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APPLICATION OF ION-SELECTIVITY PREDICTIONS TO THE ANALYSIS OF ION BINDING BY GELS

JACOB A. MARINSKY

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

SUMMARY

The development of a model for the prediction of ion-exchange selectivity has been described in some detail. Limitation of this model to moderately concentrated gels ($> 0.5 m$ on a monomer basis) and/or simple salt-containing polyelectrolytes is specified to define the range of its utility. Its successful application in the defined operational range has been fully demonstrated. In addition the method has been successfully employed to facilitate the ultimate objective of this manuscript, the interpretation of data comparing the uptake by complexation of an ion such as Ni^{2+} with the uptake of the uncomplexed Na^+ ion. The great quantity of such data that are reported in the literature has not been amenable to correct assessment. With the predictive quality of selectivity computations with the model presented it is now possible to resolve the complexation equilibria encountered in these studies from such data.

INTRODUCTION

Many investigators have resorted to an ion-exchange model for the assessment of ion-binding phenomena in natural systems¹⁻³. For evaluation of the selectivity of metal-ion interaction in these systems, the exchange of a metal ion for a reference ion, *e.g.* Na^+ , has usually been examined¹. Unfortunately, the interpretation of such data can be extremely complicated. As a consequence the investigator has usually oversimplified his analysis and little useful information has been forthcoming from these studies.

For example, in natural systems such as organic acid soils (humic substances) which consist of a three-dimensional array of aromatic rings with numerous functional groups and side chains⁴ at least two types of metal ion-humic reactions have been identified^{5,6}: electrostatic binding due to polyelectrolyte effects⁷ (charged polymer surfaces) and complex formation⁸⁻¹¹ including chelation^{8,9}. Such interaction with metal ions must therefore be accounted for in any examination of these kind of systems with an ion-exchange model. Indeed if the exchange of Na^+ and an M^{2+} ion is compared the quantity of M^{2+} complexed by the organic acid functional units will lead to an ion-exchange selectivity pattern that is a strong function of the pH and ionic strength employed in the study. Unless an attempt is made to understand the

observed variability in a quantitative way no unified physiochemical description of the system is possible. Indeed such compilation of gross selectivity data has contributed significantly to the lack of uniformity in data presentation for these systems¹²⁻¹⁵. As a consequence a comparison and/or correlation of the metal ion binding properties of these systems has not been possible.

It is the objective of this presentation to show in a fundamental way the remedy to this problem. A basis for the uniform description of metal-ion binding reactions in systems of this kind that is sought has been developed to facilitate this objective.

THEORETICAL BASIS

Background information

In order to provide a meaningful interpretation of ion-exchange selectivity patterns it is essential to know the factors that control selectivity in the ion-exchange process. Indeed, numerous investigators have sought to identify these factors¹⁶⁻²⁷. A rather complete review of these efforts has been presented by Helfferich²⁸.

We believe the Gibbs-Donnan model^{29,30} has been most useful for facilitating an analysis of the ion-exchange phenomenon. In this model, K_{NExM} , the selectivity coefficient, *i.e.*, the molality product ratio at equilibrium for the Z_{M}^- , Z_{N}^- valent cation-exchange reaction, is expressed by

$$K_{\text{NExM}} = \frac{\bar{\gamma}_{\text{N}}^{-Z_{\text{M}}} \gamma_{\text{M}}^{\pm(Z_{\text{N}}+Z_{\text{N}}Z_{\text{M}}/Z_{\text{X}})}}{\bar{\gamma}_{\text{M}}^{-Z_{\text{N}}} \gamma_{\text{N}}^{\pm(Z_{\text{M}}+Z_{\text{N}}Z_{\text{M}}/Z_{\text{X}})}} \exp.[-\pi(Z_{\text{N}}\bar{V}_{\text{M}} - Z_{\text{M}}\bar{V}_{\text{N}})/RT] \quad (1)$$

where π is the swelling pressure of the exchanger^{16,17,21}, \bar{V}_{M} and \bar{V}_{N} are the partial molal volumes of the exchanging ions in the gel phase and γ_{M}^{\pm} and γ_{N}^{\pm} are the mean molal activity coefficients of salts $\text{M}_{Z_{\text{X}}}\text{X}_{Z_{\text{M}}}$ and $\text{N}_{Z_{\text{X}}}\text{X}_{Z_{\text{N}}}$. Barred symbols denote the resin phase, $\bar{\gamma}_{\text{M}}$ and $\bar{\gamma}_{\text{N}}$ corresponding to the mean molal activity coefficients of the exchanging pairs of ions in the gel. The charge of the co-ion of salts $\text{M}_{Z_{\text{X}}}\text{X}_{Z_{\text{M}}}$ and $\text{N}_{Z_{\text{X}}}\text{X}_{Z_{\text{N}}}$ is designated by Z_{X} .

The validity of this model has been fully demonstrated by us in earlier studies with zeolites³¹ by facilitating the precise prediction of K_{NExM} . The special properties of the zeolite, rigidity and high resistance to electrolyte invasion affected by the large negative charge of the ring of oxygen atoms in the faces and corners of its cubic unit cell and the small openings available to the exchanging ions³², make it possible to evaluate the terms on the right hand side of eqn. 1 for this purpose. The values of $\bar{\gamma}_{\text{M}}/\bar{\gamma}_{\text{N}}$ and π are calculable because of the zeolite properties while γ_{M}^{\pm} , γ_{N}^{\pm} , \bar{V}_{M} and \bar{V}_{N} are accessible in the literature^{33,34}.

This success led to our further application of the model to the examination of the cation-exchange phenomenon in an organic ion-exchange resin, the polystyrene sulfonate (PSS) exchanger cross-linked with varying quantities of divinyl benzene. These materials are flexible and easily invaded by simple electrolyte making the evaluation of $\bar{\gamma}_{\text{M}}/\bar{\gamma}_{\text{N}}$ and π more difficult in these cation-exchange resins.

The water sorption properties of PSS exchangers with different degrees of cross-linking have been observed to coincide in the lower water activity region where

the $\pi V_{\text{H}_2\text{O}}$ term is negligibly small²¹. There is coincidence as well between osmotic coefficient data³⁵ for the linear PSS and those obtained by Soldano and Larson³⁶ for the $\leq 0.5\%$ cross-linked PSS gel; only at the highest water activity where a $\pi V_{\text{H}_2\text{O}}$ term is operative in the gel as a consequence of solvent restraint is a lower amount of water taken up by the gel. These experimental results showed that the cross-linking agent, divinyl benzene, does not affect the physical chemical properties of the PSS and provided fundamental justification for their use in the computation of resin-phase swelling pressure (π) with eqn. 2

$$RTm\varphi_m W_{\text{H}_2\text{O}}/1000 = -RT \ln a_{\text{H}_2\text{O}} = \pi V_{\text{H}_2\text{O}} \quad (2)$$

where $W_{\text{H}_2\text{O}}$ is the molecular weight of water and φ_m is the osmotic coefficient of the polyelectrolyte analogue at m , the counter-ion molality in the resin.

There is justification as well for utilization of the osmotic coefficient data for the linear polyelectrolyte analogue in the Gibbs–Duhem equation to compute resin-phase activity coefficients for the exchanging ions. However, since the trend, with dilution, of osmotic coefficient data for fully dissociated polyelectrolytes cannot be deduced beyond the lowest measurable concentration as it can with simple electrolytes, where the Debye–Hückel limiting law applies, the computation with this equation of mean molal activity coefficients meaningfully related to a value of unity for the polyelectrolyte at infinite dilution was impossible. It was necessary to use the equation as shown below to compute mean molal activity coefficient values, $\gamma_{\pm m}$, as a function of counter-ion concentration, m , relative to an indeterminate mean molal activity coefficient, $\gamma_{\pm m_r}$, at the low reference concentration m_r .

$$\ln \gamma_{\pm m}/\gamma_{\pm m_r} = \varphi_m - \varphi_{m_r} + \int_{m_r}^m (\varphi_m - 1) d \ln m \quad (3)$$

By this approach the inherent deficiency of the earlier attempts to evaluate this term by assuming a particular osmotic behaviour in the dilute concentration range^{21–25,36,37} was avoided.

Only trends in ion-exchange selectivity were predicted by this approach when it was used to examine the interpretive quality of the Gibbs–Donnan model for analysis of the ion-exchange phenomenon in flexible, cross-linked ion-exchange resins^{38,39}. To circumvent the intrinsic deficiency of this test of the Gibbs–Donnan model for the anticipation of ion-exchange selectivity, the exchange of pairs of ions, one present in macroscopic quantity and the other in trace, between a cross-linked gel and its linear polyelectrolyte analogue was examined⁴⁰. In these systems the activity coefficients of the reference state cancel with eqn. 1 taking the form

$$K_{\text{NEXM}} = \frac{(\bar{\gamma}_{\text{N}}^{\pm})_{\text{M}}^{Z_{\text{M}}}}{(\bar{\gamma}_{\text{M}}^{\pm})_{\text{N}}^{Z_{\text{N}}}} \frac{\gamma_{\text{M}}^{\pm(Z_{\text{N}}+Z_{\text{N}}Z_{\text{M}}/Z_{\text{X}})}}{\gamma_{\text{N}}^{\pm(Z_{\text{N}}+Z_{\text{N}}Z_{\text{M}}/Z_{\text{X}})}} \exp [-\pi(Z_{\text{N}}\bar{V}_{\text{M}} - Z_{\text{M}}\bar{V}_{\text{N}})]/RT \quad (4)$$

In this presumably definitive test of the model the value of $\gamma_{\pm m}^{\pm}/\gamma_{m_r}$ for the macroion in each phase was obtained from integration of eqn. 3 to the experimental concentration of the macro counter-ion component. Computation of this term for the trace-ion component employed the hybrid function given by eqn. 5

$$\ln \gamma_{\pm m}^{\pm}/\gamma_{m_r} = \ln (\gamma^{\pm el})_m (\gamma^h)_m / (\gamma^{\pm})_{m_r} \quad (5)$$

In eqn. 5, $(\gamma^{\pm et})_m$ and $(\gamma^h)\varphi m$ refer to deviation from ideality attributed respectively to trace ion–polyion interaction based on the experimental concentration of the macro counter-ion component and to trace ion–solvent interaction presumed to be determined by the molality the trace-ion component would assume at the experimental water activity (φm) of the solvent when present as the macro component. This equation was justified in the following way:

The characteristic shape of the curve obtained for the $\log \gamma_{\pm m}/\gamma_{\pm m_r}$ versus $\log m$ plot that is used to characterize these polyelectrolytes is similar to the shape of the curve that is obtained from a plot of $\log \gamma_{\pm m}$ versus $m^{1/2}$ for simple electrolytes. In simple electrolytes this property of $\log \gamma_{\pm m}$ is attributed to the product of competing ion–ion and ion–solvent interactions³³. At low concentrations, $\gamma_{\pm m}^{et}$ is the dominant factor and $\ln \gamma_{\pm m}$ is inversely proportional to $m^{1/2}$; as the molality is raised γ_m^h becomes increasingly important and eventually $\ln \gamma_{\pm m}$ passes through a minimum and then increases exponentially with $m^{1/2}$. By presuming these factors to be similarly operative in the polyelectrolyte as well, $\ln \gamma_{\pm m}^{et}/\gamma_{\pm m_r}$ is assumed, a priori, to be represented by the initial straight line portion of the curve at low values of m (ref. 40). Extension of this line is believed to provide the value of $\ln \gamma_{\pm m}^{et}/\gamma_{\pm m_r}$ over the complete concentration range. Division of $\gamma_{\pm m}/\gamma_{\pm m_r}$ by the extrapolated values of $\gamma_{\pm m}^{et}/\gamma_{\pm m_r}$ over this concentration range yields the corresponding value of γ_m^h which in turn can be analyzed as a function of the water activity associated with the polyelectrolyte at these concentrations. Thus an appropriate estimate of the $\ln \gamma_{\pm m}/\gamma_{\pm m_r}$ term for the trace ion in eqn. 4 was thought to be provided by the product of $\gamma_{\pm m}^{et}/\gamma_{\pm m_r}$ obtained by extrapolation of the linear portion of the $\ln \gamma_{\pm m}/\gamma_{\pm m_r}$ versus $\ln m$ curve for the trace-ion form of the polyelectrolyte to the stoichiometrically equivalent concentration of the macro-ion component in the distribution study and $\gamma^h \varphi m$, obtained at the water activity of the equilibrium mixture from the γ^h versus φm curve analyzed as described above, for the trace-ion system⁴⁰.

There was satisfactory agreement between observation and prediction when computation was based on this presumption that the stoichiometry determines $\gamma_{\pm m}^{et}/\gamma_{\pm m_r}$ and the water activity defines $(\gamma^h)\varphi m$. The accurate prediction of ion-exchange selectivity by this application of the Gibbs–Donnan model would appear to provide strong evidence for its validity.

Recently these studies were extended to the examination of the exchange of two counter-ions over their complete composition range⁴¹. The distribution of Na^+ and Zn^{2+} , between polystyrene sulfonate resin cross-linked with divinylbenzene (1, 2, 4, 8, 12 and 16%, w/w) and the linear PSS analogue of the resin at three different concentration levels (0.02, 0.06 and 0.12 *N*) was measured. The equivalent fraction of Zn and Na was varied from 0 to 1 and 1 to 0 to examine the distribution pattern of these exchanging counter-ions over the complete composition range. The polyelectrolyte analogue was used in these studies to permit direct assessment of selectivity with eqn. 4, the reference state mean molal activity coefficient ratio of the sodium and zinc being expected to cancel as before.

Over most of the composition range examined there was good agreement between the computed and measured selectivity values. Only when the fraction of Zn^{2+} approached unity was there sizeable discrepancy between the two values, the predicted value deviating by as much as a factor of five or six. Explanation of the discrepancy between prediction and experiment in the Zn-rich range was sought in

the theoretical treatment of Manning⁴². These results were rationalized⁴¹ with the “condensation of counter-ions” concept developed by Manning.

The complication introduced by counter-ion “condensation” in the prediction of ion-distribution patterns is, however, sizeably diminished at the concentration levels encountered with gels^{40,41}, even at their lowest degree of cross-linking; for example, the distribution ratio of ions in the gel in contact with a simple mixed electrolyte is rather accurately predicted with the hybrid activity coefficient function once the reference activity coefficient ratios have been evaluated with one selectivity measurement⁴⁰.

An alternative explanation for the discrepancy between the predicted and observed distribution of Na and Zn, when the concentration ratio of Zn to Na is high was suggested by the interpretation given by Boyd and Bunzl⁴³ to volume changes observed to accompany the selective binding of ions by PSS gels. They concluded on the basis of the volume changes observed, that complexation of multiply-charged cations was extensive in this ion exchanger. Examination of the complexation of Zn(II), Ca(II) and Co(II) by the linear analogue of the polystyrene sulfonate gels showed, however, that such complexation by the polystyrene sulfonate polyion is very small indeed. The formation constant of 0.1 measured is much too small to account for the discrepancy between prediction and observation⁴⁴.

Recent simplifications⁴⁵

The effective concentration of mobile counter-ions in charged polymers. The first fundamental insight to the analysis of non-ideality in charged polymeric systems such as proteins was due to Linderstrøm-Lang⁴⁶. His complicated treatment was restated much later in a more convenient form by Scatchard⁴⁷ to facilitate the study of ion binding in complicated protein systems. The more rigorous derivations of Scatchard have been essentially duplicated by Tanford⁴⁸ with a simplified version of the Linderstrøm-Lang treatment. With this treatment the pK of ionizable groups of a protein, assumed to be completely independent of one another, is a function of the charge, Z , as shown

$$\text{p}K = \text{p}K_0 - \frac{2Zw}{2.303} (kT) \quad (6)$$

where w is a measure of the electrostatic free energy required to increase the charge of the polyion from 0 to Z . From the well-known Hasselbach–Henderson equation

$$\text{p}K = \text{p}H - \log \frac{\alpha}{1 - \alpha} \quad (7)$$

where α represents the degree of dissociation; thus

$$\text{p}H - \log \frac{\alpha}{1 - \alpha} = \text{p}K_0 - \frac{2Zw}{2.303} (kT) \quad (8)$$

The potential difference between the surface of a polyion and the region in which the potential is measured during pH measurements in the course of neutralization of a weak polyacid with standard base provides an experimental evaluation of this deviation term ($0.8686 Zw$) in such polymeric systems. The deviation from

ideality of mobile H^+ ions at the site of the neutralization reaction is obtained from the well-known equation given below:

$$pH - \log \frac{[A^-]}{[HA]} - pK_{HA} = pK_{HA_{app}} - pK_{HA} = -0.4343 \frac{\varepsilon\psi(a)}{kT} = -0.886Zw/kT \quad (9)$$

In this equation ε is the unit charge of the proton, $\psi(a)$ corresponds to the potential at the surface of the polyion, K_{HA} is the intrinsic dissociation constant of the acid, $K_{HA_{app}}$ is its apparent dissociation constant, and $[A^-]$ and $[HA]$ are molar concentrations of the dissociated and undissociated polyacid expressed on a monomer basis.

Arnold and Overbeek⁴⁹ in their pioneer demonstration of this plotted potentiometric titration data obtained with polymethacrylic acid as $pH - \log a/1 - a$ versus a . Ideally $pH - \log a/1 - a = pK_{HA}$ and any deviation from a straight line of zero slope in such a plot is presumed to be a quantitative measure of the deviation from ideal behavior of the system as the polyacid is progressively dissociated. The K_{HA} of $1.48 \cdot 10^{-5}$ that is determined from extrapolation of the potentiometric data to intercept the ordinate axis at $a = 0$ is in good agreement with the dissociation constant reported for isobutyric acid, the repeating monomer unit in this polymer. Since there is no ionization of the polymer at $a = 0$ this number should correspond to the negative logarithm of the intrinsic dissociation constant of the repeating acid group of PMA, as it does, if the source of deviation is exclusively electrostatic in nature. Thus the change in the value of pK (ΔpK) with a , is attributed to the change in the electrostatic free energy of the molecule as a consequence of group-group interactions accompanying the ionization process.

Equivalence in the deviation from ideality of counterions. We have shown that in the presence of neutral electrolyte, the fundamental deviation term, $\exp - \varepsilon\psi(a)/kT$, derived from the study of H^+ ion in weak polyacid systems, also provides an accurate basis for estimate of the deviation from ideality of other mobile M^{Z+} counterions present concurrently in these complicated systems: The deviation term then is $\exp - Z\varepsilon\psi(a)/kT$ where Z is the charge of the metal, M^{Z+} , counterion. In a study of complexation of Ca^{2+} , Co^{2+} and Zn^{2+} by polymethacrylic and polyacrylic acid as a function of A made in our laboratory⁵⁰ the distribution of trace-level concentrations of these respective metal ions between a cation-exchange resin (Na-ion form) and solution ($M NaClO_4$) in the absence and presence of various concentrations of the respective polyacids was measured at different degrees of neutralization to demonstrate this. The partition coefficient D_0 (absence of polyacid) and D (presence of ligand) bear the following relationship to β and A for M^{2+} -polyligand systems:

$$\frac{D_0 - D}{DA} = \beta_1(\exp - 2\varepsilon\psi(a)/kT) + \beta_2 A(\exp - 2\varepsilon\psi(a)/kT) \quad (10)$$

Analysis of the distribution results, with $\exp - \varepsilon\psi(a)/kT$ and A values directly available from pH measurements (binding of trace metal ion does not affect the stoichiometry of the system) made concurrently with the distribution measurements provided unambiguous verification of the general applicability of the nonideality term so obtained in these systems. The experimental value of $(D_0 - D)/DA$ were plotted versus A . The data were extrapolated and the intercept of the ordinate defined the values of

β_1 . A plot of $\log(D_0 - D)/DA\beta_1$ versus $\text{pH} - \log \alpha/(1 - \alpha) - \text{p}K_{\text{HA}}$ then yielded a line with a slope of 2 which intersected the origin. The ordinate, $\log(D_0 - D)/DA\beta_1$ is equal to $-2\varepsilon\psi_{(a)}/2.3kT + \log(1 + \beta_2A/\beta_1)$ while the abscissa $\text{pH} - \log \alpha/(1 - \alpha) - \text{p}K_{\text{HA}}$ is equal to $\varepsilon\psi_{(a)}/2.3kT$; the observed result demonstrates that (1) essentially only the MA^+ species exists in these systems and (2) that the non-ideality of the divalent ions is defined by $Z\varepsilon\psi_{(a)}/kT$.

Evaluation of the molal activity coefficient ratio of pairs of mobile counter ions in the charged polymer phase. As has been pointed out earlier the linear portion of a plot of $\log \gamma_m^\pm/\gamma_{m_r}^\pm$ versus $\log m$, defined by $(\varphi_i^* - 1) \log m/m_r$, is presumed to identify the electrostatic contribution to the mean molal activity coefficient ($\gamma_m^{\pm el}/\gamma_{m_r}^\pm$) over the complete concentration range. Subtraction of $(\varphi_i - 1) \log m/m_r$ from $\log(\gamma_m^\pm/\gamma_{m_r}^\pm)$ starting at values of $\log m$ near zero then lead to evaluation of $\log \gamma_{\varphi m}^{\pm h}/\gamma_{m_r}^{\pm h}$ as a function of the charged polymer concentration at the water activity of the equilibrated system. The $\log \bar{\gamma}_M/\bar{\gamma}_N$ term in eqn. 1 is composed of electrostatic and hydration terms as shown below:

$$\log \frac{\bar{\gamma}_M}{\bar{\gamma}_N} = \log \frac{(\gamma_m^{\pm el})_M}{(\gamma_m^{\pm el})_N} \frac{(\gamma_{\varphi m}^{\pm h})_M}{(\gamma_{\varphi m}^{\pm h})_N} \frac{(\gamma_{m_r}^{\pm el})_N (\gamma_{m_r}^{\pm h})_N}{(\gamma_{m_r}^{\pm el})_M (\gamma_{m_r}^{\pm h})_M} \quad (11)$$

In the polymer the electrostatic terms cancel in the presence of simple electrolyte; also

$$\gamma^\pm = (\gamma^+)^{\frac{\nu}{\nu+1}} (\gamma^-)^{\frac{\nu}{\nu+1}} \quad (12)$$

where ν is the degree of polymerization. If $\nu > 200$

$$\gamma^\pm = (\gamma^+)^1 (\gamma^-)^0 = \gamma^+ \quad (13)$$

and

$$\log \frac{\bar{\gamma}_M}{\bar{\gamma}_N} = \log \frac{(\gamma_{+\varphi m}^h)_M}{(\gamma_{+\varphi m}^h)_N} \frac{(\gamma_{+m_r}^h)_N}{(\gamma_{+m_r}^h)_M} \quad (14)$$

At the reference concentration (0.01 for divalent and 0.02 for univalent ions), a_w , the activity of water, is very nearly unity and $\gamma_{\pm m_r}$ has to be unity as well so that $\gamma_{\varphi m}^h/\gamma_{m_r}^h = \gamma_{\varphi m}^h$ and

$$\log \frac{\bar{\gamma}_M}{\bar{\gamma}_N} = \log \frac{(\gamma_{+\varphi m}^h)_M}{(\gamma_{+\varphi m}^h)_N} \quad (15)$$

at the experimental water activity; the value of $\bar{\gamma}_M/\bar{\gamma}_N$ is thus directly calculable in the ion-exchange resin at every experimental condition with the $(\gamma_{+\varphi m}^h)$ values so resolved from such analysis of osmotic coefficient data.

Marinsky and Högfeldt⁵¹ have shown that at the higher concentrations of polystyrene sulfonate the polyanion is essentially unhydrated so that $\gamma_{\pm}^h \approx \gamma_{+}^h$. There may be a finite but small contribution to γ^h from the polyanion, however, at the

* φ_i is the limiting value of the osmotic coefficient at low solution concentrations.

lower concentrations and the prediction of ion distribution patterns in the lower polymer concentrations with the less cross-linked resins may be affected by neglect of such a contribution.

Tests of simplified approach to ion-exchange selectivity predictions

The utility of eqn. 15 for predicting ion-exchange selectivity has been fully tested⁴⁵ by demonstrating the anticipation of K_{NExM} without resort to a calibration step. For example, Boyd *et al.*⁵² recently conducted an extensive study program designed to provide a rigorous thermodynamic basis for the prediction of the selectivity pattern of Zn^{2+} and Na^+ during equilibration in $\text{Zn}(\text{NO}_3)_2$, NaNO_3 mixtures (0.1 *N*) of polystyrene sulfonate exchanger cross-linked to various degrees (0.5 to 24 %) with divinylbenzene. The complete composition range of the resin (X_{Zn} from zero to 1) was covered in these studies. In order to facilitate the prediction of ion-exchange selectivity in this dilute electrolyte mixture they measured the water content of the pure ion forms and the mixed ion forms of the resins as a function of degree of cross-linking. These data were used in the Gibbs–Duhem equation for ternary mixtures through application of the cross differential identities which apply for exact differentials. In this way, they computed the activity coefficient ratio and the partial molar volume difference in the resin of the exchanging ions to predict ion-exchange selectivity coefficients for comparison with the experimental coefficients. In order to employ these data, however, it was necessary to calibrate first the activity estimates through experimental observations made over the complete composition range of the exchanger at one fixed cross-linking value (0.5 % divinylbenzene).

We have compared in Table I the selectivity measurements made by Boyd *et al.*⁵² of the NaPSS , $\text{Zn}(\text{PSS})_2$, $\text{Zn}(\text{NO}_3)_2$, NaNO_3 system with predictions based upon (1) their rigorous thermodynamic analysis of the system and (2) our direct assessment of the ratio of $(\gamma_{\text{Na}}^h)^2/(\gamma_{\text{Zn}}^h)$ (as described earlier in this section) where $\log K_{\text{NaExZn}} = (\log(\gamma_{\text{Na}}^h)^2(\gamma_{\pm\text{Zn}(\text{NO}_3)_2})^3/(\gamma_{\text{Zn}}^h)(\gamma_{\pm\text{NaNO}_3})^4)$, neglecting the $\pi\Delta V/2.3 RT$ term which is relatively unimportant.

We see at once from Table I that the predictive quality of the procedure that we have developed here is fully as good as that provided by the Boyd *et al.*⁵² approach. Their predictions are based upon calibration of the system through measurements of selectivity made with the 0.5 % cross-linked resin, whereas our predictions depend

TABLE I (ref. 53)

COMPARISON OF LOG K_{Ex} PREDICTIONS WITH EXPERIMENTAL MEASUREMENTS

Divinyl- benzene (%)	$\log K_{\text{NaExZn}}$					
	$X_{\text{Na}} = 1$			$X_{\text{Zn}} = 1$		
	Exp.	Predicted		Exp.	Predicted	
		Boyd <i>et al.</i> ⁵²	This lab		Boyd <i>et al.</i> ⁵²	This lab
2	0.096	0.153	0.04	0.10	0.19	-0.01
4	0.00	0.057	0.00	0.09	0.19	0.00
8	-0.22	-0.18	-0.13	-0.11	0.01	-0.20
12	-0.30	-0.33	-0.23	-0.21	-0.11	-0.36
16	-0.35	-0.47	-0.34	-0.42	-0.18	-0.52

only upon resolution of $\bar{\gamma}_h$ from the $\log \gamma_{\pm m} / \gamma_{\pm m_r}$ versus $\log m$ curves derived from our analysis of osmotic coefficient data obtained for the polymer analogues of the cross-linked resins. The indication is that the PSS resins are essentially fully dissociated in their divalent forms as we have shown⁴⁴.

In Table II we have presented selectivity predictions as well for several pairs

TABLE II (ref. 53)

SELECTIVITY PREDICTIONS FOR PAIRS OF IONS IN DILUTE ELECTROLYTE^{38,39,40}

<i>Divinyl- benzene</i> (%)	<i>0.168 M HClO₄</i>	<i>0.1 M Ca(ClO₄)₂</i>	<i>0.1 M Zn(ClO₄)₂</i>	<i>0.1 M Cd(ClO₄)₂</i>	<i>0.1 M Sr(ClO₄)₂</i>					
	<i>K_{NE_xM^T}</i> (Pred.)	<i>K_{NE_xM^T}</i> (Exp.)	<i>K_{NE_xM^T}</i> (Pred.)	<i>K_{NE_xM^T}</i> (Exp.)	<i>K_{NE_xM^T}</i> (Pred.)	<i>K_{NE_xM^T}</i> (Exp.)	<i>K_{NE_xM^T}</i> (Pred.)	<i>K_{NE_xM^T}</i> (Exp.)	<i>K_{NE_xM^T}</i> (Pred.)	<i>K_{NE_xM^T}</i> (Exp.)
<i>Trace ion = Sr²⁺</i>										
1	1.41	3.21	0.90	1.56	0.88	2.83	1.30	2.14		
2	1.81	3.51	0.94	1.78	0.99	3.01	1.49	2.41		
4	3.06	4.30	1.05	1.72	1.34	3.59	1.80	2.91		
8	5.81	6.52	1.13	1.84	2.20	4.85	2.40	3.15		
12	9.49	10.88	1.27	1.87	3.30	7.13	2.88	3.99		
16	16.28	13.13	1.27	1.83	3.59	11.1	3.20	3.35		
<i>Trace ion = Cd²⁺</i>										
1	1.22	1.82	1.01	0.76	1.04	1.03			0.99	0.60
2	1.39	1.89	0.99	0.73	0.99	1.14			1.02	0.55
4	2.02	1.97	0.91	0.62	1.12	1.16			0.90	0.53
8	2.81	2.19	0.80	0.56	1.21	1.42			0.74	0.44
12	3.31	2.54	0.72	0.56	1.50	1.80				
16	3.72	2.65	0.71	0.55	1.41	2.24				
<i>Trace ion = Co²⁺</i>										
1	1.27	1.44	1.12	0.75	1.00	1.20			0.89	0.57
2	1.50	1.87	1.04	0.72	0.88	1.08			0.96	0.49
4	1.84	1.82	0.81	0.63	1.00	1.11			0.75	0.47
8	2.56	1.78	0.67	0.52	0.98	1.11			0.57	0.20
<i>Trace ion = Ca²⁺</i>										
1	1.26	2.09	1.03*	1.18*			1.03	0.93	0.93	0.70
2	1.60	2.59	1.14*	1.26*			1.04	0.92	1.05	0.65
4	2.51	2.97	1.22*	1.37*			1.18	0.89	1.01	0.69
8	4.10	3.92	1.51*	1.49*			0.87	0.74	0.89	0.61
12	5.48	6.01	1.61*	1.88*					0.79	0.58
16	7.42	7.26	1.65*	1.40*					0.74	0.60
<i>Trace ion = Zn²⁺</i>										
1	1.17	1.71	0.96	0.81	0.98	0.49			0.96	0.54
2	1.35	1.75	0.88	0.71	0.86	0.38			0.93	0.50
4	1.84	1.68	1.03	0.68	0.91	0.51			0.79	0.61
8	2.15	1.72	1.29	1.24	1.11	0.50			0.68	0.57
12	2.35	1.66	2.22	1.81	1.35	0.65			0.71	0.64
16	2.64	1.50	2.56	2.53	1.51	0.90			0.71	0.71
<i>Trace ion = Na⁺</i>										
1			1.01	0.49						
2			0.87	0.48						
4			0.66	0.42						
8			0.81	0.42						
12			0.85	0.48						
16			0.86	0.49						

* In 0.1 M Co(ClO₄)₂.

of ions made by the method we have introduced here. In this table we also include the experimentally measured values. Upon comparison of prediction with experiment one observes that when the macro-ion component is univalent (H^+) and the trace-ion component is divalent (Sr^{2+} , Cd^{2+} , Co^{2+} , Ca^{2+} and Zn^{2+}) agreement is quite good at the higher degrees of cross-linking ($> 4\%$). At the lower degrees of cross-linking (1 and 2%), the predicted value of K_{NEXMT} is too small. When the opposite experimental condition is tested, *i.e.* the macro-ion component is divalent (Zn^{2+} , Cd^{2+} , Sr^{2+} and Ca^{2+}) and the trace-ion component is univalent (Na^+), agreement is good for the Zn^{2+} , Na^+ system; with Cd^{2+} and Ca^{2+} the predicted K_{MEXNaT} , while a factor of two too large, parallels the trend in selectivity with cross-linking. The computed value of $K_{SrEXNaT}$ is too large by a factor of almost 2 at low degrees of cross-linking but converges with the experimentally determined value at the highest degree of cross-linking ($> 8\%$). In the divalent-divalent systems the agreement between prediction and experiment is quite good for almost every pair of ions examined. Only for the $Zn-Sr^T$ pair is there considerable discrepancy between prediction and experiment. However, the trend in selectivity is predictable with a ratio of approximately three existing between computation and experiment over the complete cross-linking range (1 to 16%).

We have found in many instances that the serious discrepancy between prediction and experiment for the various systems at the lower degrees of cross-linking can be removed by evaluation of γ_M^h at the molality of the macro-ion component rather than at the molality that the macro-ion form of the trace element corresponds to at the water activity of the equilibrium system. This observation, summarized in Table III, may only indicate that the model we have employed becomes more fully applicable only after the concentration of PSS reaches a sufficiently large value.

It must be pointed out that use of eqn. 15 really needs to be restricted to the sulfonate concentration levels encountered in ion-exchange resins ($\geq 0.5 m$); in the more dilute linear polyelectrolyte analogue systems the presence of simple electrolyte

TABLE III (ref. 53).

SELECTIVITY PREDICTIONS AT LOW DEGREES OF CROSS-LINKING

<i>System</i>	<i>Divinyl- benzene (%)</i>	K_{NEXMT} (<i>Pred.</i>)	K_{NEXMT} (<i>Exp.</i>)
$Zn^T, HClO_4$	1	2.00	1.71
$Cd^T, HClO_4$	1	2.03	1.82
$Ca^T, HClO_4$	1	1.90	2.09
$Na^T, Cd(ClO_4)_2$	1	0.49	0.49
$Na^T, Ca(ClO_4)_2$	1	0.48	0.49
$Na^T, Sr(ClO_4)_2$	1	0.39	0.54
$Na^T, Sr(ClO_4)_2$	2	0.42	0.50
$Sr^T, Cd(ClO_4)_2$	1	1.52	2.14
$Sr^T, Cd(ClO_4)_2$	2	1.89	2.41
$Sr^T, Cd(ClO_4)_2$	4	2.47	2.91
$Cd^T, Sr(ClO_4)_2$	1	0.67	0.60
$Cd^T, Sr(ClO_4)_2$	2	0.66	0.55
$Cd^T, Sr(ClO_4)_2$	4	0.52	0.53

is required for eqn. 15 to be applicable. Only the presence either of salt or high concentrations of the fully ionized repeating functional unit with its mobile counter-ion provides sufficient screening of the highly charged polyion to reduce the remarkably selective "condensation" properties of the polyion. In fact the deviation of selectivity behavior from prediction in the lowest cross-linked resins is probably a consequence of such a residual ion-condensation effect.

The remarkable effect of ion-condensation behavior on selectivity may be seen from a comparison of the exchange with PSS resins at different degrees of cross-linking of Zn^{2+} and Na^+ in 0.1 M NO_3^- and in 0.02, 0.05 and 0.12 M PSS⁴¹ and of Co^{2+} and H^+ in 0.16 M ClO_4^- and in dilute concentrations of PSS³⁹.

A good deal of additional research is required to examine more carefully the concepts we have introduced. There can be no question however, that the predictive quality of the new approach we have developed for the assessment of counterion distribution patterns in ion-exchange resins compares favorably with the less direct methods employed rather successfully in our earlier work.

We believe that fundamental assessment of the factors important in defining counterion distribution in charged polymers (cross-linked and linear) has been resolved with our interpretation of osmotic coefficient data. By our analysis, ion-solvent interactions are believed to contribute most importantly in the PSS-based resins to their ion-exchange selectivity patterns. The agreement obtained between the prediction of these patterns and their observed distribution without need to resort to a single measurement for calibration of the activity coefficient terms in the polymer provides strong support for the validity of the interpretations made.

Method for analysis of ion-exchange selectivity measurements complicated by complexation reactions with the repeating gel functional unit

With the complexation of one (M) of the pair of exchanging cations (M^{Z_M} and N^{Z_N}) by the repeating exchanger functional unit (R^-) the experimentally observed gross concentration of M in the exchanger corresponds to $(M^{Z_M} + \sum_{n=1} MR_n^{Z_M-n})$ so that

$$K_{NEX}M = \frac{(M^{Z_M} + \sum_{n=1} MR_n^{Z_M-n})^{Z_N} (N^{Z_N})^{Z_M}}{(M^{Z_M})^{Z_N} (N^{Z_N})^{Z_M}} \quad (16)$$

$$\text{Since } \sum_{n=1} MR_n^{Z_M-n} = \sum_{n=1} \beta_n (R^-)^n (M^{Z_M}) \quad (17)$$

where β represents the overall formation constant of the n th complexed species

$$K_{NEX}M = \frac{(M^{Z_M})^{Z_N} (N^{Z_N})^{Z_M}}{(M^{Z_M})^{Z_N} (N^{Z_N})^{Z_M}} (1 + \sum_{n=1} \beta_n (R^-)^n \exp(-Z_M \epsilon \psi_{(a)}/kT))^{Z_N} \quad (18)$$

The quotient defined by eqn. 1 is contained in eqn. 18 as shown

$$K_{NEX}M_{(18)} = K_{NEX}M_{(1)} (1 + \sum_{n=1} \beta_n (R^-)^n \exp(-Z_M \epsilon \psi_{(a)}/kT))^{Z_N}$$

$$\text{and } K_{\text{NExM}}^{(18)} = \frac{(\bar{\gamma}_{\text{N}})^{\text{Z}} (\gamma_{\text{M}}^{\pm})^{\text{N} + \text{Z}_{\text{N}} \text{Z}_{\text{M}} / \text{Z}_{\text{X}}}}{(\bar{\gamma}_{\text{M}}) (\gamma_{\text{N}}^{\pm})^{\text{Z}_{\text{M}} + \text{Z}_{\text{N}} \text{Z}_{\text{M}} / \text{Z}_{\text{X}}}} \times \exp(-\pi[\text{Z}_{\text{N}} \bar{V}_{\text{M}} - \text{Z}_{\text{M}} \bar{V}_{\text{N}}] / RT) (1 + \sum_{n=1} \beta_n (\text{R}^-)^n \exp(-\text{Z}_{\text{M}} \varepsilon \psi_{(a)} / kT))^{\text{Z}_{\text{N}}} \quad (19)$$

In most exchange systems the osmotic pressure term is small enough to neglect. Also, from eqn. 15 $\frac{(\gamma_{\varphi m}^h)_{\text{N}}}{(\gamma_{\varphi m}^h)_{\text{M}}}$ can be substituted for $\left(\frac{\bar{\gamma}_{\text{N}}}{\bar{\gamma}_{\text{M}}}\right)$

and

$$K_{\text{NExM}}^{(18)} \approx \frac{(\gamma_{\varphi m}^h)_{\text{N}}^{\text{Z}_{\text{M}}} (\gamma_{\text{M}}^{\pm})^{\text{Z}_{\text{N}} + \text{Z}_{\text{N}} \text{Z}_{\text{M}} / \text{Z}_{\text{X}}} (1 + \sum_{n=1} \beta_n (\text{R}_n^-)^n \exp(-\text{Z}_{\text{M}} \varepsilon \psi_{(a)} / kT))^{\text{Z}_{\text{N}}}}{(\gamma_{\varphi m}^h)_{\text{M}}^{\text{Z}_{\text{N}}} (\gamma_{\text{N}}^{\pm})^{\text{Z}_{\text{M}} + \text{Z}_{\text{N}} \text{Z}_{\text{M}} / \text{Z}_{\text{X}}}} \quad (20)$$

If the total concentration of M and N does not exceed $\approx 1 m$

$$(\gamma_{\varphi m}^h)_{\text{N}} (\gamma_{\varphi m}^h)_{\text{M}} \approx 1 \text{ and}$$

$$K_{\text{NExM}}^{(18)} \approx \frac{(\gamma_{\text{N}}^{\pm})^{\text{Z}_{\text{M}} + \text{Z}_{\text{N}} \text{Z}_{\text{M}} / \text{Z}_{\text{X}}} (1 + \sum_{n=1} \beta_n (\text{R}^-)^n \exp(-\text{Z}_{\text{M}} \varepsilon \psi_{(a)} / kT))^{\text{Z}_{\text{N}}}}{(\gamma_{\text{M}}^{\pm})^{\text{Z}_{\text{N}} + \text{Z}_{\text{N}} \text{Z}_{\text{M}} / \text{Z}_{\text{X}}}} \quad (21)$$

TEST OF THE METHOD

A number of years ago this author examined the complexation of Co(II), Ni(II) and Cu(II) by the weakly acidic IRC-50 resin, a copolymer of polymethacrylic acid and divinyl benzene marketed by Rohm & Haas^{10,11}. In the examination of these systems 0.100 g of the resin (hydrogen form) was equilibrated in 100.0 ml of 0.05 M Na₂SO₄ solution containing MSO₄ at a total millimol content respectively 1/2, 1/4 and 1/6 that of the measured hydrogen capacity (0.1000 ± 0.0005) of the resin sample. In each set of solutions the system was allowed to come to equilibrium after the resin sample was brought to different degrees of neutralization (0.1 to 0.9) with standard sodium hydroxide. The concentration of M(II) was measured polarographically and the activity of H⁺ was measured potentiometrically in each equilibrated sample.

Analysis of the data was affected by comparing the exchange of H⁺, rather than Na⁺, with M(II). With this approach

$$[\bar{\text{M}}] \approx \sum_{n=1} \bar{\text{M}}\text{R}_n \text{ and } [\text{H}] \approx [\bar{\text{H}}\text{R}]$$

$$\text{since } [\bar{\text{M}}(\text{II})] \ll \sum_{n=1} \bar{\text{M}}\text{R}_n \text{ and } \text{H}^+ \ll [\bar{\text{H}}\text{R}]$$

and the treatment of the data is straightforward. By describing the equilibrium as follows:

$$K_{\text{HExM}(\text{II})} = \sum_{n=1} \bar{\text{M}}\text{R}_n (\text{H}^+)^2 (\text{R}^-) / \text{M}(\text{II}) (\bar{\text{H}}\text{R})^2 \quad (22)$$

the presence of complex species can be resolved through a plot of $K_{\text{H}^{\text{EXM}}(\text{II})}$ versus (\bar{R}) (refs. 10, 11, 54). Such a plot yields a line intercepting the ordinate at a value equal to $\beta_{\text{MR}^+}/(\beta_{\text{HR}})^2$. If only the MR^+ species is present the line will be straight and its slope will be zero. If a second species is present concurrently the slope of the line will correspond to $\beta_{\text{MR}_2}/(\beta_{\text{HR}})^2(\bar{V}_g)$ where \bar{V}_g is the volume of the exchanger phase.

It was found that Co(II) and Ni(II) formed only one complexed species, the M(II)R^+ ion pair, whereas the M(II)R_2 species was believed to be the predominant one with Cu(II) . We have tested the applicability of eqn. 21 by comparing the formation constant in the Ni(II) system resolved earlier with the value derived from the same data expressed in eqn. 16 where the binding of metal to resin is compared with the simultaneous incorporation of Na^+ .

In expressing $K_{\text{Na}^{\text{EXM}}(\text{II})}$ with eqn. 16 the concentration of $\bar{\text{M}}_b$ and $\bar{\text{Na}}^+$ is based on the volume of the gel, \bar{V}_g . To evaluate the total millimols of Na entering the gel the quantity of Na is presumed to be equal to R^- by preserving electroneutrality in the gel phase; any invasion of the gel by Na_2SO_4 is neglected.

In the earlier studies^{10,11} \bar{V}_g was not measured. However, in a recent examination of the potentiometric property of IRC-50 volume measurements were made over its complete neutralization range⁵⁵. We have presumed that in this rather inflexible resin these volume measurements are applicable in the presence of M(II) as well.

TABLE IV

THE FORMATION CONSTANT OF THE NiR^+ SPECIES FORMED IN A PMA GEL

α	β_{NiR^+} (eqn. 23)	β_{NiR^+} (eqn. 10)
$4.86 \cdot 10^{-3} \text{ M NiSO}_4 (\text{HR}/\text{Ni} = 2)$		
0.201	8.71	12.6
0.300	7.85	8.64
0.400	9.13	10.5
0.500	9.14	10.0
0.600	9.55	11.2
0.700	5.07	9.54
0.800	9.15	8.07
0.900	9.02	13.1
$2.43 \cdot 10^{-3} \text{ M NiSO}_4 (\text{HR}/\text{Ni} = 4)$		
0.102	9.44	9.00
0.201	14.3	11.6
0.300	10.7	10.8
0.400	9.14	10.2
0.500	14.7	11.1
0.600	11.1	9.82
0.700	10.6	9.23
0.800	11.0	8.88
0.900	10.6	10.3
$1.63 \cdot 10^{-3} \text{ M NiSO}_4 (\text{HR}/\text{Ni} = 6)$		
0.300	8.19	12.3
0.400	9.80	13.0
0.500	9.68	8.35
0.600	10.7	12.7
0.700	11.4	10.5

For the analysis of the data expressed in this manner eqn. 21 has been transformed as follows: The total concentration of M(II) and Na⁺

$$\left\{ \left[K_{\text{NaExM(II)}} \frac{(\gamma \pm_{\text{Na}_2\text{SO}_4})^4}{(\gamma \pm_{\text{MSO}_4})^3} \right] - 1 \right\} \left[\frac{1}{R^-} \right] = \sum_{n=1} \beta_{\text{MR}_{n-1}}(R)^{n-1} \exp(-\varepsilon\psi_{(a)}/kT) \quad (23)$$

in the gel never exceeded $\approx 1M$ and this equation is applicable since $(\gamma_{\text{qm}}^h)_M/(\gamma_{\text{qm}}^h)_{\text{Na}}$ is close to unity and constant at this concentration level (Table I).

These computations are summarized in Table IV for the NiSO₄, IRC-50, 0.05 M Na₂SO₄ system investigated previously¹⁰. The earlier computations of β_{NiR^+} are also included in the table for comparison. To assure an equivalent basis for comparison a correction of the earlier formation constant values resolved has been made by correcting for the deviation of NiSO₄ from ideal behavior. The values of β_{NiR^+} deduced with eqn. 23 are in excellent agreement with the earlier computation of this parameter that employed a more direct approach. The analysis we recommend for studies comparing the binding of metal ions with Na⁺ is thus essential for a proper interpretation of such data. Unfortunately, most investigators are not aware of this.

REFERENCES

- 1 H. Zadnard, *Kolloid-Beihfte*, 49 (1939) 315.
- 2 J. R. Dunstone, *Biochem. J.*, 85 (1962) 336.
- 3 J. R. Dunstone, *Biochem. J.*, 77 (1960) 164.
- 4 M. Schnitzer and S. V. Khan, *Humic Substances in the Environment*, Marcel Dekker, New York, 1972.
- 5 D. S. Gamble, *Can. J. Chem.*, 50 (1972) 2680.
- 6 D. S. Gamble, *Can. J. Chem.*, 51 (1973) 3217.
- 7 J. A. Marinsky, in J. A. Marinsky (Editor), *Ion Exchange*, Vol. 1, Marcel Dekker, New York, 1966, ch. 9.
- 8 C. Eger, W. M. Anspach and J. A. Marinsky, *J. Nucl. Inorg. Chem.*, 30 (1968) 1899.
- 9 C. Eger, W. M. Anspach and J. A. Marinsky, *J. Nucl. Inorg. Chem.*, 30 (1968) 1910.
- 10 J. A. Marinsky and W. M. Anspach, *J. Phys. Chem.*, 79 (1975) 433.
- 11 J. A. Marinsky and W. M. Anspach, *J. Phys. Chem.*, 79 (1975) 439.
- 12 O. Smidsrød and A. Haug, *Acta Chem. Soc.*, 19 (1965) 341.
- 13 J. L. Morgan and A. Wasserman, *J. Chem. Soc.*, (1952) 492.
- 14 G. R. Seely and R. L. Hart, *Macromolecules*, 7 (1974) 766.
- 15 J. L. Mongar and A. Wasserman, *Discussions Faraday Soc.*, 7 (1949) 118.
- 16 H. P. Gregor, *J. Amer. Chem. Soc.*, 70 (1948) 1293.
- 17 H. P. Gregor, *J. Amer. Chem. Soc.*, 73 (1951) 642.
- 18 E. Ekedahl, E. Högfeldt and L. G. Sillen, *Acta Chem. Scand.*, 4 (1950) 828.
- 19 E. Högfeldt, E. Ekedahl and L. G. Sillen, *Acta Chem. Scand.*, 4 (1950) 556.
- 20 O. D. Bonner, W. J. Argersinger, Jr. and A. W. Davidson, *J. Amer. Chem. Soc.*, 74 (1952) 1044.
- 21 E. Glueckauf, *Proc. Roy. Soc., Ser. A.*, 214 (1952) 207.
- 22 J. F. Duncan, *Aust. J. Chem.*, 8 (1955) 293.
- 23 B. Soldano and D. Chestnut, *J. Amer. Chem. Soc.*, 77 (1955) 1334.
- 24 G. E. Myers and G. E. Boyd, *J. Phys. Chem.*, 60 (1956) 521.
- 25 G. E. Boyd, S. Lindenbaum and G. E. Myers, *J. Phys. Chem.*, 65 (1961) 577.
- 26 J. Feitelson, *J. Phys. Chem.*, 66 (1962) 1295.
- 27 J. A. Marinsky, *J. Phys. Chem.*, 71 (1967) 1572.
- 28 F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
- 29 F. G. Donnan and E. A. Guggenheim, *Z. Phys. Chem.*, (Leipzig), 162A (1932) 356.
- 30 F. G. Donnan, *Z. Phys. Chem. (Leipzig)*, 168A (1934) 369.
- 31 S. Bukata and J. A. Marinsky, *J. Phys. Chem.*, 68 (1964) 994.

- 32 D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J. Amer. Chem. Soc.*, 78 (1956) 5963, 5972.
- 33 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth Scientific Publications, London, 2nd ed., 1959.
- 34 P. Mukherjee, *J. Phys. Chem.*, 65 (1961) 740.
- 35 M. M. Reddy, J. A. Marinsky and A. Sarker, *J. Phys. Chem.*, 74 (1970) 3891.
- 36 B. Soldano and Q. V. Larson, *J. Amer. Chem. Soc.*, 77 (1955) 1331.
- 37 B. Soldano, Q. V. Larson and J. S. Myers, *J. Amer. Chem. Soc.*, 77 (1955) 1339.
- 38 M. M. Reddy, S. Amdur and J. A. Marinsky, *J. Amer. Chem. Soc.*, 94 (1972) 4087.
- 39 M. M. Reddy and J. A. Marinsky, *J. Macromol. Sci. Phys.*, B-5(1) (1971) 135.
- 40 J. A. Marinsky, M. M. Reddy and S. Amdur, *J. Phys. Chem.*, 77 (1973) 2128.
- 41 R. Yang and J. A. Marinsky, *J. Phys. Chem.*, 83 (1979) 2737.
- 42 G. S. Manning, *J. Chem. Phys.*, 51 (1969) 924, 3249.
- 43 G. E. Boyd and K. Bunzl, *J. Amer. Chem. Soc.*, 96 (1974) 2054.
- 44 R. Baldwin, *Ph. D. Thesis*, State University of New York at Buffalo, Buffalo, NY, 1978.
- 45 J. A. Marinsky, M. M. Reddy and R. Baldwin, *Water in Polymers*, Amer. Chem. Soc. Advances in Chemistry Symposium Series No. 127, 1980, p. 387.
- 46 K. Linderstrøm-Lang, *C. R. Trav. Lab. Carlsberg*, 15 (1924) No. 7.
- 47 G. Scatchard, *Ann. N.Y. Acad. Sci.*, 51 (1949) 660.
- 48 C. Tanford, *J. Amer. Chem. Soc.*, 72 (1950) 441.
- 49 R. Arnold and J. Th. G. Overbeek, *Rec. Trav. Chim. Pays-Bas.*, 69 (1950) 592.
- 50 L. Travers and J. A. Marinsky, *J. Polym. Sci., Part C*, 47 (1974) 285.
- 51 J. A. Marinsky and E. Högfeldt, *Chemica Scripta*, 9 (1976) 233.
- 52 G. E. Boyd, G. E. Myers and S. Lindenbaum, *J. Phys. Chem.*, 78 (1974) 110.
- 53 J. A. Marinsky, M. M. Reddy and R. S. Baldwin, in S. Rowland (Editor), *Water in Polymers*, ACS Symposium Series No. 127, Amer. Chem. Soc., Washington, DC, in press.
- 54 J. A. Marinsky, *Coord. Chem. Rev.*, 19 (1976) 125.