dienes (a), a surprisingly large five-bond coupling originates from the FC term through the transitions from the F···F antibonding σ orbitals to the corresponding bonding ones. From a valence-bond consideration, this kind of long-range coupling mechanism, called a "fragment coupling" mechanism here, is expected to appear generally in the X-Y coupling in XC≡CC≡CY and XCCCY, if the fragment X-Y in the above configuration is stable.

A more detailed examination of the angular dependence of F-F couplings would be of value and is one of the problems left unanswered in this paper. Further investigation in this respect has been completed and the results will be published subsequently.

Application of Thermodynamic Measurements of Polyelectrolyte Solutions for the Prediction of Ion-Exchange Selectivity[1a]

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Abstract: A thermodynamic calculation of the modified selectivity coefficient, K_{AC}, has been made employing the Gibbs–Donnan equation for the exchange of several trace divalent ions and trace sodium ion with macro divalent ion in cross-linked polystyrenesulfonate ion-exchange resins. Evaluation of activity coefficient ratios of the exchanging ions in the resin phase was accomplished using the Gibbs–Duhem equation and osmotic coefficients of polystyrenesulfonates. The osmotic free energy of the exchange reaction was estimated using polystyrenesulfonate osmotic coefficients and ionic partial molal volumes. Calculated modified selectivity coefficients for divalent-divalent ion exchange in general agree with experimentally determined values. Significant discrepancies were found between calculated and experimental selectivities for trace sodium–divalent ion exchange at high resin-phase concentrations. The theoretical treatment of polyelectrolytes by Manning has been used to explain this result.

Ion-exchange equilibria have been extensively studied in recent years[2a] with numerous methods proposed for the interpretation of observed ion-exchange selectivity values.[2b-15] The Donnan membrane model of the ion-exchange process has been found to be particularly useful for this purpose. Thermodynamic expressions obtained from this model lead to the relationship[12]

$$RT \ln K_A = \pi(z_2 \bar{V}_1 - z_1 \bar{V}_2) \qquad (1a)$$

where K_A is the activity product ratio at equilibrium for the ion-exchange reaction, π is the swelling pressure of the resin, $\bar{V}_1$ and $\bar{V}_2$ are the partial molal volumes of the exchanging ions within the resin phase, and z_1 and z_2 are the charges on ions 1 and 2, respectively. For a symmetrical ion-exchange reaction eq 1 can be written

$$RT \ln K_A = \pi(\bar{V}_1 - \bar{V}_2) \qquad (1b)$$

The ion-exchange reaction that occurs in the resin and solution phases when a trace divalent ion, M_1^{2+}, exchanges with a divalent ion, M_2^{2+}, may be expressed as

$$[M(ClO_4)_2]_1 + \overline{[M(ClO_4, PSS)_2]_2} \rightleftharpoons$$
$$\overline{[M(ClO_4,PSS)_2]_1} + [M(ClO_4)_2]_2 \qquad (2)$$
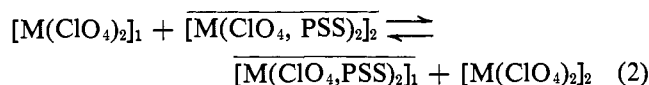
where

$$[\overline{M_2^{2+}}] = [\overline{ClO_4^-}] + [\overline{PSS^-}] \cong \overline{PSS^-}$$

neglecting trace metal ion concentration since $[\overline{PSS^-}] \gg [\overline{ClO_4^-}]$. Species within a squared bracket represent molal concentration. The bar over a symbol refers to the resin phase. The selectivity terms, distribution coefficient, K_D, selectivity coefficient, K_{EX}, and modified selectivity coefficient, K_{AC}, that are used to express the data are defined as

$$K_D = [\overline{M_1^{2+}}]/[M_1^{2+}] \qquad (3)$$

$$K_{EX} = [\overline{M_1^{2+}}][M_2^{2+}]/[M_2^{2+}] \cdot [\overline{M_2^{2+}}] \qquad (4)$$

(1) (a) Presented in part at The Symposium on the Physical and Colloid Chemistry of Ion Exchangers, during the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970. (b) Visiting Professor, Chemistry Department, McGill University, 1970–1971, Montreal, Quebec, Canada.
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$$K_{AC} = \frac{[M_1{}^{2+}][M_2{}^{2+}]}{[M_1{}^{2+}][M_2{}^{2+}]} \frac{\gamma_\pm{}^3 M_2(ClO_4)_2}{\gamma_\pm{}^3 M_1(ClO_4)_2} = K_A \frac{\bar{\gamma}_2}{\bar{\gamma}_1} \quad (5)$$

with all anion concentrations cancelling and γ representing the mean molal activity coefficient of the trace and macro salts in the two phases.

Equation 1b may be expanded with eq 4 and 5 to yield

$$K_{EX} = \frac{\bar{\gamma}_2}{\bar{\gamma}_1} \frac{\gamma_{\pm 1}{}^3}{\gamma_{\pm 2}{}^3} \exp(-\pi[\bar{V}_1 - \bar{V}_2]/RT) \quad (6)$$

for divalent–divalent ion exchange.

In the ion-exchange resin phase the term $\bar{\gamma}_\pm{}^2_{ClO_4^-}(M(ClO_4)_2)_2/\bar{\gamma}_\pm{}^2_{ClO_4}(M(ClO_4)_2)_1$ is common to both components and cancels. Since in the experimental program $\overline{PSS^-} \gg \overline{ClO_4^-}$, the effect of $\overline{ClO_4^-}$ on the chemical potential of the polyelectrolyte is negligible. The deviation from ideal behavior of the exchanging cations is then related to their single ion activity coefficients by the ratio of the mean molal activity coefficients of the pure components because

$$(\gamma_M{}^Z\gamma_P)^{1/(Z+1)} = (\gamma_M)^{Z(Z+1)}(\gamma_P)^{1/Z} = \gamma_\pm$$

and

$$\gamma_\pm \simeq \gamma_M$$

(subscripts M and P refer to counterion and polyanion, respectively) since Z, the degree of polymerization, is much greater than unity.

Solution-phase activity coefficients, solution–resin phase osmotic pressure differences, and resin-phase partial ionic molal volume differences appearing in eq 6 can be estimated from published data.[16] To predict and interpret ion-exchange selectivity coefficients, it is necessary to have a measure of the ionic activity coefficients in the ion-exchange resin phase. In the most successful application of eq 1 to ion-exchange selectivity phenomena, ion-exchange resin-phase activity coefficient ratios were evaluated by employing the Gibbs–Duhem equation with osmotic coefficients of low cross-linked ion-exchange resins, enabling prediction of ion-exchange selectivity in a number of monovalent systems.[12,13] This approach is limited by the unavailability of osmotic data at low concentrations.

Polyelectrolyte analogs of ion-exchange resins have been proposed as model systems for the thermodynamic analysis of cross-linked ion-exchange resin behavior.[16] If the polyelectrolyte analog does indeed provide a valid model for transcending their properties to those of the cross-linked exchanger, osmotic coefficient data obtained with them and used in the Gibbs–Duhem equation should allow precise calculation of ion-exchange resin phase activity coefficients. This approach to the calculation of resin-phase activity coefficients has been successfully tested.[17-19] Recently precise measurements of the osmotic coefficients of polystyrenesulfonic acid and its salts (the polyelectrolyte analog of Dowex-50 ion-exchange resin) have been reported.[17,18] These results enabled calculation of ion-exchange resin-phase activity coefficient ratios for a number of ions.

By using the Gibbs–Duhem equation

$$(d \phi/d \ln m) + (\phi - 1) = (d \ln \gamma/d \ln m) \quad (7)$$

in the integrated form

$$\ln \gamma_\pm/\gamma_{\pm ref} = \phi - \phi_{ref} + \int_{m_{ref}}^m (\phi - 1) \, d \ln m \quad (8)$$

mean activity coefficients relative to a reference state were computed.[19] This permitted calculation of ion-exchange selectivity coefficients for several hydrogen-divalent ion-exchange reactions in good agreement with experimental values.[19]

In this paper the utility of this approach has been tested further. For this purpose ion-exchange resin-phase activity coefficient ratios were calculated from polyelectrolyte osmotic coefficient data by employing eq 8; the ion-exchange selectivity coefficient for several divalent–divalent and divalent–sodium ion exchange reactions using eq 6 and available polyelectrolyte data were computed and comparisons of the calculated coefficients with values arrived at experimentally were made. Experimental and calculated ion-exchange selectivity coefficients were determined for distributions of trace Ca^{2+}, Sr^{2+}, Co^{2+}, Cd^{2+}, and Na^+ ions between dilute aqueous divalent perchlorate solutions and a series of cross-linked (with divinylbenzene) polystyrenesulfonate ion-exchange resins in several divalent forms.

Experimental Section

Materials. Distilled, deionized water was used in all experiments. Reagent grade divalent metal perchlorate salts (purchased from the G. F. Smith Co., Columbus, Ohio) and Dowex-50 Bio-Rad AG cation exchange resins with 1–16% divinylbenzene cross linking (purchased from the Bio-Rad Laboratories, Richmond, California) were employed in all selectivity measurements. Trace metal ion concentrations were monitored using radionuclides purchased from Nuclear Science and Engineering Co., Pittsburgh, Pa., and the Oak Ridge National Laboratory, Oak Ridge, Tenn. γ activity measurements were carried out for solutions containing ^{22}Na and ^{60}Co radioisotopes with a Packard automatic γ counter. Assays of solutions containing ^{45}Ca, ^{90}Sr, and ^{109}Cd radionuclides were made with a liquid scintillation counting procedure,[20] the measurements being determined with a Packard tricarb liquid scintillation spectrometer. Reagent grade toluene and Packard scintillation grade PPO, POPOP, and Triton-X were used to prepare the liquid scintillation solution.

Procedure. Ion-exchange resin equivalent capacity was measured using an isotope dilution method. Ion-exchange resin-phase equilibrium water contents were determined using a centrifugation procedure.[21] Resin-phase concentrations were expressed on a molal basis. Table I contains the resin-phase parameters determined for the resin ionic forms at the various cross linkings employed in this study. Batch distribution experiments were used to obtain the experimental ion-exchange selectivity coefficients.[22,23] Ionic distribution experiments were carried out for 3 days with ion-exchange resin and labeled solution in sealed polyethylene bottles placed on a shaking platform maintained at 25°. At equilibrium the solution was separated from the resin–solution mixture using a Millipore filter with accurately measured aliquot portions of the filtered solution then being placed into vials for activity measurement.

Results

Tables II–V present experimental distribution, selectivity, and modified selectivity coefficients for several trace ions with zinc, cadmium, calcium, and strontium

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Table I. Ion-Exchange Resin Parameters

(1) Calcium Form Ion-Exchange Resin

% DVB	1	2	4	8	12	16
Ca^{2+} (mm)/dry CaR (g)	2.45	2.29	2.27	2.19	2.15	2.07
H_2O (g)/dry CaR (g)	2.04	1.45	1.03	0.716	0.570	0.542
Resin molality	1.20	1.57	2.20	3.05	3.77	3.81

(2) Strontium Form Ion-Exchange Resin

% DVB	1	2	4	8	12	16
Sr^{2+} (mm)/dry SrR (g)	2.33	2.11	2.07	2.04	1.98	1.97
H_2O (g)/dry SrR (g)	1.57	1.20	0.891	0.638	0.482	0.448
Resin molality	1.42	1.76	2.32	3.20	4.11	4.40

(3) Zinc Form Ion-Exchange Resin

% DVB	1	2	4	8	12	16
Zn^{2+} (mm)/dry ZnR (g)	2.37	2.25	2.21	2.11	2.08	2.00
H_2O (g)/dry ZnR (g)	2.36	1.64	1.16	0.820	0.645	0.599
Resin molality	1.00	1.37	1.91	2.58	3.23	3.35

(4) Cadmium Form Ion-Exchange Resin

% DVB	1	2	4	8	12	16
Cd^{2+} (mm)/dry CdR (g)	2.14	1.99	1.96	1.95	1.94	1.86
H_2O (g)/dry CdR (g)	2.09	1.43	1.03	0.686	0.586	0.531
Resin molality	1.02	1.39	1.90	2.84	3.31	3.50

Table II. Selectivity Terms for Trace Na^+, Co^{2+}, Cd^{2+}, and Sr^{2+} Exchange with Calcium Form Ion-Exchange Resin in 0.1000 m Calcium Perchlorate

		1	2	4	8	12	16
				% DVB			
K_D	Na^+	2.43	2.76	3.06	3.60	4.25	4.31
	Co^{2+}	9.02	11.3	13.8	15.9	15.6	13.0
	Cd^{2+}	9.12	11.5	13.7	17.2	21.2	20.8
	Sr^{2+}	18.7	28.2	37.8	56.5	70.5	20.0
K_{EX}	Na^+	0.491	0.482	0.424	0.423	0.478	0.486
	Co^{2+}	0.751	0.715	0.626	0.519	0.413	0.340
	Cd^{2+}	0.764	0.728	0.621	0.562	0.561	0.545
	Sr^{2+}	1.56	1.78	1.72	1.84	1.87	1.83
K_{AC}	Na^+	0.352	0.345	0.304	0.303	0.342	0.348
	Co^{2+}	0.668	0.636	0.557	0.462	0.373	0.303
	Cd^{2+}	0.720	0.687	0.586	0.530	0.529	0.514
	Sr^{2+}	1.83	2.09	2.02	2.16	2.19	2.15

Table III. Selectivity Terms for Trace Na^+, Co^{2+}, Cd^{2+}, and Ca^{2+} Exchange with Strontium Form Ion-Exchange Resin in 0.1000 m Strontium Perchlorate

		1	2	4	8	12	16
				% DVB			
K_D	Na^+	2.78	2.97	3.76	4.26	5.14	5.58
	Co^{2+}	8.04	8.58	10.9	6.3	2.9	2.6
	Cd^{2+}	8.51	9.70	12.4	14.1	0.93	1.3
	Ca^{2+}	10.0	11.5	16.1	19.5	23.9	26.3
K_{EX}	Na^+	0.544	0.502	0.609	0.567	0.643	0.708
	Co^{2+}	0.566	0.488	0.469	0.197	0.071	0.059
	Cd^{2+}	0.599	0.552	0.534	0.440	0.02	0.03
	Ca^{2+}	0.704	0.654	0.693	0.609	0.581	0.598
K_{AC}	Na^+	0.331	0.305	0.371	0.345	0.391	0.431
	Co^{2+}	0.492	0.369	0.355	0.149	0.05	0.04
	Cd^{2+}	0.481	0.443	0.429	0.353	0.02	0.02
	Ca^{2+}	0.603	0.560	0.594	0.522	0.498	0.512

Table IV. Selectivity Terms for Trace Na^+, Co^{2+}, Cd^{2+}, and Sr^{2+} Exchange with Zinc Form Ion-Exchange Resin in 0.1000 m Zinc Perchlorate

		1	2	4	8	12	16
				% DVB			
K_D	Na^+	1.35	3.13	3.59	5.66	7.65	9.20
	Co^{2+}	12.1	14.8	21.1	28.8	36.3	36.5
	Cd^{2+}	10.3	15.6	22.2	36.7	58.2	74.7
	Sr^{2+}	28.4	41.3	67.6	125.0	230.0	371.0
K_{EX}	Na^+	0.18	0.714	0.676	1.24	1.81	2.53
	Co^{2+}	1.20	1.08	1.11	1.11	1.13	1.09
	Cd^{2+}	1.03	1.14	1.16	1.42	1.80	2.24
	Sr^{2+}	2.83	3.01	3.59	4.85	7.13	11.1
K_{AC}	Na^+	0.499	0.542	0.513	0.941	1.37	1.92
	Co^{2+}	1.13	1.02	1.05	1.05	1.07	1.03
	Cd^{2+}	1.03	1.14	1.16	1.42	1.80	2.24
	Sr^{2+}	3.52	3.75	4.41	6.04	8.87	13.8

Table V. Selectivity Terms for Trace Na^+, Co^{2+}, Ca^{2+}, and Sr^{2+} Exchange with Cadmium Form Ion-Exchange Resin in 0.1000 m Cadmium Perchlorate

		1	2	4	8	12	16
				% DVB			
K_D	Na^+	2.25	2.31	3.13	3.76	4.65	6.90
	Co^{2+}	9.52	12.8	17.0	21.1	23.0	21.6
	Ca^{2+}	12.1	17.6	26.1	42.4	62.4	74.6
	Sr^{2+}	21.9	33.5	55.3	89.6	132.0	178.0
K_{EX}	Na^+	0.494	0.383	0.514	0.497	0.653	0.896
	Co^{2+}	0.930	0.920	0.893	0.742	0.695	0.406
	Ca^{2+}	1.18	1.26	1.37	1.49	1.88	1.40
	Sr^{2+}	2.14	2.41	2.91	3.15	3.99	3.35
K_{AC}	Na^+	0.375	0.291	0.390	0.377	0.496	0.680
	Co^{2+}	0.878	0.868	0.843	0.700	0.656	0.383
	Ca^{2+}	1.25	1.37	1.45	1.58	1.99	1.48
	Sr^{2+}	2.66	3.00	3.62	3.92	4.96	4.17

form ion-exchange resins. The mean molal activity coefficients for the simple salts have been taken from the literature.[24,25]

The modified selectivity coefficient has been expressed as a function of the activity coefficients of the exchanging ions in the resin phase and the pressure–volume work of the exchange reaction by dividing both sides of

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eq 2 by the mean molal activity coefficient ratio term for the two salts in the aqueous phase. Evaluation of $\bar{\gamma}_2/\bar{\gamma}_1$ and $\pi(\Delta V)$ permitted computation of K_{AC} for comparison with the experimentally determined values. The pressure–volume work contribution to the observed modified selectivity was calculated from estimates of the resin-phase swelling pressure (π) and the partial molal volume difference of the exchanging ions in the resin phase (ΔV). Resin-phase swelling pressures were calculated from the osmotic coefficient data for the polystyrenesulfonate salts.[15] Partial molal volumes of the ions in the resin phase were taken as the partial molal volumes of the ions in aqueous solution at infinite dilution.[26] In most instances the calculated pressure–volume work of the exchange reaction made only a slight contribution to the calculated modified ion-exchange selectivity.

Resin-phase activity coefficients for the exchanging ions were determined by integration of the Gibbs–Duhem equation (eq 8) employing osmotic coefficients of polystyrenesulfonate salts from a reference concentration of 0.01 m[27] to the concentration of the resin phase. The integration was performed graphically using a polar planimeter. This integration gives, $\bar{\gamma}_m/\bar{\gamma}_{m_{ref}}$, the resin-phase activity coefficient at the concentration of the ion-exchanger divided by the activity coefficient at the reference concentration. To use this result for the selectivity calculation it is necessary to determine the reference state activity coefficient

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Table VI. Computation of the Modified Selectivity Coefficient for Trace Divalent Ion Exchange with Calcium Form Ion Exchange Resin in 0.1000 m Calcium Perchlorate

$$K_{AC} = (\bar{\gamma}_{Ca^{2+}}/\bar{\gamma}_T) \exp(-\pi[V_T - V_{Ca^{2+}}]/RT)$$

% DVB	Resin molality	Trace ion M^{2+}	$\dfrac{\bar{\gamma}_{Ca}/\bar{\gamma}_{Ca_{ref}}}{\bar{\gamma}_{M^{2+}}/\bar{\gamma}_{M^{2+}_{ref}}}$	π, atm	ΔV, ml	$e^{-\pi\Delta V/RT}$	K_{AC} (calcd)	K_{AC} (obsd)[a]
1	1.196	Co²⁺	0.72	10.6	−6.9	1.00	0.72	0.668
		Cd²⁺	0.81	10.6	−2.9	1.00	0.81	0.72
		Sr²⁺	1.21	10.6	−0.5	1.00	1.21	1.83 (±3.5)
2	1.581	Co²⁺	0.58	20.9	−6.9	1.01	0.58	0.636 (±2.5)
		Cd²⁺	0.69	20.9	−2.9	1.00	0.69	0.687
		Sr²⁺	1.29	20.9	−0.5	1.00	1.29	2.09
4	2.201	Co²⁺	0.41	48.1	−6.9	1.01	0.41	0.557 (±6.5)
		Cd²⁺	0.56	48.1	−2.9	1.01	0.56	0.586 [±3.7)
		Sr²⁺	1.52	48.1	−0.5	1.00	1.52	2.02
8	3.053	Co²⁺	0.19	106.0	−6.9	1.03	0.20	0.462 (±8)
		Cd²⁺	0.40	106.0	−2.9	1.01	0.41	0.530
		Sr²⁺	1.94	106.0	−0.5	1.00	1.94	2.16 (±5)
12	3.77	Co²⁺	0.10	164.0	−6.9	1.05	0.10	0.373
		Cd²⁺	0.29	164.0	−2.9	1.02	0.30	0.529
		Sr²⁺	2.20	164.0	−0.5	1.00	2.20	2.19 (±3.5)
16	3.81	Co²⁺	0.10	167.5	−6.9	1.05	0.11	0.303
		Cd²⁺	0.31	167.5	−2.9	1.02	0.31	0.514
		Sr²⁺	2.38	167.5	−0.5	1.00	2.38	2.15

[a] Discrepancy between duplicate measurements was within ±2% of the averaged value except where noted.

Table VII. Computation of the Modified Selectivity Coefficient for Trace Divalent Ion Exchange with Strontium Form Ion Exchange Resin in 0.1000 m Strontium Perchlorate

$$K_{AC} = (\bar{\gamma}_{Sr^{2+}}/\bar{\gamma}_T) \exp(-\pi[V_T - V_{Sr^{2+}}]/RT)$$

% DVB	Resin molality	Trace ion M^{2+}	$\dfrac{\bar{\gamma}_{Sr}/\bar{\gamma}_{Sr_{ref}}}{\bar{\gamma}_{M^{2+}}/\bar{\gamma}_{M^{2+}_{ref}}}$	π, atm	ΔV, ml	$e^{-\pi\Delta V/RT}$	K_{AC} (calcd)	K_{AC} (obsd)[a]
1	1.42	Co²⁺	0.52	11.15	−6.4	1.00	0.52	0.429
		Cd²⁺	0.57	11.15	−2.4	1.00	0.57	0.481
		Ca²⁺	0.79	11.15	+0.5	1.00	0.79	0.603
2	1.76	Co²⁺	0.39	20.1	−6.4	1.01	0.40	0.369
		Cd²⁺	0.48	20.1	−2.4	1.00	0.48	0.443 (±3)
		Ca²⁺	0.75	20.1	+0.5	1.00	0.75	0.560
4	2.32	Co²⁺	0.24	40.5	−6.4	1.01	0.24	0.355
		Cd²⁺	0.34	40.5	−2.4	1.00	0.34	0.40 (±25)
		Ca²⁺	0.63	40.5	+0.5	1.00	0.63	0.594 (±2.5)
8	3.20	Co²⁺	0.083	86.0	−6.4	1.02	0.083	0.20 (±27)
		Cd²⁺	0.19	86.0	−2.4	1.01	0.19	0.353
		Ca²⁺	0.50	86.0	+0.5	1.00	0.50	0.522
12	4.11	Co²⁺	0.040	150.0	−6.4	1.04	0.041	0.10 (±50)
		Cd²⁺	0.11	150.0	−2.4	1.01	0.11	0.018 (±2.3)
		Ca²⁺	0.43	150.0	+0.5	1.00	0.43	0.498
16	4.40	Co²⁺		175.0	−6.4	1.05		0.045 (±7)
		Cd²⁺	0.11	175.0	−2.4	1.02	0.11	0.024 (±5)
		Ca²⁺	0.42	175.0	+0.5	1.00	0.42	0.512

[a] Discrepancy between duplicate measurements was within ±2% of the averaged value except where noted.

ratio. The reference state activity coefficient ratio for the exchanging ions can be obtained from the activity coefficient ratio calculated using the Gibbs–Duhem equation and the experimental ion-exchange selectivity determined for a 1% cross-linked ion-exchange resin. In practice it is found that for the reference concentration employed in this study the reference state activity coefficient ratio for the exchanging pair of divalent ions is very close to unity and it was possible to predict selectivity without resort to this normalization procedure. Only in the case of unsymmetrical ion exchange[19] was it necessary to compute the reference state activity coefficient ratio.

Tables VI–IX show the calculated resin-phase activity coefficient ratios, the osmotic free energy of the exchange reaction, and modified selectivity coefficients for the exchange of divalent ion at tracer-level concentrations with ion-exchange resins in the calcium-,

strontium-, zinc-, and cadmium-ion forms. Table X provides similar information for the exchange of Na ion at tracer-level concentration with these divalent ion-exchange resin forms. The reference state activity coefficient ratios for trace sodium-ion exchange with calcium, strontium, zinc, and cadmium are an additional entry in Table X.

Error limits of the resin-phase activity coefficient ratios are determined by the uncertainties in the polystyrenesulfonate osmotic coefficients employed for the integration of the Gibbs–Duhem equation. The polystyrenesulfonate osmotic coefficient at the reference concentration has a maximum uncertainty of 10% for divalent polystyrenesulfonates while, in general, the uncertainty of the osmotic data is 3%. These error limits indicate that the calculated resin-phase activity coefficient ratios have a maximum uncertainty of 10%. The precision of the experimentally determined modi-

Table VIII. Computation of the Modified Selectivity Coefficient for Trace Divalent Ion Exchange with Zinc Form Ion-Exchange Resin in 0.1000 m Zinc Perchlorate

$$K_{AC} = (\bar{\gamma}_{Zn}/\gamma_T) \exp(-\pi[V_T - V_{Zn^{2+}}]/RT)$$

% DVB	Resin molality	Trace ion M²⁺	$\dfrac{\bar{\gamma}_{Zn}/\bar{\gamma}_{Zn\,ref}}{\bar{\gamma}_{M^{2+}}/\bar{\gamma}_{M^{2+}_{ref}}}$	π, atm	ΔV, ml	$e^{-\pi\Delta V/RT}$	K_{AC} (calcd)	K_{AC} (obsd)[a]
1	1.003	Sr²⁺	1.44	10.6	+3.9	1.00	1.44	3.52
		Cd²⁺	1.07	10.6	+1.5	1.00	1.07	1.03 (±9)
		Co²⁺	1.00	10.6	−2.5	1.00	1.00	1.13 (±3.5)
2	1.37	Sr²⁺	1.82	24.3	+3.9	1.00	1.82	3.75
		Cd²⁺	1.16	24.3	+1.5	1.00	1.16	1.14
		Co²⁺	1.00	24.3	−2.5	1.00	1.00	1.02
4	1.911	Sr²⁺	2.71	56.5	+3.9	0.99	2.68	4.41
		Cd²⁺	1.26	56.5	+1.5	1.00	1.26	1.16 (±6.7)
		Co²⁺	1.00	56.5	−2.5	1.00	1.00	1.01
8	2.581	Sr²⁺	6.06	114.0	+3.9	0.98	5.94	6.04
		Cd²⁺	1.75	114.0	+1.5	1.00	1.75	1.42
		Co²⁺	1.00	114.0	−2.5	1.01	1.01	1.05
12	3.23	Sr²⁺	12.4	208.0	+3.9	0.97	12.0	8.82
		Cd²⁺	2.30	208.0	+1.5	0.99	2.28	1.80
		Co²⁺	1.00	208.0	−2.5	1.02	1.02	1.07
16	3.35	Sr²⁺	14.4	275.0	+3.9	0.96	13.8	13.8 (±6)
		Cd²⁺	2.45	275.0	+1.5	0.98	2.40	2.24
		Co²⁺	1.00	275.0	−2.5	1.03	1.03	1.03

[a] Discrepancy between duplicate measurements was within ±2% of averaged value except where noted.

fied selectivity coefficient is better than 2% except where noted in the tables.

The calculated and the observed modified selectivities, for divalent–divalent exchange (columns 8 and 9 of Tables VI–IX), are in reasonable agreement. Indeed a sizable fraction of the calculated ion-exchange selectivity coefficients are identical with the observed values within experimental error. The calculated selectivity trend with increased cross linking is, however, exaggerated. In those instances where good agreement between experiment and computation is obtained at low cross linking, the computed value is usually lower than the experimental value in the higher cross-linking situations. Where the computed selectivity coefficient value is significantly lower than the experimental value at the lower cross linking, there is usually good agreement between prediction and observation at the highest cross linkings. This divergent trend between computation and experiment, clearly demonstrated by representative data selected for this purpose (Figure 1), is essentially similar to that observed in our earlier study of hydrogen–ion exchange with trace amounts of divalent ion,[19] except that the normalization procedure used to facilitate correlative analysis of the unsymmetrical exchange system (2H⁺, M²⁺ and 2Na⁺, M²⁺) was unnecessary.

The correlation between the computed and experimentally observed K_{AC} values for the Na⁺–M(II) systems (Table X) is significantly poorer than that obtained with the divalent–divalent ion exchange and the previously examined H⁺–M(II) ion-exchange systems.[19] For these exchanges the calculated modified selectivity coefficients, while still exhibiting the same characteristic trends as the experimental values, diverge much more rapidly from the experimental values as the cross linking of the resin becomes larger.

Discussion

Osmotic coefficient values of the trace ion selected for employment in the Gibbs–Duhem equation were those for this ion form of the polyelectrolyte at a concentration equal to the macroion concentration in the

resin during an exchange experiment. Use of this approach assumes that the osmotic properties of the trace ion form of the polyelectrolyte are undisturbed by the
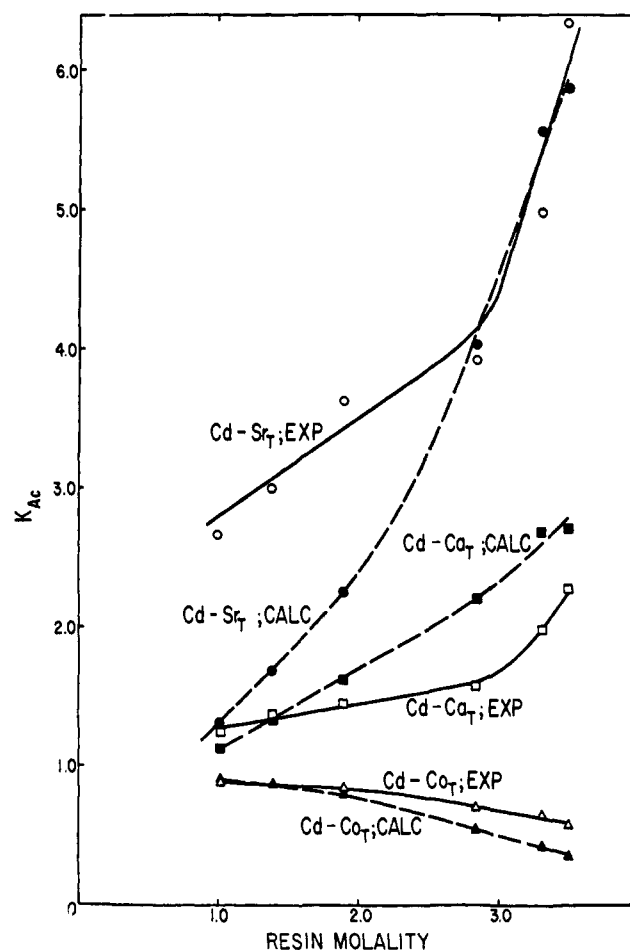

Figure 1. Comparison of calculated (calc) and experimental (exp) modified selectivity coefficients for trace calcium, strontium, and cobalt exchanges on cadmium form ion-exchange resin.

presence of the other ion. Differences between calculated and experimental ion-exchange selectivities may

Table IX. Computation of the Modified Selectivity Coefficient for Trace Divalent Ion Exchange with Cadmium Form Ion-Exchange Resin in 0.1000 m Cadmium Perchlorate

$$K_{AC} = (\bar{\gamma}_{Cd^{2+}}/\gamma_T) \exp(-\pi[V_T - V_{Cd^{2+}}]/RT)$$

% DVB	Resin molality	Trace ion M²⁺	$\dfrac{\bar{\gamma}_{Cd}/\bar{\gamma}_{Cd_{ref}}}{\bar{\gamma}_{M^{2+}}/\bar{\gamma}_{M^{2+}ref}}$	π, atm	ΔV, ml	$e^{-\pi\Delta V/RT}$	K_{AC} (calcd)	K_{AC} (obsd)[a]
1	1.02	Co²⁺	0.91	9.55	−4.0	1.00	0.91	0.878
		Ca²⁺	1.13	9.55	+2.9	1.00	1.13	1.25
		Sr²⁺	1.31	9.55	+2.4	1.00	1.31	2.66
2	1.39	Co²⁺	0.87	21.6	−4.0	1.00	0.87	0.868
		Ca²⁺	1.34	21.6	+2.9	0.99	1.34	1.37
		Sr²⁺	1.68	21.6	+2.4	0.99	1.68	3.00
4	1.90	Co²⁺	0.79	45.4	−4.0	1.01	0.80	0.843
		Ca²⁺	1.63	45.4	+2.9	0.99	1.62	1.45
		Sr²⁺	2.26	45.4	+2.4	0.99	2.25	3.62 (±2.5)
8	2.84	Co²⁺	0.54	118.0	−4.0	1.02	0.55	0.700
		Ca²⁺	2.22	118.0	+2.9	0.98	2.20	1.58
		Sr²⁺	4.08	118.0	+2.4	0.98	4.03	3.92
12	3.31	Co²⁺	0.42	167.0	−4.0	1.03	0.43	0.654
		Ca²⁺	2.74	167.0	+2.9	0.98	2.69	1.99
		Sr²⁺	5.65	167.0	+2.4	0.98	5.56	4.98
16	3.50	Co²⁺	0.35	189.4	−4.0	1.03	0.36	0.582 (±7)
		Ca²⁺	2.77	189.4	+2.9	0.98	2.71	2.28
		Sr²⁺	5.97	189.4	+2.4	0.98	5.86	6.34

[a] Discrepancy between duplicate measurements was within ±2% of the averaged value except where noted.

Table X. Computation of the Modified Selectivity Coefficient for Trace Sodium Ion Exchange with Various Divalent Ion Form Ion-Exchange Resins in 0.1000 m Divalent Perchlorate

$$K_{AC} = (\gamma_M/\gamma_{Na}^2) \exp(-\pi[2V_{Na} - V_m]/RT)$$

% DVB	Resin molality	Divalent resin form	$\dfrac{\bar{\gamma}_{M^{2+}}/\bar{\gamma}_{M^{2+}ref}}{(\bar{\gamma}_{Na^+}/\bar{\gamma}_{Na^+re})^2}$	$\dfrac{\bar{\gamma}_{M^{2+}ref}}{\bar{\gamma}_{Naref}^2}$	π, atm	ΔV, ml	$e^{-\pi\Delta V/RT}$	K_{AC} (calcd)	K_{AC} (obsd)[a]
1	1.00	Zn²⁺	6.20	0.0811	10.6	+19.1	0.992	0.499	0.499 (±3.7)
	1.02	Cd²⁺	5.73	0.0659	9.55	+17.6	0.993	0.375	0.375
	1.20	Ca²⁺	5.32	0.0665	10.6	+14.7	0.994	0.352	0.352
	1.42	Sr²⁺	4.61	0.0723	11.15	+15.2	0.993	0.331	0.331 (±2.9)
2	1.37	Zn²⁺	8.65	0.0811	24.3	+19.1	0.981	0.73	0.54
	1.39	Cd²⁺	7.73	0.0659	21.6	+17.6	0.985	0.50	0.291 (±3.9)
	1.57	Ca²⁺	6.18	0.0665	20.9	+14.7	0.988	0.45	0.345
	1.76	Sr²⁺	5.11	0.0723	20.1	+15.2	0.988	0.37	0.305
4	1.91	Zn²⁺	15.5	0.0811	56.5	+19.1	0.958	1.29	0.54 (±8.0)
	1.90	Cd²⁺	12.1	0.0659	45.4	+17.6	0.968	0.78	0.390 (±5.4)
	2.20	Ca²⁺	9.16	0.0665	48.1	+14.7	0.971	0.66	0.304
	2.32	Sr²⁺	6.20	0.0723	40.5	+15.2	0.975	0.45	0.371
8	2.58	Zn²⁺	42.2	0.0811	114.0	+19.1	0.914	2.78	0.94
	2.84	Cd²⁺	31.1	0.0659	118.0	+17.6	0.919	1.84	0.377 (±3.4)
	3.05	Ca²⁺	15.5	0.0665	106.0	+14.7	0.938	1.02	0.303 (±5.5)
	3.20	Sr²⁺	8.3	0.0723	86.0	+15.2	0.948	0.57	0.345
12	3.23	Zn²⁺	102.0	0.0811	208.0	+19.1	0.85	7.04	1.37
	3.31	Cd²⁺	47.0	0.0659	167.0	+17.6	0.887	2.74	0.496 (±3.2)
	3.77	Ca²⁺	27.5	0.0665	164.0	+14.7	0.906	1.48	0.342
	4.11	Sr²⁺	14.9	0.0723	150.0	+15.2	0.911	0.69	0.391 (±3.0)
16	3.35	Zn²⁺	120.0	0.0811	275.0	+19.1	0.807	8.18	1.92 (±6.5)
	3.50	Cd²⁺	50.8	0.0659	189.4	+17.6	0.869	3.19	0.680 (±4.0)
	3.81	Ca²⁺	27.8	0.0665	167.5	+14.7	0.904	1.49	0.348
	4.40	Sr²⁺	14.6	0.0723	175.0	+15.2	0.897	0.66	0.431

[a] Discrepancy between duplicate measurements was within ±2% of averaged value except where noted.

be due to neglect of changes in the osmotic properties of the trace ion going from the pure salt form to the trace-ion form, at a fixed total polyelectrolyte concentration. The discrepancy between calculated and experimental ion-exchange selectivities is not large (with the exception of the M^{2+}–Na^+_T system) suggesting that neglect of interaction effects on the osmotic properties of the trace ion is a useful approximation.

The sizable and rapidly increasing divergence between predicted and experimental modified selectivity coefficients with resin cross linking that was obtained for the M^{2+}–Na^+_T systems is a surprising result. In our earlier research of the analogous unsymmetrical ion-

exchange reaction between resin in the univalent hydrogen-ion form and various divalent ions at tracer-level concentrations predictions were in as good agreement with experiment[19] as with the symmetrical divalent-divalent ion-exchange system. Selectivity prediction for the M^{2+}–Na^+_T exchange reaction as a consequence was expected to correlate with the experimental K_{AC} values as well.

A possible explanation to this apparent anomaly may come from the theoretical treatment of polyelectrolytes by Manning.[28] He has shown that there is theoretical

(28) G. S. Manning, *J. Chem. Phys.*, **51**, 924, 3249 (1969).

Table XI. Revised Computation of Modified Selectivity Coefficient for Trace Sodium Ion Exchange with Various Divalent Ion Forms of Ion-Exchange Resin in 0.1000 m Divalent Perchlorate

% DVB	Divalent resin form	$\dfrac{\bar{\gamma}_{M}{}^{+2}{}_{ref}}{\bar{\gamma}_{(Na}{}^{+}{}_{ref)}{}^{2}}$	K_{AC} (calcd)	K_{AC} (obsd)
1	Zn^{2+}	6.69	0.499	0.499
	Cd^{2+}	5.44	0.375	0.375
	Ca^{2+}	6.11	0.352	0.352
	Sr^{2+}	7.86	0.331	0.331
2	Zn^{2+}	6.69	0.55	0.54
	Cd^{2+}	5.44	0.39	0.291
	Ca^{2+}	6.11	0.31	0.345
	Sr^{2+}	7.86	0.29	0.305
4	Zn^{2+}	6.69	0.66	0.51
	Cd^{2+}	5.44	0.43	0.39
	Ca^{2+}	6.11	0.30	0.304
	Sr^{2+}	7.86	0.27	0.371
8	Zn^{2+}	6.69	1.19	0.94
	Cd^{2+}	5.44	0.64	0.377
	Ca^{2+}	6.11	0.34	0.303
	Sr^{2+}	7.86	0.23	0.345
12	Zn^{2+}	6.69	2.21	1.37
	Cd^{2+}	5.44	0.84	0.496
	Ca^{2+}	6.11	0.36	0.342
	Sr^{2+}	7.86	0.20	0.391
16	Zn^{2+}	6.69	2.35	1.92
	Cd^{2+}	5.44	0.87	0.68
	Ca^{2+}	6.11	0.35	0.348
	Sr^{2+}	7.86	0.18	0.431

justification for expecting "condensation" of counterions on a polyion only until the charge density is reduced below a certain critical value. When a fully dissociated polyelectrolyte or cross-linked gel is essentially in a divalent ion form, as in this phase of the research program that is discussed here, its charge density is lower than this critical limiting value for "condensation" of trace univalent ion and no ion binding of the univalent ion by the polyion matrix can be expected to occur. In his treatment the uncondensed mobile ions are treated in the Debye-Hückel approximation and the predicted mean molal activity coefficient reflects a combination of this binding and the effect of Debye-Hückel interactions on the "uncondensed" counterions.

To examine this possibility we have used Manning's "limiting law" expression to evaluate the osmotic coefficient of the trace univalent ion when the charge density, $e^2/\epsilon kTb$ (ξ) (where e is the charge of the proton, ϵ is the macroscopic dielectric constant of water, b is the distance between neighboring charged groups of the polyion, and kT has its characteristic meaning), is equal to $1/2$ as a consequence of the saturation condensation of divalent ions in the ion-exchange systems studied. With this analysis $\phi_p = 1 - 1/2\xi = 0.75$. By presuming that the "uncondensed" univalent ions will behave in the same way as the fraction of "uncon-

densed" ions in the pure univalent ion form of the polyelectrolyte, the osmotic coefficient $vs.$ molality plot for the sodium polystyrenesulfonate has been modified by increasing each experimental value by the difference between the "limiting law" ϕ_p and the ϕ_p value of $\sim$0.24 that is obtained when the experimental ϕ_p values are extrapolated to zero concentration.

By using this synthesized osmotic coefficient plot to compute with the Gibbs-Duhem equation the activity coefficient ratio, $(\gamma_{Na})_m/(\gamma_{Na})_r$, for modified selectivity predictions satisfactory correlation between prediction and experiment is once again obtained. This result is summarized in Table XI.

Calculated and experimental ion-exchange selectivities of the $H^+-M^{2+}{}_T$ systems are in good agreement. This result is an apparent contradiction to predictions based on the "condensation" model. When H^+ ions are present in macro quantities a charge density limitation should be reached which effectively should prevent further "condensation" of H^+ ions. This limiting charge density is not low enough, however, to prevent "condensation" of divalent ions. The success of the simple approach in the $H^+-M^{2+}{}_T$ systems may be a consequence of screening of the potential field at the surface of the polyion by the hydrogen ion (macro concentration).

This screening lowers the effective charge density on the polyion to a point where the divalent ion is not completely "condensed" as predicted by Manning's treatment. Thus, osmotic coefficient values employed in the Gibbs-Duhem integration should be nearly equal to the values for the pure divalent form of the polyelectrolyte. Shielding by the macro concentration of divalent ion in the $M^{2+}-Na^+{}_T$ system would only tend to slightly increase the estimate of the sodium polystyrenesulfonate osmotic coefficient used to calculate the selectivities shown in Table XI.

With attainment of the previously listed objectives of this research program, it has been shown that the linear polyelectrolyte analog of a cross-linked ion-exchange gel will serve as a useful model of the ion-exchange resin itself. The thermodynamic approach that has been employed suffers inaccuracy only from the inability to assess the effect of the presence of one counterion on the colligative properties of the other. Even in the absence of such information the predictive quality of the Gibbs-Donnan model of ion exchange that is employed is seriously impaired only when the potential determining ion reduces the charge density at the surface of the polyion below the limiting "condensation" value of the exchanging counterion.