrophobic response in the presence of F^- ion. These results are consistent with expectations based on the logic employed earlier to predict the pattern of halide ion selectivity developed by positively charged polyions.^{11,26}

Discussion and Conclusions

On the basis of the results obtained in this study, factors that lead to conversion of the surface of charged polymers from a hydrophilic to a hydrophobic state that effectively resists

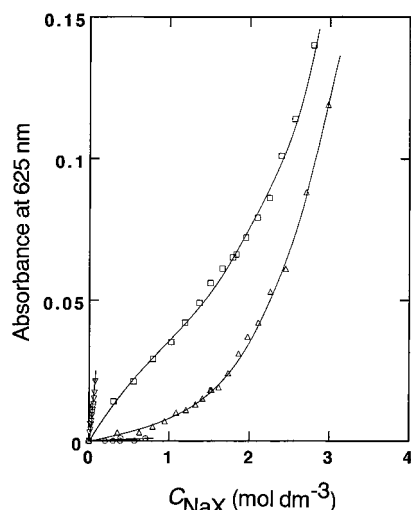


Figure 12. Comparison of the effect of the concentration level of I^- (∇), Br^- (\square), Cl^- (\triangle), and F^- (\circ) ions on the intensity of the shifted peak (625 nm). $\text{CoCl}_2 = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$; $\text{NaSCN} = 2 \times 10^{-2} \text{ mol dm}^{-3}$; $\text{PVBtMA}^+\text{Cl}^- = 0.10 \text{ monomol dm}^{-3}$.

interaction with water have become predictable. For example, by substituting tetraalkylammonium counterions for Na^+ ion, the normally encountered concentration level of the counterion in the solvent-sheathed domain of the linear, weak acid polyelectrolyte PAA is increased by factors as large as 100, as the degree of dissociation approaches unity. The removal of water from the charged polyion domain to yield this result is understandable by presuming interaction of the C, H, and N presence in the counterion with the C, H, and O content of the PAA changes the polyion domain surface from hydrophilic to hydrophobic. The negatively charged surface sites interact strongly with the positive charge of the tetraalkylammonium counterion while repelling water.

The concentration levels reached by Cl^- ion, the Donnan potential determining counterion employed in examining the positively charged domains of the conjugate acids of PVIIm and PAAM, were elevated, as well, to provide strong supportive evidence for the hydrophobicity of their positively charged surfaces. With PVIIm and PAAM considered to be representative of the many linear, weak and strong base polyelectrolytes and their cross-linked gel analogues, the Donnan determined concentration levels of counterions in their hydrophobic polyion domains are expected to be extremely high as well. Earlier attempts to rationalize the fact that metal ion complexes that form with Donnan potential controlling counterions that also function as ligand frequently appear in the positively charged polyion domain of these macromolecules as a single anionic complex whose coordination by the counterion (ligand) has reached the maximum value possible in its tetrahedral configuration can now be answered in a straightforward manner. With Cl^- ion concentration levels reaching 30 mol dm^{-3} and higher, such a result is understandable. Their hydrophobicity rejects those complexes where H_2O replaces the ligand.

On the basis of the observations made in the course of this study, it has also been possible to identify some of the factors that determine whether hydrophilic or hydrophobic characteristics will prevail in a particular charged polymer. With hydrophobicity considered to be an intrinsic characteristic of the positively charged surface of linear, weak and strong base polyelectrolytes and their cross-linked gel analogues, the influence of the size of Donnan potential determining counterions on this property has been sought. Measurement of halide ion selectivity coefficient patterns affected by their anion-exchange

reactions has shown that the larger the halide ion the larger is its interaction with the positively charged macromolecule. The selectivity pattern defined as shown, $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, informs one that the larger the halide ion the greater is the release of water from the charged polymer domain. This relates halide ion size to increase in hydrophobicity of the positively charged polymer surface.

The effect of the size of the Donnan potential determining counterion on the hydrophilic properties normally exhibited by linear weak and strong acid polyelectrolytes has been examined as well. Whereas its effect on the negatively charged polymer surfaces associated with the monofunctional acid repeated along the full length of the macromolecule is negligible, there is a sizable effect observed when the acid functionality repeated in the polyelectrolyte is bifunctional. Once its second dissociation step is involved, water removal from the polyion domain becomes greatly enhanced by replacing the small Donnan potential determining alkali metal ion, e.g., Li^+ , with the large Cs^+ ion. Hydrophilicity of the poly(maleic acid) has been replaced by hydrophobicity through the substitution of Cs^+ ion for Li^+ ion.

One can conclude from the above that additional insight with respect to the factors that lead to hydrophobicity in charged polymers should be forthcoming from extension of the program described. The eventual preparation of charged polymers with exactly the hydrophobic/hydrophilic properties being sought appears to be a feasible goal.

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