

Proton and metal ion binding to natural organic polyelectrolytes—I. Studies with synthetic model compounds*

J. A. MARINSKY¹ and M. M. REDDY²

¹Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14214, U.S.A.

²U.S. Geological Survey, Denver, CO 80225, U.S.A.

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Abstract—A unified physico-chemical model, based on a modified Henderson-Hasselbalch equation, for the analysis of ion complexation reactions involving charged polymeric systems is presented and verified. In this model $\text{pH} = \text{p}K_a + \text{p}(\Delta K_a) + \log(\alpha/1 - \alpha)$ where K_a is the intrinsic acid dissociation constant of the ionizable functional groups on the polymer, ΔK_a is the deviation of the intrinsic constant due to electrostatic interaction between the hydrogen ion and the polyanion, and α is the polyacid degree of ionization. Using this approach $\text{p}K_a$ values for repeating acidic units of polyacrylic (PAA) and polymethacrylic (PMA) acids were found to be 4.25 ± 0.03 and 4.8 ± 0.1 , respectively. The polyion electrostatic deviation term derived from the potentiometric titration data (i.e. $\text{p}(\Delta K_a)$) is used to calculate metal ion concentration at the complexation site on the surface of the polyanion. Intrinsic cobalt-polycarboxylate binding constants (7.5 for PAA and 5.6 for PMA), obtained using this procedure, are consistent with the range of published binding constants for cobalt-monomer carboxylate complexes. In two phase systems incorporation of a Donnan membrane potential term allows determination of the intrinsic $\text{p}K_a$ of a cross-linked PMA gel, $\text{p}K_a = 4.83$, in excellent agreement with the value obtained for the linear polyelectrolyte and the monomer. Similarly, the intrinsic stability constant for cobalt ion binding to a PMA-gel ($\beta_{\text{CoPMA}^+} = 11$) was found to be in agreement with the linear polyelectrolyte analogue and the published data for cobalt-carboxylate monodentate complexes.

Key words: Donnan potential, heterogeneity, 2-dimensional, 3-dimensional aggregate (gel), polyelectrolyte, complexation, electrostatic potential.

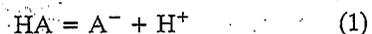
INTRODUCTION

An important component of natural organic complexing materials are the weakly acidic high molecular weight humic and fulvic acids. Their chemical properties, in particular their acid-base behavior and their ability to bind metal ions are of major importance in natural processes such as rock weathering, soil formation, and metal transport in the biosphere (Stevenson, 1982; Saar and Weber, 1980). Moreover, characterization of ion-binding in organic-rich sediments and soils, such as those in acid precipitation impacted regions of the northeastern United States, requires an accurate description of the processes involved in these polyelectrolyte reactions.

Until recently understanding of metal ion binding to weak acid organic natural polyelectrolytes has suffered from the lack of a generalized thermodynamic treatment. Techniques useful for characterization of mixtures of metal ions and discrete ligands have been reported to be unsuitable for use with these materials (McCarthy and Mark, 1976). Several recent studies have reported ion association constants for metal ions bound to these natural polyacids which vary over several orders of magnitude during the course of a single experiment. Moreover, metal

stability constants exhibit marked dependence upon experimental conditions (e.g. solution ionic strength and total acid concentration). In addition, comparisons of published acid dissociation and metal ion binding constants for natural polyacids show no systematic variation from one metal or acid to another. Nor do these results exhibit any concordance with the well-established literature for simple organic ion-metal ion complex formation (Florence and Batley, 1980; Jackson *et al.*, 1978; Ryan and Weber, 1982; Stevenson, 1982).

In part deficiencies in the treatment of data for natural organic polyion-metal ion complex formation arise from an inability to assess the concentrations of the metal ion at a complexing site located on a charged organic polyelectrolyte. In addition, there has been difficulty in assessment of ligand and ligand-metal complex species concentrations. Gregor *et al.* (1955), employing synthetic polyelectrolytes, sought to overcome the second of these problems by using an extended Henderson-Hasselbalch equation for the dissociation of a weak acid (HA) into a (hydrated) proton and its acid anion $[A^-]$



The usual form of the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log \left(\frac{[HA]}{[A^-]} \right) = \text{p}K_a - \log((1 - \alpha)/\alpha) \quad (2)$$

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where the square brackets are used to designate species concentrations and a is the degree of neutralization of the acid, was modified (Gregor and coworkers, 1955) by adding a constant (n) to the second term on the right hand side of equation (2) as shown below:

$$\text{pH} = \text{p}K_a - n \log((1 - \alpha)/\alpha) \quad (3)$$

This equation provides empirical representation of the titration curves of many polyelectrolytes, K_a , corresponding to the intrinsic dissociation constant of the polyacid functional groups and the constant corrective parameter, n , accounting for deviation of the system from ideality at a selected acid concentration and ionic strength as the degree of dissociation of the acid is varied.

Mandel and Leyte (1964) used a more direct approach to the evaluation of $[A^-]$. A titration curve of the polyacid in the presence of neutral salt was transformed into a plot of $P([H^+]/[HA])$ versus $p[A^-]$. This plot was then used to estimate the concentration of $[A^-]$ for the metal containing solutions at the polyacid and neutral salt concentration of the reference system.

Inability to analyze the effect of the electric field at the surface of the polyion on the activity of the complexing metal ion has limited interpretation of metal ion binding in polyelectrolyte systems such as those examined by Gregor *et al.* (1955), and by Mandel and Leyte (1964). Scatchard *et al.* (1964) in their studies of the binding of small ions to proteins attempted to correct for such perturbations by estimating the electrical field at the surface of the protein. In this approach they assumed charge to be uniformly distributed over a spherical surface to facilitate computation of the effective concentration of mobile ions at the site of complexation. Since such an estimate was not usually representative of the actual conformational properties of the macromolecule, the utility of this method of site concentration analysis was limited. Manning and Holtzner's (1973) proposal to use the Henderson-Hasselbalch equation for determining an apparent average value for the acid dissociation constant of weak acid polyelectrolytes provided no real solution to this problem as well.

An experimental method to determine the distribution of mobile metal ions at the sites of complexation was proposed by Marinsky (1973). This technique, which utilizes potentiometric titrations of weakly acidic organic polyelectrolytes in the presence and absence of metal ions, provides the most reliable data for stability constant determinations in these complex systems. The method was based on the following logic: The neutralization of a weak polyacid can be described by the following modification of the Henderson-Hasselbalch equation (Arnold and Overbeek, 1950).

$$\text{pH} = \text{p}K_a + p(\Delta K_a) + \log(\alpha/1-\alpha) \quad (4)$$

where K_a is the intrinsic acid dissociation constant of the ionizable functional groups on the polyion and $p(\Delta K_a)$ the deviation in its value due to the electrostatic interaction of the simple ions in solution and the charge on the polyion surface;

$$p\Delta K_a = -0.4343 (e\psi/kT) \quad (5)$$

e is the electrical charge of the mobile ion, ψ the electrical potential at the surface of the polyion, k the Boltzmann constant and T the absolute temperature. As α approaches a value of zero, ψ , and consequently $p(\Delta K_a)$, must also approach zero as their limiting value. Thus a plot of $\text{pH} - \log(\alpha/1-\alpha)$ versus α , when extrapolated to intercept the ordinate axis at $\alpha = 0$ yields the intrinsic $\text{p}K$ ($\text{p}K_a$) of the metal-free system at the point of intersection.

Parallel analysis of the metal ion (M^{n+}) containing, but otherwise equivalent, polyacid system by measurement of both free H^+ and M^{n+} permitted assessment of $0.4343(e\psi/kT)$ at each experimental condition. Correct assignment of the metal-binding reactions permitted accurate assessment of A^- and HA in the systems so that the resultant plot of $\text{pH} - \log [A^-]/[HA]$ versus $[A^-]$ over the range of study, when extrapolated to $[A^-] = 0$ yielded the $\text{p}K_a$ value previously assigned to the polyacid from such a plot obtained with the metal-free, but otherwise equivalent system (Marinsky, 1982). The vertical displacement of the ordinate from the intercept value could then be used to provide a numerical assignment of the exponential term at each experimental situation. By presuming Poisson-Boltzmann statistics to apply to these systems the concentrations of ions at the site of reaction (M_a^{n+}) were computed by multiplying the measured (bulk) ion concentrations (M^{n+}) by the exponential term, the value of $e\psi/kT$ being multiplied by the ion valence, as shown:

$$(M_a^{n+}) = (M^{n+}) \exp(-0.4343 n^+ e\psi/kT) \quad (6)$$

In gel systems, a macroscopic or microscopic second phase exists and a Donnan membrane potential term has to be included in the computation as well (Marinsky, 1973).

It is our objective in this manuscript to demonstrate experimentally the validity of the approach proposed by Marinsky (1982) for the accurate assessment of stability constants characterizing the complexed species formed by metal ions with repeating ligands of polyelectrolytes and their gel analogs. The synthetic organic polyelectrolytes selected to demonstrate this are described in Fig. 1.

MATERIALS AND METHODS

The synthetic polyacids employed (polyacrylic acid, PAA, and polymethacrylic acid, PMA) were gifts of the Rohm & Haas Company. A molecular weight of 5000 was specified by the manufacturer for each product. An earlier publication gives details of

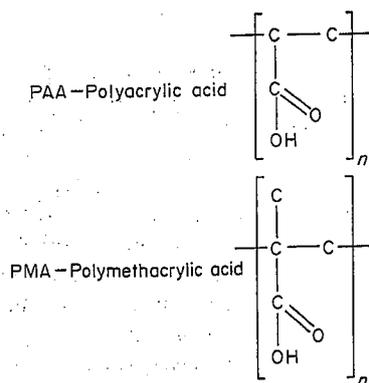


Fig. 1. Synthetic polyelectrolytes used for ion binding studies.

purification and preparation of these materials for study (Torrence *et al.*, 1971). Analytical reagent grade chemicals and grade A glassware were used in all experiments. Special precautions were taken to prevent carbon dioxide contamination of the standard sodium hydroxide used in the investigation. The preparation of sodium perchlorate for use as background electrolyte is described elsewhere (Travers and Marinsky, 1974).

Sodium-form ion exchange resin (Dowex 50-8X, BioRad) used in the cation-exchange distribution studies had an exchange capacity of 4.56 m-equiv/g of dry resin. Solvent and electrolyte imbibement were compensated for when necessary.

Radioactive isotopes—cobalt-60 and zinc-65—were from the Radioisotope Division of the Oak Ridge National Laboratory.

Potentiometric, and cation-exchange distribution measurements were made concurrently to quantify metal ion binding to the weak polyacids. Batch equilibration techniques were used in two configurations (Helfferich, 1962). In one configuration metal ion present at trace-level concentrations in background electrolyte (sodium perchlorate), contained polyacid at a fixed concentration while its degree of neutralization was varied by appropriate addition of sodium hydroxide. Alternatively, with trace metal ion contained in the background electrolyte at a fixed concentration, the polyacid concentration (at a fixed degree of neutralization) was varied. In both experiments polyacid-free, but otherwise equivalent, controls were also equilibrated with the resin. Measurement of cation-exchange distribution in the controls facilitated estimate of free hydrated ion in the polyacid systems.

The pH of solutions at equilibrium was typically determined using a Radiometer Model 4 pH meter with a standard calomel electrode (separated from the solution by an ammonium nitrate-agar salt bridge) and a Beckmann glass hydrogen electrode. Both measurements and standardizations with reference buffers (pH's of 4.008, 6.865, and 9.18 at 25°C) were performed in a nitrogen atmosphere.

Complexation of macro quantities of divalent ions

by PMA and its gel analog, Amberlite IRC-50, a resin product of Rohm & Haas, was studied in a series of experiments designed to be comparable. The resin, prepared for use in the acid form by standard procedures (Anspach and Marinsky, 1975), was equilibrated in the background electrolyte (sodium sulfate) while the degree of polyacid neutralization was varied. The metal ion to resin molar ratio, fixed at the start of each neutralization series, was varied for this study. The potentiometric measurement of the system pH at equilibrium was made after at least 40 days of reaction. The concentration of metal ion remaining in the solution was measured polarographically at this time as well.

In the parallel experiments with the polyacid the potentiometric measurements of pH were made on a single sample after each addition of standard base, carbon dioxide being excluded by blanketing the solution with a stream of nitrogen gas. In these systems the quantity of free metal ion in the solution was deduced from comparison of pH measurements obtained with the metal-containing and metal-free but otherwise equivalent controls during neutralization.

An Amberlite IRC-50 resin was used to demonstrate, for the first time, an accurate method for the measurement of Donnan membrane potential terms encountered with gels (Slota and Marinsky, 1980).

RESULTS AND DISCUSSION

(I) Single phase systems

(A) *Potentiometric properties of synthetic polyelectrolytes.* Potentiometric titration data obtained during the neutralization of polyacrylic and polymethacrylic acids have been interpreted with the Henderson-Hasselbalch equation (equation 4) rearranged as shown

$$\begin{aligned} \text{pH} - \log(\alpha/1-\alpha) &= \text{p}K_a - 0.4343 e\psi/kT \\ &= \text{p}K_a(\text{app}) \end{aligned} \quad (7)$$

Plots of the left hand side of this equation versus alpha, extrapolated to zero alpha, yield as the ordinate intercept value the intrinsic microscopic acid dissociation constant, K_a , of the repeating functional group as shown in Fig. 2 for PAA and in Fig. 3 for PMA.

As we have pointed out earlier graphical resolution of $\text{p}K_a$ in this manner is valid since $e\psi/kT$ approaches zero in value as α approaches zero and

$$\lim(\text{pH} - \log(\alpha/1-\alpha))_{\alpha \rightarrow 0} = \text{p}K_a \quad (8)$$

Titration behavior for the PAA is consistent with expectation over the entire neutralization range. The PMA, on the other hand, undergoes a conformational transition near $\alpha = 0.3$; this results in a plateau

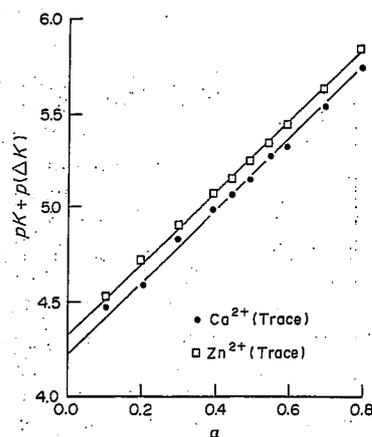


Fig. 2. Henderson-Hasselbalch function plotted versus degree of neutralization, α , for polyacrylic acid (0.03 M) in the presence of trace concentrations of cobalt and zinc ions and 0.1 M sodium perchlorate solution, where $pK + p(\Delta K) = pH - \log(\alpha/(1 - \alpha))$ (Travers and Marinsky, 1975).

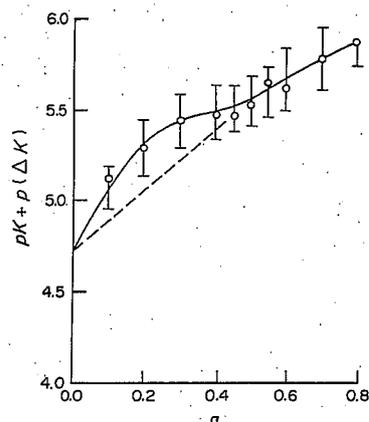


Fig. 3. Henderson-Hasselbalch function plotted against degree of neutralization, α , polymethacrylic acid (0.04 M) in the presence of trace concentrations of zinc ions and 0.1 M sodium perchlorate solution. Error bars enclose data for other experiments with trace cobalt and zinc ions over a range of acid concentrations from 0.02 to 0.05 M. Upper and lower portions of the curve are shown extrapolating to the same ordinate intercept (i.e. the same intrinsic binding constant) (Travers and Marinsky, 1975).

in the curve until an alpha value of about 0.5 is reached. The intercept of the curve extrapolated from the two sloping portions of the plot intersect the ordinate at the same point as they should. The pK_a values of 4.25 ± 0.03 and 4.8 ± 0.1 resolved in this way for the respective repeating acidic units of PAA and PMA are in good agreement with the literature values of 4.258 (25°C; zero ionic strength, propenoic acid) and 4.849 (25°C, zero ionic strength, 2-methyl propanoic acid) for the monomer acids they most closely resemble.

This result is to be expected with a sufficient number of identical sites in the molecule since each should behave in an equivalent manner from a

statistical point of view. The accessibility ratio of these acidic units, A^- and HA , are thus equal and the characteristic intrinsic pK_a of the repeating acid moiety in the polymer should be resolved, as it is.

(B) *Divalent metal ion-synthetic polyion complex formation.* Study of the complexation of metal ions by weak acid polyelectrolytes requires accurate assessment of the free metal ion concentration in the bulk solution. Ion-exchange distribution techniques using trace level concentrations of metal ions can be conveniently used for this purpose (Helferich, 1962; Marinsky *et al.*, 1983). A detailed examination of the theoretical and experimental aspects of the various ion-exchange techniques employable for free metal ion assessment in the study of complex equilibria in solution has been given by Ringbom (1979).

The distribution coefficient for a metal ion at trace level concentrations between a solution and ion-exchange resin, in the presence and absence of a complexing ligand, can be expressed as

$$D = D_0 / (1 + \sum_{n=1}^i MA_n / M_f) \quad (9)$$

where D and D_0 are the metal distribution coefficients in the presence and absence of complexing organic polyion, M_f is the concentration of uncomplexed metal ion in solution, and MA_n is the solution concentration of the n th complexed metal species. Conversion of the free metal ion concentration deduced for the bulk solution in this way to its concentration of the complexing site on the polyion surface is then facilitated by employing the Boltzmann statistical term (i.e. $e^{\psi/Kt}$) obtained from the potentiometric titration data. The polyion correction term derived from the potentiometric titration of the weak polyacid (equations 4 and 5) multiplied by the valence of the metal ion determines the non-ideality of the metal ion at the binding site adjacent to the polyion.

Incorporation of this term into eq. 9 leads to the following expression

$$\frac{D_0 - D}{DA(\Delta pK)^2} = \sum_{n=1} \beta_{(HA)_n} (A)^{n-1} \quad (10)$$

where β_n is the overall polyion-metal ion complex formation constant for the n th species. Table 1 illustrates unambiguously the validity of the potentiometrically based method for converting bulk solution metal ion concentrations to their concentration at the site of complexation adjacent to the charged surface of the polymer. For cobalt ions binding to PAA and PMA in 0:1 molar sodium perchlorate solution only the monoligated species is presumed to be formed so that $(D_0 - D)/(D [A^-][\Delta K_a]^2) = \beta_1$. Employment of the polyion correction term (ΔK_a) completely removes this otherwise strong dependence of the binding constant upon the degree of polyion neutralization (column 3 for PMA and

Table 1. Trace concentration level cobalt (^{60}Co) binding functions for polymethacrylic acid (PMA) in 0.1 M sodium perchlorate solution (Travers and Marinsky, 1975)

	0.05M PMA		0.03M PAA	
	$\frac{D_0 - D}{D[A^-]}$	$\frac{D_0 - D}{D[A^-] [\Delta K^{-1}]^2}$	$\frac{D_0 - D}{D[A^-]}$	$\frac{D_0 - D}{D[A^-] [\Delta K^{-1}]^2}$
0.1	29.8	6.0	25.1	10.4
0.2	—	—	41.6	7.7
0.3	1042	10.9		
0.6	413.9	5.3	1380	9.6
0.7	570.4	4.2	2847	8.7
0.8	886.1	4.5	8019	10.8

column 5 for PAA): This result provides strong support for our assumption that the polyion potential seen by the proton is experienced by the divalent metal ion as well.

An alternative approach to evaluation of the intrinsic polyion-metal ion binding constant is graphical. When the logarithm of the metal-ion binding function ($\log((D_0 - D)/D(A^-))$) is plotted versus alpha and the resultant curve is extrapolated to the ordinate axis at alpha = 0 the intrinsic metal ion binding constant is resolved in much the same way as pK_a is (i.e. from a plot of the modified Henderson-Hasselbalch function versus alpha.) Such plots are presented in Figs 4 and 5 for the cobalt-PAA and cobalt-PMA systems, respectively. The values resolved in this way for the intrinsic formation constants in these two systems ($\log \beta_{\text{CoPAA}} + = 0.88$; $\beta_{\text{CoPAA}} + = 7.5$ and $\log \beta_{\text{CoPMA}} + = 0.75$; $\beta_{\text{CoPMA}} + = 5.6$) agree with the average intrinsic $\beta_{\text{MA}} +$ values obtained for these respective systems

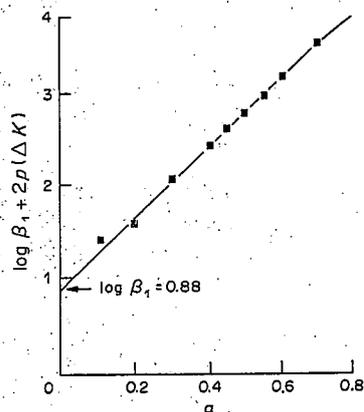


Fig. 4. Cobalt (at trace level concentrations) ion binding function versus degree of neutralization, α , for 0.03 M polyacrylic acid in 0.1 molar sodium perchlorate solution, where $\log \beta_1 + 2p(\Delta K) = \log((D_0 - D)/D[A^-])$ (Travers and Marinsky, 1975).

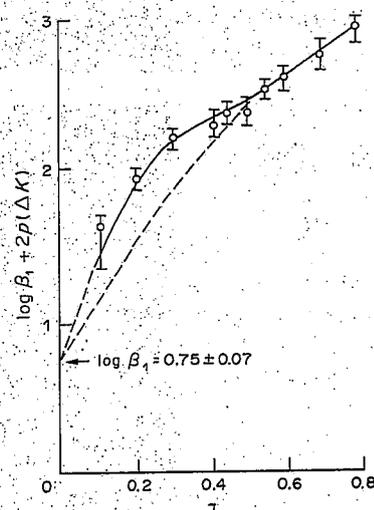


Fig. 5. Cobalt (at trace level concentrations) ion binding function versus degree of neutralization, α , for polymethacrylic acid (0.04 M) in 0.1 M sodium perchlorate solution. As in Fig. 3, error bars enclose data for other experiments over a range of acid concentrations from 0.03 to 0.05 M. Upper and lower portions of the curve are shown extrapolating to the same ordinate intercept (i.e. the same intrinsic binding constant) (Travers and Marinsky, 1975).

($\beta_{\text{CoPAA}} + = 9.9$ and $\beta_{\text{CoPMA}} + = 5.4$) by our earlier approach. This good agreement between intrinsic stability constant assignments demonstrates clearly that the proton and divalent metal ion do indeed experience the same electrical potential at the reaction site on the surface of the polyion.

Additional support for the use of the (ΔpK) correction term to calculate metal ion concentrations at the site of reaction is most effectively shown by a plot of $\log((D_0 - D)/D(A^-)) \beta_{\text{MA}} +$ versus $\text{pH} - \log(\alpha/1 - \alpha) - pK_a$. Since it is assumed that $\log((D_0 - D)/D(A^-)) \beta_{\text{MA}} + = 2 p(\Delta K_a)$ and that $\text{pH} - \log(\alpha/1 - \alpha) - pK_a = p(\Delta K_a)$ such a plot, on the basis of the above assumption, must yield a straight line of slope

2.0 which intersects the origin. In Figs 6 and 7 this relationship is shown to be valid, within experimental error, for trace concentration of cobalt ion binding to PAA and PMA, respectively.

(II) Two phase (gel) systems

(A) *Potentiometric properties of synthetic polyelectrolyte gels.* If there is a macroscopic gel phase present, then the influence of this second phase upon the ion distribution within the solution must be considered in addition to the polyion effect. For example, in a system containing a solution and a gel potentiometric data will differ from that observed for similar single phase solutions. For a single phase solution the Henderson-Hasselbalch function plotted

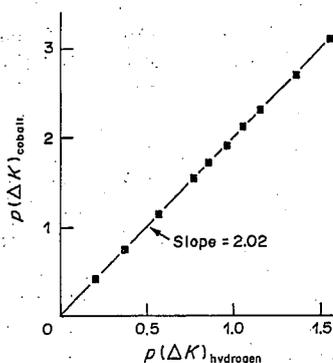


Fig. 6. Modified cobalt ion binding function plotted versus the modified Henderson-Hasselbalch expression for 0.03 M polyacrylic acid in 0.1 M sodium perchlorate solution, where $p(\Delta K)_{\text{cobalt}}$ is $\log((D_0 - D)/(D[A^-]\beta_1))$ and $p(\Delta K)_{\text{hydrogen}}$ is $\text{pH} - \log(\alpha/(1 - \alpha) - \text{pK})$ (Travers and Marinsky, 1975).

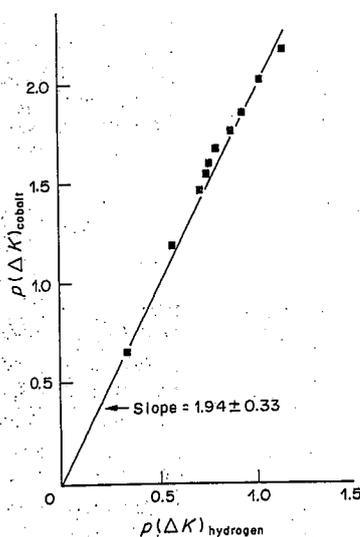


Fig. 7. Modified cobalt ion binding function plotted against the modified Henderson-Hasselbalch term for polymethacrylic acid in 0.1 M sodium perchlorate solution, where $p(\Delta K)_{\text{cobalt}}$ is $\log((D_0 - D)/(D[A^-]\beta_1))$ and $p(\Delta K)_{\text{hydrogen}}$ is $\text{pH} - \log(\alpha/(1 - \alpha) - \text{pK})$ (Travers and Marinsky, 1975).

versus degree of polyacid neutralization over a range of polyacid concentrations, or solution ionic strengths, yields lines which diverge one from another. As the degree of neutralization increases the extent of divergence increases with decreasing ionic strength (Arnold and Overbeek, 1950). These results are due to the fact that the increasing polyelectrolyte charge is less and less effectively screened by counter ions as the ionic strength of the system is lowered. As the alpha value approaches zero, polyacid charge also approaches zero, and the Henderson-Hasselbalch functions for each polyacid concentration tend to converge at the intercept.

The pH of a gel is inaccessible to direct measurement. As a consequence, study of their potentiometric properties has had to be based upon the pH of the solution phase in (Donnan membrane) equilibrium with the gel phase in question. A result of this experimental restriction is that the observed potentiometric characteristics are a sensitive function of: (1) the water content of the gel (which is regulated in large measure by the flexibility of its matrix), and (2) the ionic strength of the aqueous solution in equilibrium with the gel.

For a synthetic organic gel at a fixed ionic strength and alpha value, the pK of the repeating monomer unit appears to increase with the matrix rigidity, which is in turn controlled by the quantity of crosslinking agent used in the gel manufacture. The effect of increasing ionic strength, on the other hand, is to decrease the measured pK. This behavior will also be seen for natural organic polyelectrolyte gels with matrix rigidity (i.e. network crosslinking) being regulated by the source of the organic material and its subsequent diagenesis.

Plots of pK ($\text{pH} - \log(\alpha/(1 - \alpha))$) versus alpha, calculated from directly measured solution concentrations, over a range of solution ionic strengths or gel crosslinking values, parallel each other. The value of pK determined in this way is a function of alpha, being higher the lower the ionic strength and the higher the rigidity (crosslinking) of the gel. Unlike the single phase linear polyelectrolyte, no convergence of the Henderson-Hasselbalch plot curves is observed as alpha approaches zero. Thus a unique microscopic pK cannot be resolved for the repeating functional unit of the gel macromolecule.

Determination of the intrinsic pK in the gel phase requires the hydrogen ion concentration of the gel phase, H_g^+ . This quantity must be calculated (using the Donnan membrane equilibrium condition for two phases) from the direct measurement of hydrogen ion concentration in the solution phase. In this way potentiometric measurements in the solution can be applied to calculate terms needed for plotting the Henderson-Hasselbalch function of the gel phase.

This result was demonstrated for the first time by Marinsky and Slota (1980) who employed the Donnan membrane model to relate the equilibrium distribution of diffusible components, water, a fully

ionized acid and its salt, in the gel and solution phases. By using this approach they were able to show that

$$\text{pH} - \text{pM}^+ = \text{pH}_g - \text{pM}^+_g \quad (11)$$

The intrinsic microscopic dissociation constant of the repeating functional group in the gel was then redefined correctly in the modification of equation (4) shown:

$$\text{pH}_g - \log(\alpha/1-\alpha) + 0.4343(e\psi/kT) = \text{p}K_a \quad (12)$$

where

$$\text{pH}_g + 0.4343(e\psi/kT) = \text{pH}_{sg} \quad (13)$$

the subscripts g and sg referring, respectively, to the gel bulk solution and the solution immediately adjacent to the charged surface of the polymer matrix. By substituting $(\text{pH} - \text{pM}^+ + \text{pM}^+_g)$ for pH_g in equation (12) to yield equation (14)

$$\begin{aligned} &\text{pH} - \text{pM}^+ + \text{pM}^+_g \\ &- \log(\alpha/1-\alpha) + 0.4343(e\psi/kT) = \text{p}K_a \quad (14) \end{aligned}$$

for analysis of potentiometric data in gel systems unique resolution of the $\text{p}K_a$ characteristic of the repeating functional unit could be expected.

The value of the free metal ion concentration within the gel phase (M^+_g), like the value of the gel phase hydrogen ion concentration, is not amenable to direct measurement. However, its value can be computed in the following way: The volume of the gel phase can be measured and a charge balance, based upon (1) the stoichiometry of the neutralization reaction and, (2) the requirement that the condition of electroneutrality be satisfied, defines the quantity of metal ion entering the gel phase during neutralization of the acid groups. A simple Donnan equilibrium corrected for the introduction of additional metal ion by gel phase imbibement of salt. The total quantity of metal ion within the gel phase calculated in this way is divided by the gel volume to obtain the gel phase (bulk) concentration for use in equation (14).

This procedure applied to the crosslinked polymethacrylic acid gel, using dilute sodium polystyrenesulfonate solution in place of simple dilute electrolyte, resolved an intrinsic $\text{p}K_a$ value of 4.83, in excellent agreement with the $\text{p}K_a$ value obtained for the (single phase) linear analogs. The validity of this approach is firmly established by this result.

The discrepancy between $\text{p}K$ values computed directly from measured solution pH, and values computed using the appropriate, model-deduced gel phase pH can be substantial. For example, Two sets of $\text{p}K$ values, one using the solution pH values and the other using the appropriate gel phase pH, for the polymethacrylic acid gel system are plotted in Fig. 8

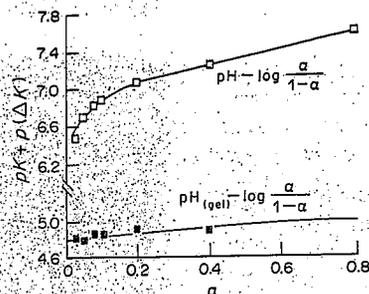
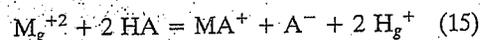


Fig. 8. Henderson-Hasselbalch function plotted as a function of degree of neutralization, α , for a cross-linked polymethacrylic acid (IRC-50) in 0.03 normal sodium polystyrene sulfonate. The upper curve is calculated from the solution pH, the lower linear plot is calculated employing the pH value within the gel phase, (Slota and Marinsky, 1980).

as a function of alpha, and demonstrate differences in calculated $\text{p}K$ values between the two procedures of more than two orders of magnitude.

(B) *Divalent metal ion binding to a cross-linked PMA gel.* Earlier studies of the binding of cobalt and nickel to polymethacrylic acid had demonstrated the existence of one complexed species, MA^+ the complex formation reaction was written as follows to facilitate analysis:



With this reaction the mass action expression is

$$K = (\text{MA})(\text{H}_g^+)^2(\text{A}^-)/(\text{M}_g^{+2})(\text{HA})^2 \quad (16)$$

The $(\Delta K_a^{-1})^2$ terms applicable to the hydrogen ion and the metal ion concentrations within the gel phase cancel; the Donnan membrane potential term to transform bulk ion concentrations in the solution to the corresponding concentrations within the gel phase cancel as well so that the experimentally measured solution concentrations can be used directly in the equation as shown; and finally, V_g , the gel phase volume term required to determine the molar concentration of MA, A, and HA cancel so that the total quantities of each may be employed in the equation. Since

$$K = \beta_{\text{MA}} + \beta_{\text{HA}}^2 \quad (17)$$

multiplying the experimentally observed K by β_{HA} ($\log \beta = 4.8$) squared led to the value of β_{MA} . Good agreement between the values for β_{MA} in the gel phase and the polyelectrolyte was obtained after correction for ion pair formation of the divalent ion in the sodium sulfate medium used in the gel studies. The monodentate cobalt-PMA (gel) stability constant value ($\beta_{\text{CoPMA}^+} = 11$) is in agreement with the value obtained for the linear polyelectrolyte analogue (Anspach and Marinsky, 1975).

CONCLUSION

The results presented here demonstrate that mass action equations, suitable for describing simple electrolyte equilibria in aqueous solution, may be modified to apply to solutions containing soluble polyelectrolytes and their gels. For hydrogen ion dissociation from, and metal ion binding to weak acid polyelectrolytes the appropriate modification is incorporation of a term compensating for the polyanion electrostatic effects at the site of complexation. This electrostatic correction term, $p(\Delta K_a)$, can be calculated directly from potentiometric titration data for the weak acid polyelectrolyte. With the appropriately modified mass action expression polyion intrinsic acid dissociation constants and metal ion binding constants are independent of experimental conditions and exhibit the expected correspondence with the simple electrolyte carboxylate-metal ion complexes. These results demonstrate the soundness of this technique for describing polyelectrolyte equilibria. With this understanding, polyelectrolyte effects encountered in natural polyacids (e.g. humic and fulvic acids) can be quantitatively incorporated into mathematical models of solution equilibria.

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