Macromolecules 1986, *19*, 2974–2977

Phosphoric Acid Ester Cation-Exchange Resins. 2. Physicochemical Characterization[†]

Russell B. Selzer and Darryl G. Howery*

Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, New York 11210. *Received June 9, 1986*

ABSTRACT: Water contents, ion-exchange selectivity coefficients, and specific electrical conductances of phosphate monoester (PME) and phosphate diester (PDE) cation-exchange resins are measured. The group 1 cation forms contain the most water (e.g., 39.2% for Na^+-PME and 28.8% for Na^+-PDE), while the hydrogen and polyvalent cation forms have the lowest water contents (e.g., 24.9% for Ca^{2+}-PME and 17.9% for H^+-PDE). The selectivity coefficients for eight cation-pair systems on the PME resin and three cation-pair systems on the PDE resin are determined. The resins exhibit high selectivities for the proton and polyvalent cations (e.g., $\log K^{H}{}_{Na} = 0.98$ for PME and $\log K^{Mg}{}_{Na} = 1.42$ for PDE). The specific electrical conductances for four ionic forms of each resin are measured, the Na^+ forms exhibiting the highest values (e.g., $5.0 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ for Na^+-PME) and the divalent forms having much lower values (e.g., $2.4 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ for Cu^{2+}-PDE).

Introduction

The synthesis and preliminary characterization of two phosphate cation-exchange resins were described in a recent publication.[1] These resins, based on a poly(styrene-*co*-2% divinylbenzene) matrix (designated R), contain functional groups that are esters of phosphoric acid, attached to the copolymer matrix through C–O–P linkages. One resin, $RCH_2CH_2OP(O)(OH)_2$, is designated the PME resin for its *p*hosphate *m*ono*e*ster groups and the other, $RCH_2CH_2OP(O)(OCH_2CH_3)(OH)$, is designated the PDE resin for its *p*hosphate *d*i*e*ster groups. These materials were shown to be stable for use in a detailed physicochemical characterization of the two types of phosphate groups. To this end, we have studied the capacity and acid–base properties of the resins[1] and have analyzed the infrared spectra of the exchangers.[2] In the present paper, we extend the resin characterization to include water contents, ion-exchange equilibrium selectivities, and electrical conductances.

Phosphate groups, which can act as cation exchangers, are a major component of many biological systems. Thus, we anticipate that a study of the physicochemical properties of synthetic ion-exchange resins containing phosphate exchange sites could lead to information useful for interpreting physiological processes. The fact that models based on the biological ion exchanger have been used to explain a number of properties of living cells[3,4] originally motivated us to synthesize and characterize phosphate ion exchangers. Suitable materials have heretofore not been available, the common phosphorus-containing cation exchangers bearing phosphonate ester groups (having C–P linkages) and the phosphoric acid materials generally being inhomogeneous and/or unstable with respect to hydrolysis of the phosphate functions from the polymer backbone.

Experimental Section

Resin-Form Preparations. The synthesized resins[1] were conditioned with three cycles of 0.5 M HCl/H_2O/0.5 M NaOH (4 L each) before use. All salts were Baker Reagent Grade (J. T. Baker Co., Phillipsburg, NJ). The H^+ forms were prepared by treatment in a column with 1 M HCl followed by water rinse until the effluent was neutral to methyl orange. The Na^+ forms were prepared with particular care to avoid hydrolysis of the weak-acid exchange sites of the PME resin. The resin sample was treated in a column with 0.5 M NaOH, followed by application of succeedingly more dilute NaOH solutions (down to ca. 0.001 M). The sample was then transferred to a glass filter and rinsed with two portions of deionized water, each followed by suction to remove adherent liquid. A mixed Na^+/H^+ form of the PME resin was prepared by treatment of the Na^+ form in a column with deionized water for 2 days (ca. 6 L) until the effluent was neutral to phenolphthalein. The other ionic forms were prepared by treatment of small resin samples (ca. 1 g) with 3 L of 0.5 N nitrate salts. The samples were then suction washed with a minimum of water to prevent extensive hydrolysis.

Water Contents. The centrifugation technique was applied.[5] About 1.0 g of resin in a particular ionic form was equilibrated with water for at least 1 h. The resin/water slurry was then transferred to a small tube fitted with a sintered-glass frit, which was inserted into a 15-mL centrifuge tube. The assembly was sealed with plastic film to prevent excessive drying of the sample from evaporation. A small hole in the inner tube provided for pressure equalization in the system. The wet resin was spun in a centrifuge for 20 min; then the resin beads were quickly transferred to a tared vial, weighed, and placed in a vacuum oven at 70 °C for 48 h. The dry resin was then weighed and the water content, w ((g of H_2O)/(g of wet resin)), was calculated from the weight loss.

Equilibrium Selectivities. The ion-exchange equilibrium reaction for two cations $M1^{z1}$ and $M2^{z2}$ is

$$z2\,\overline{M1^{z1}} + z1\,M2^{z2} \rightleftharpoons z1\,\overline{M2^{z2}} + z2\,M1^{z1} \qquad (1)$$

in which the barred terms represent cations in the resin phase and the nonbarred terms represent cations in the external aqueous phase. We applied batch and column techniques to measure the ion-exchange isotherms for the phosphoric acid ester resins.

The progressive batch technique[6] provided a convenient and rapid means of obtaining the exchange isotherms. In this method, a sample of resin in a particular ionic form is equilibrated with a succession of solutions containing the exchanging counterion. A portion of each solution is drawn off and subjected to quantitative analysis, from which the solution composition and, by material balance, the resin composition can be computed. The equations developed by Cosgrove and Strickland for monovalent cations[7] can be readily modified to account for polyvalent cations. The selectivity coefficient, K (also referred to as the ion-exchange equilibrium constant), for each point in the determination is then calculated for the counterion system M2/M1 from the equation

$$K^{M2}{}_{M1} = \{\bar{x}^{z1}{}_{M2}x^{z2}{}_{M1}\}/\{\bar{x}^{z2}{}_{M1}x^{z1}{}_{M2}\} \qquad (2)$$

where all concentration terms are expressed as equivalent fractions.

For the determinations on the PME and PDE resins, samples of resins corresponding to a total capacity of ca. 10 mequiv were placed in a 250-mL Erlenmeyer flask. The experimental parameters were chosen[8] so that 6–9 values of K spanning the resin-fraction range 0.1–0.9 could be found. For typical isotherms, the total volume was 125 mL, and after each equilibration, a 100-mL sample of solution was withdrawn through a pipet. The concentration of the exchanging-cation solution (M2) was standardized in the 0.30 N range, in order to keep the ionic strength in all systems below 0.03 N and thereby minimize activity coefficient variations. The method of quantitative analysis varied according to the cation. Titration was used for H^+, flame pho-

---

[†] Based on the Ph.D. Thesis of R.B.S., City University of New York, New York, 1982.

[*] To whom correspondence should be addressed.

0024-9297/86/2219-2974$01.50/0

tometry for Na^+ and K^+, and atomic absorption for Mg^{2+}, Ca^{2+}, and Cu^{2+}. Equilibration times ranging from 4 to 12 h were found to yield consistent results. The temperature during equilibration was 21–25 °C; variations within this range did not measurably affect the isotherms. The capacity of the resin was measured for each individual sample by transferring the sample to a column and eluting with 1 M HCl. Displaced counterion was collected and measured.

To check the validity of the progressive batch technique, an alternative column method was applied to a few of the systems. A resin sample is equilibrated by exhaustive column treatment with a solution containing both counterions. For each point on an isotherm, the resin compositions for both cations are determined. An amount of resin in the $M1^{z1}$ or $M2^{z2}$ form was placed in a column, and 3 L of a solution containing M1 and M2 in a known composition (total ionic strength = 0.05 N) was slowly passed through the resin for 2 days. A brief washing followed, which eluted interstitial electrolyte in the resin but avoided any changes in composition from hydrolysis. Then the counterions were eluted from the resin with 500 mL of 1 M HCl into a volumetric flask, the eluate composition was determined, and a point on the isotherm was calculated. The process was repeated with new solution compositions until four isotherm points were obtained.

Electrical Conductances. The conductances of packed beds of the PME and PDE resins were determined by the dip cell method. The conductivity cell consists of a 2.5 cm diameter × 5.0 cm long weighing bottle, fitted with a Barnstead plastic dip cell (no. B2-03412, Barnstead Co., Boston, MA). The body of the electrode module is inserted through a rubber stopper, which is notched to fit into the weighing bottle in a reproducible manner. The levels of the packed resin bed and interstitial solution in the cell were kept constant for all measurements.

To determine the resin bead conductance, between 4 and 8 samples of each ionic form were studied. Each sample was equilibrated with a solution of the corresponding cation at a certain concentration by slowly running 250 mL of the solution through the resin in a column (ca. 10-mL bed volume). The resin samples were transferred in the equilibrating (interstitial) solution to weighing bottles, covered, and equilibrated for an additional 24 h in a constant-temperature bath at 30 °C. Samples of the interstitial solutions were also equilibrated in separate weighing bottles. The resin beds were carefully tapped to eliminate air bubbles and to ensure efficient packing of the copolymer spheres.

The inherent conductances of the resin beads were determined by plotting the conductance of the packed bed vs. the conductance of the interstitial solution for a particular ionic form.[10,11] From the curves so obtained, the unique point at which the bed conductivity equals the solution conductivity, termed the isoconductance point, is read.[10-13] At the isoconductance point, the conductance of the resin bead itself must necessarily equal that of the interstitial solution. Equilibrating solution concentrations were chosen to bracket the isoconductance point.

Electrical measurements were made with a Wayne-Kerr bridge (Wayne-Kerr Laboratories, Chessington, England). At least 15 min was required for stable readings. By measuring the conductance of a 0.1 M KCl solution at 30 °C and using the data of Kortum and Bockris[9] to find the specific conductance, we obtained a value of $c = 0.314\ \text{cm}^{-1}$ for the cell constant at 30 °C. All conductance values measured were converted to specific conductances by using this value of c.

Results and Discussion

Water Contents. Three sets of water-content determinations were performed on several ion forms of the PME and PDE resins. For the PME resin, the water contents of the H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, $NH_4{}^+$, Cu^{2+}, La^{3+}, and mixed Na^+/H^+-forms were measured; for the PDE resin, the H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and La^{3+} forms were characterized. As a check on the stability of the resins, samples from one set of determinations were reequilibrated with water and used in a second determination.

Average values for the water-content determinations are presented in Table I. The PME forms have considerably higher water contents than the PDE forms, in line with the fact that the PME resin has about twice the capacity of the PDE resin[1]. The water contents vary inversely with the ionic charge (excepting the H^+ form). For example, as seen in Table I, the resin forms of the group 1 cations have the highest water contents, while the La^{3+} form has the lowest. The water contents obtained by repeating measurements on the same sample agreed nearly within experimental error, providing further confirmation, with one exception, of the stability of the materials. The significantly lower value for the second measurement on the NH_4^+ form of the PME resin is the result of partial conversion to the H^+ form in the heated dry state. The first value for the NH_4^+ form water content (39.7%) correlates with those of the alkali cations, as would be expected. The second value (26.3%) correlates with that of a mixed NH_4^+/H^+ form. Our infrared spectral measurements[2] confirm this conversion.

Table I
Water Contents of Phosphate Resins (% H_2O)

ionic form	PME resin[a]	PDE resin[b]
H^+	22.3 ± 0.4	17.9 ± 0.1
Na^+	39.2 ± 0.3	28.8 ± 0.4
K^+	37.9 ± 0.6	29.8 ± 0.5
Mg^{2+}	32.1 ± 0.2	19.6 ± 0.2
Ca^{2+}	24.9 ± 0.4	19.0 ± 0.2
Cu^{2+}	24.6 ± 0.3	c
La^{3+}	22.5 ± 0.4	17.2 ± 0.2
Na^+/H^+	36.7 ± 0.3	c

[a] Capacity of PME resin (H^+ form) = 2.30 mequiv g. [b] Capacity of PDE resin (H^+ form) = 1.26 mequiv g. [c] Not measured.

The mixed Na^+/H^+ form of the PME resin, in which the Na^+ counterions occupy the strong-acid exchange sites and the H^+ counterions the weak-acid sites, has a water content that is only ca. 10% lower than that of the fully converted Na^+ form. If all Na^+ counterions in the PME resin were bound in an equivalent manner, an approximately 30% reduction in water content would be expected upon replacement of half of the Na^+ ions with protons (based on the H^+-form water content). The hydration of the PME resin appears to be determined primarily by the strong-acid exchange sites.

From the capacity and water content of a particular resin form, the cationic hydration number may be estimated from the formula

$$\mathrm{HN_M} = \{1000w\}/\{18c(1 - w)\} \qquad (3)$$

where $\mathrm{HN_M}$ is the average hydration number of counterion M in the resin ((mol of H_2O)/(equiv of M)), c is the capacity of the M form (mequiv/g), and w is the water content of the M form (g of H_2O)/(g of wet resin)). The hydration numbers for the H^+, Na^+, and K^+ forms are 7, 16, and 17, respectively, for the PME resin and 10, 18, and 19, respectively, for the PDE resin. Assuming that the protons of the PDE resin are roughly equivalent to the strong-acid protons of the PME resin and that the $\mathrm{HN_H}$ of 7 for the PME resin is the average of the hydration numbers for the strong- and weak-acid protons, then the hydration number for the weak-acid protons of the PME resin is estimated to be 4 (mol of H_2O)/(equiv of H^+). Similar reasoning gives $\mathrm{HN_{Na}} = 14$ and $\mathrm{HN_K} = 15$ for the Na^+ and K^+ counterions occupying the weak-acid sites of the PME groups.

Equilibrium Selectivities. Equilibrium isotherms were determined at 25 °C for the following M2/M1 counterion systems: for the PME resin, Li^+/Na^+, K^+/Na^+, Rb^+/Na^+, H^+/Na^+, Mg^{2+}/Na^+, Ca^{2+}/Mg^{2+}, Cu^{2+}/Ca^{2+}, and H^+/Cu^{2+}; for the PDE resin, K^+/Na^+, Mg^{2+}/Na^+, and Ca^{2+}/Mg^{2+}. The isotherms for the PME resin reflect the

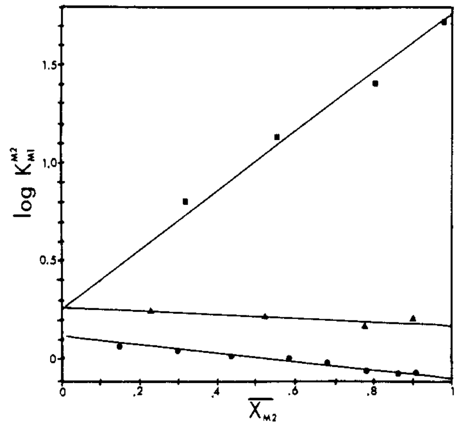

Figure 1. log *K* plots at 25 °C. PDE resin: (●) K^+/Na^+. PME resin: (■) H^+/Na^+; (▲) Ca^{2+}/Mg^{2+}.

Table II
Integrated Selectivity Coefficients for Phosphate Resins (25 °C)

resin	counterion M1	counterion M2	log $K^{M2}{}_{M1}$[a]	slope	intercept[b]
PME[c]	Na^+	H^+	0.98	1.25	0.25
	Na^+	K^+	0.12	−0.07	0.13
	Na^+	Rb^+	0.02	−0.14	0.10
	Li^+	Na^+	0.01	0.07	0.05
	H^+	Cu^{2+}	0.20	−0.00	1.24
	Na^+	Mg^{2+}	1.60	*d*	0.00
	Mg^{2+}	Ca^{2+}	0.24	−0.26	0.28
	Ca^{2+}	Cu^{2+}	0.93	−0.53	1.20
PDE	Na^+	K^+	0.02	−0.21	0.12
	Na^+	Mg^{2+}	1.42	2.18	0.31
	Mg^{2+}	Ca^{2+}	0.42	0.53	0.15

[a] Integrated selectivity coefficient for equilibrium given by eq 2. Experimental error: 10–15% (20% for the H^+/Na^+ and Mg^{2+}/Na^+ systems on the PME resin). [b] Value of log *K* extrapolated to $\bar{x}_{M2} = 0$. [c] For strong-acid exchange sites (see text). [d] Plot is somewhat nonlinear.

selectivity characteristics of the strong-acid exchange sites only since the resin forms were prepared by conversion of the H^+ form at low pH. The K^+/Na^+ isotherm for the PME resin was also measured at high pH by using KOH solutions to determine the overall selectivity characteristics of both the strong- and weak-acid exchange sites.

An integrated selectivity coefficient for each system was estimated by plotting log $K^{M2}{}_{M1}$ values calculated for each experimental point on the isotherm (eq 2) vs. the resin composition $\bar{x}_{M2}$ and constructing the best line through the points. The area under this curve over the entire composition range of the resin gives the integrated selectivity coefficient. In Figure 1 are presented three representative log *K* plots. The integrated selectivity coefficients calculated for the various counterion systems on the phosphate resins are summarized in Table II. To indicate the general shape of the log *K* plots, the slopes and intercepts for those reasonably linear plots are given in Table II. The majority of the isotherms were determined by the batch method. The K^+/Na^+ isotherms were determined by the batch method in the forward and reverse directions with excellent reproducibility. For the PME resin, the Mg^{2+}/Na^+ and Ca^{2+}/Cu^{2+} systems were measured by the batch method and a few points were checked by the column method, with satisfactory agreement. The Ca^{2+}/Mg^{2+} isotherms for both resins were measured by the column method.

From the integrated selectivity coefficients presented in Table II, the following affinity orders may be formulated: Cr > H > Cu > Ca > Mg > K > Rb > Na > Li for the PME resin and H > Ca > Mg > K > Na for the PDE resin. The Cr^{3+} ion was included in the PME affinity order since this ion could not be fully eluted from the PME resin with H^+. The H^+ ion was included in the PDE affinity order based on the highly efficient column elution by H^+ of all counterions studied on this material.

There have been a few reports in the literature concerning the selectivity characteristics of phosphorus-containing cation exchangers.[14] The high selectivity of various phosphonic and phosphoric acid exchangers for polyvalent ions[15] is particularly noteworthy. For example, phosphorus-containing resins have long been of interest as recovery systems for uranium and other metals.[16,17] The selectivity properties observed for the PME and PDE resins generally correspond to those reported for related materials. Examination of Table II reveals that the resins have a high affinity for the proton. As a consequence, most univalent and divalent counterions could be efficiently eluted from the resins with acid solutions. However, complete elution of UO_2^{2+}-, Cr^{3+}-, and La^{3+}-loaded resins could not be affected, even with treatment for 3 days with 5 M acid solutions. This behavior implies strong coordinative interactions of these polyvalent ions with the phosphate groups. Both the PME and PDE resins display an extremely high selectivity for Mg^{2+} ion over Na^+ ion (see Table II). We observed similar behavior in preliminary measurements on the Ca^{2+}/Na^+, Ca^{2+}/K^+, and Cu^{2+}/Na^+ systems as well. In addition to electrostatic effects, specific interactions of the divalent counterions with the phosphate functional groups, including ion-pair formation and covalent association, would contribute to this high selectivity. These extra stabilizing effects are expected considering the complexing ability of phosphate ion[18] and the fact that polyvalent cations tend to form insoluble phosphate salts.

The log *K* plots for the Mg^{2+}/Na^+ and H^+/Na^+ systems indicate that, as the loading of Mg^{2+} or H^+ on the resins increases, the selectivity for Mg^{2+} or H^+ increases. This behavior is unusual with respect to the common strong-acid cation exchangers.[13] A similar phenomenon in anion-exchanger systems[19] and for H^+/NH_4^+ exchange on a poly(acrylic acid) resin[20] has been observed. This increased selectivity with increased loading may be related to the marked reduction in resin water content (see Table I) and contraction in volume (≈40%) that accompanies replacement of Na^+ with either H^+ or Mg^{2+}. The resin matrix, to avoid increased constraint with increased loading, becomes even more selective for the counterion that can bind to the resin functional group with the exclusion of hydration water.

The resins exhibit small selectivities among the alkali cations, the maximum value in the integrated log *K* for the alkali–alkali systems of the PME resin being 0.12. The PME resin at low pH follows the selectivity sequence K > Rb > Na > Li, which does not correspond to the Hofmeister order.[13] The isotherm for the PDE K^+/Na^+ system displayed a selectivity reversal at $\bar{x}_K = 0.6$. Among the group 2 cations, both the PME and PDE resins are distinctly more selective for the smaller hydrated counterion; e.g., for the PDE resin, log $K^{Ca}{}_{Mg} = 0.42$.

The relative preference of the PME resin for K^+ and Na^+ differs at pH ≈ 5.5 compared to pH ≈ 12. Consistent with the previous studies on other phosphorus-containing materials,[21] the PME resin acts as a monofunctional strong-acid exchanger under slightly acidic conditions with log $K^K{}_{Na} = 0.12$. Under basic conditions, the overall selectivity is altered by activation of the weak-acid exchange sites, giving log $K^K{}_{Na} = -0.20$.

Electrical Conductances. The specific electrical conductances for the H^+, Na^+, Ca^{2+}, and Cu^{2+} forms of the

Table III
Resin Specific Electrical Conductances (30 °C)

ionic form	specific conductance,[a] Ω^{-1} cm^{-1} × 10^3		
	PME resin	PDE resin	λ[b]
H^+	2.7	1.3	349.8
Na^+	5.0	3.5	50.1
Ca^{2+}	0.21	0.46	59.5
Cu^{2+}	0.16	0.24	53.6

[a] Determined from isoconductance-point values for packed beds. Uncertainties ±1 in the last digit. [b] Equivalent ionic conductances at 25 °C in aqueous solution (cm^2 Ω^{-1} equiv^{-1}).[25]

Table IV
Conductance Ratios (30 °C)

counterion pair M2/M1	(conductance of M2)/(conductance of M1)			log $K^{M2}{}_{M1}$ (PME resin)[b]
	PME resin[a]	PDE resin[a]	aqueous cations[a]	
H^+/Na^+	0.55	0.37	6.98	0.98
H^+/Ca^{2+}	12.9	2.76	5.88	
H^+/Cu^{2+}	17.3	5.29	6.48	0.20
Na^+/Ca^{2+}	23.7	7.50	0.84	−1.23
Na^+/Cu^{2+}	31.7	14.4	0.93	−1.76
Ca^{2+}/Cu^{2+}	1.34	1.92	1.10	−0.93

[a] Based on data from Table III. [b] Logarithm of selectivity coefficient for PME resin. Values from Table II, except for the Na^+/Ca^{2+} and Na^+/Cu^{2+} systems, which were calculated by the triangle rule (ref 13, p 185).

resins are listed in Table III, along with the equivalent ionic conductances for the corresponding aqueous cations. Conductance ratios for pairs of resin ionic forms and for the corresponding pairs of aqueous cations are shown in Table IV along with the selectivity coefficients for the relevant counterion pairs. The patterns evident in these data are in agreement with the resins' selectivity, water content, and infrared spectral characteristics.[2] For instance, the H^+/Na^+ conductance ratios are much lower for both resins than the ratio for the aqueous ions, consistent with the high H^+/Na^+ selectivity coefficients, the considerably higher water contents of the Na^+ forms relative to the H^+ forms, and the covalent bonding in the H^+ forms vs. the ionic bonding in the Na^+ forms reflected in the IR spectra.[2]

Comparisons between the PME and PDE resins for the H^+/Ca^{2+}, H^+/Cu^{2+}, Na^+/Ca^{2+}, and Na^+/Cu^{2+} systems reveal that Cu^{2+} is less mobile, i.e., is more tightly bound, than Ca^{2+} in both resins. However, the significantly higher conductance ratios for the PME systems show that Cu^{2+} and, to a lesser extent, Ca^{2+} interact especially strongly with the dibasic phosphate groups. For both the Ca^{2+} and Cu^{2+} forms of the PME resin, the specific conductances are significantly lower than for the PDE forms. Considering that the PME resin contains almost twice as many counterions per unit volume as the PDE resin and hence should display higher conductances, these low values further support complex formation between a divalent counterion and a single PME functional group. Electroneutrality requirements may hinder such strong binding to the monobasic functional groups of the PDE resin. Ideas concerning counterion binding based on resin conductance data have been discussed for other ion-exchanger systems.[22-24]

Summary. The water contents, selectivities, and electrical conductances of the phosphate resins provide a consistent model for counterion interactions. The alkali counterions give the highest water contents, lowest selectivities, and highest electrical conductances, characteristic of simple electrostatic interactions with the ionogenic groups. Highly hydrated counterions cause increased swelling pressures within the resin pores and lead to low selectivities. The low water contents of the multivalent counterion forms, the high selectivities, and the low electrical conductances imply strongly associative interactions, e.g., ion-pair formation or complexation, with the phosphate groups.

Acknowledgment. This work was supported in part by a PSC–BHE grant from the Faculty Research Award Program of the City University of New York.

Registry No. H_2O, 7732-18-5; Li^+, 7439-93-2; Na^+, 7440-23-5; K^+, 7440-09-7; Rb^+, 7440-17-7; Mg^{2+}, 7439-95-4; Ca^{2+}, 7440-70-2; Cu^{2+}, 7440-50-8.

References and Notes

(1) Selzer, R. B.; Howery, D. G. *Macromolecules* **1986**, *19*, 2673.
(2) Selzer, R. B.; Howery, D. G. *Can. J. Chem.*, submitted for publication.
(3) Ling, G. N. *A Physical Theory of the Living State*; Blaisdell: New York, 1962.
(4) Damadian, R. *Ann. N.Y. Acad. Sci.* **1973**, *204*, 211.
(5) Pepper, K. W.; Reichenberg, D.; Hale, D. K. *J. Chem. Soc.* **1952**, 3129.
(6) Cosgrove, J. D.; Strickland, J. D. H. *J. Chem. Soc.* **1954**, 1845.
(7) Equation 4 of ref 6 is the expression for the fraction of H^+ on the resin (not in solution).
(8) Selzer, R. B. Ph.D. Thesis, City University of New York, New York, 1982.
(9) Kortum, G. F.; Bockris, J. O'M. *Textbook of Electrochemistry*; Elsevier: New York, 1951.
(10) Sauer, M. C., Jr.; Southwick, P. F.; Spiegler, K. S.; Myllie, M. R. J. *Ind. Eng. Chem.* **1955**, *47*, 2187.
(11) Howery, D. G.; Tada, S. *J. Macromol. Sci., Chem.* **1969**, *A3*, 297.
(12) Gnusin, N. P.; Merkulova, T. A.; Berezina, N. P.; Beketova, V. P. *Zavod. Lab.* **1976**, *42*, 709.
(13) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962.
(14) For example: (a) Persoz, J. *Bull. Soc. Chim. Fr.* **1964**, 511. (b) Becker, K. E.; Lindenbaum, S.; Boyd, G. E. *J. Phys. Chem.* **1966**, *70*, 3834. (c) Kennedy, J.; Marriot, J.; Wheeler, V. J. *J. Inorg. Nucl. Chem.* **1961**, *22*, 269.
(15) For example: (a) Marhol, M.; Beranova, H.; Cheng, K. L. *J. Radioanal. Chem.* **1974**, *21*, 177. (b) Kennedy, J.; Davies, R. V.; Small, H.; Robinson, B. K. *J. Appl. Chem.* **1959**, *9*, 32.
(16) Bartulin, J.; Cardenas, G.; Maturana, H. *Hydrometallurgy* **1982**, *8*, 132.
(17) Head, A. J.; Kember, N. F.; Miller, R. P.; Wells, R. A. *J. Chem. Soc.* **1958**, 3418.
(18) Van Wazer, J. R. *Phosphorus and Its Compounds*; Wiley: New York, 1958; Vol. I, pp 459, 480.
(19) Gregor, H. P. *J. Am. Chem. Soc.* **1951**, *73*, 3537.
(20) Hutschnecker, K.; Deuel, H. *Helv. Chim. Acta* **1956**, *39*, 1038.
(21) Tien, H. T. *J. Phys. Chem.* **1964**, *68*, 1021.
(22) Despic, A.; Hills, G. J. *Trans. Faraday Soc.* **1955**, *51*, 1260.
(23) Heymann, E.; O'Donnell, I. J. *J. Colloid Sci.* **1949**, *4*, 405.
(24) Kitchner, J. A. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Ed.; Butterworths: London, 1959; No. 2.
(25) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold: New York, 1958; p 172.