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Ion Exchange Equilibria

I. Sodium-Zinc, Sodium-Copper, Sodium-Manganese in Nitrate Solutions

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Results from measurements of ion exchange equilibria and swelling with a sulfonated resin in solutions of Na-Zn, Na-Cu, and Na-Mn nitrate are presented. The selectivity coefficient is independent of a dilution of the outer solution, but depends on the ionic composition of the resin. As the variations in swelling are very small this dependency must be ascribed to variations in the activity coefficients in the resin phase.

Exhange equilibria in ion exchange resins have been the object of numerous investigations, but most published work deals with the exchange between ions of the same valence. In the present paper data on the exchange in nitrate solutions between sodium ions and the following bivalent ions will be given: zinc, copper and manganese. The ion exchanger was a sulfonated resin of phenolic type (Wofatit KS). The aim of the investigation was to calibrate the resin so that it could be used for determinations of the complexity of metaphosphate solutions [1,2], but as the experimental results may be of general interest it seemed appropriate to present the experiments with nitrate solutions as a separate paper. Ion exchange equilibria with metaphosphate solutions will be given in Part II of the present series.

EXPERIMENTS

Ion exchange resin. The ion exchanger used was Wofatit KS of 0.4—0.5 mm particle size, which, after purification [2], was completely converted into the sodium form by treatment with a sodium chloride solution. This treatment was followed by washing with distilled water and drying in the air. The air dried resin was stored in flasks with close-fitting stoppers. The exchange capacity was determined by displacing the sodium ions with hydrochloric acid, evaporation to dryness and chloride titration according to Mohr. The exchange capacity per gram of air dry resin is given in the tables. The same resin was used in several experimental series and the differences in exchange capacity depend upon the somewhat varying moisture content after air drying.

For resins of the same type as used in the present investigation it has been shown that under similar conditions the counter ions have a negligible effect upon the exchange

Table 1. Exchange capacity and swelling

Counter ion	Exchange capacity mequiv./g Na+ resin (air dried)		n_r equiv./1000 g water		Average
Na	2.24;	2.24	3.76;	3.78	3.77
Cu	2.24;	2.24	3.63;	3.64	3.64
Zn	2.26;	2.26	3.67;	3.65	3.66
Mn	2.25;	2.25	3.71;	3.74	3.73

capacity[3]. This was checked by percolating 0.05 M nitrate solutions of the bivalent cations through columns containing a known weight of the sodium form of the resin until the effluent concentration was unchanged. After washing with water the bivalent cations were eluted with hydrochloric acid and transformed to sulfates by addition of sulfuric acid and evaporation to dryness. The sulfates were determined using the alkalimetric ion exchange method[4]. The results presented in Table 1 confirm that the differences in exchange capacity are small.

In the same table are given results from swelling determinations performed in pure water. For this type of resin the deswelling in the dilute solutions used in the ion exchange experiments can be neglected[4]. The experiments were performed according to the centrifuge technique[5]. In all experiments the sodium form of the resin (air dried) was weighed in and transformed into other forms as described above. The moisture content of the air dried Na-resin (26.1 % H_2O) was determined by drying over magnesium perchlorate in vacuum at 55°C.

A correction was applied for the increase in weight because of the ion exchange and instead of tabulating the amount of water per unit weight of resin the results are given as equivalents of metal ions per 1 000 g of water (n_r). In a separate series of experiments the swelling was studied for resins containing varying amounts of sodium and manganese ions. The results are given in Table 2.

Table 2. Swelling of Na—Mn-resin

Equivalent fraction, X_{Mn}	0.00	0.09	0.27	0.48	0.68	0.87	1.00
Equivalent concentration, n_r	3.77	3.74	3.74	3.74	3.73	3.73	3.73

Solutions. Solutions of 0.1 M sodium nitrate (for some experiments 0.2 M) and of 0.05 M copper-, zinc- and manganese-nitrate were prepared by dissolving calculated amounts of c.p. reagents in distilled water. The concentration of the solutions was determined according to the ion exchange method by passing known volumes through a cation exchange resin in the hydrogen form and titrating the liberated acid[2].

Procedure. In each experiment 40.00 ml 0.1 M sodium nitrate solution, a certain volume (a ml) of the nitrate solution containing the bivalent metal and (10—a) ml water were mixed in an Erlenmeyerflask. After addition of 1.000 g dry resin the flasks were closed and shaken for 17—18 h in a shaking apparatus. Preliminary experiments showed that equilibrium was attained within 4 h. After shaking, the solution was analyzed. In some experiments the order of the additions was altered in order to make sure that the equilibrium was reversible. — With manganese, experiments were performed also at higher dilution (at a total volume of 150 and 500 ml).

The determination of copper was made iodometrically in a biphthalate buffer[6]. For zinc a polarographic method was applied[7], using the Radiometer polarograph, PO3. Manganese was determined colorimetrically with a Coleman spectrophotometer after oxidation to permanganate with potassium periodate in phosphoric and nitric acid solution[6]. A number of duplicate experiments were performed and at least two analytical determinations were made in each experiment. The agreement was very good and only the average values are presented in the tables and diagrams. Some duplicate experiments were made about three months after the first experiments with manganese. In the meantime the resin had been run through three or four exchange cycles with metaphosphate solutions. In spite of this only small deviations could be detected.

CALCULATIONS

From the concentration of the bivalent cation in the equilibrium solution the amount of bivalent ions in the resin is calculated by difference. In this calculation the change in volume of the outer solution caused by the swelling of the resin is not taken into consideration. For the ion exchanger used the swelling was very small compared to the volume of the outer solution. Therefore, the errors in the calculations are insignificant. Furthermore, the nitrate concentration in the resin has been neglected. For this type of resin this is permitted when working at a low concentration in the outer solution [4].

The equivalent fraction of the bivalent ion in the resin (X) is obtained as the ratio between milliequivalents of M found in the resin and the total exchange capacity of the resin. Under the conditions used in these experiments the exchange capacity can be considered as a constant independent of X.

It has proved useful to calculate the selectivity coefficient K_X which for the exchange between sodium ions and a bivalent ion (M) can be defined by the following expression:

$$K_X = \frac{X}{(1-X)^2} \frac{n^2_{\mathrm{Na}}}{n_{\mathrm{M}}} \tag{1}$$

In this equation the equivalent concentrations (n) in the outer solution and equivalent fraction (X) of the bivalent ion in the resin phase are used to express the equilibrium.

DISCUSSION

According to the thermodynamic treatment by Donnan and Guggenheim [8] the exchange between sodium ions and a bivalent ion (M) may be represented by the following equation

$$\pi(2v_{\mathrm{Na}} - v_{\mathrm{M}}) = RT \ln \left[\frac{x_{\mathrm{MR}} \cdot f_{\mathrm{MR}}}{x_{\mathrm{M}} \cdot f_{\mathrm{M}}} \times \left(\frac{x_{\mathrm{Na}} \cdot f_{\mathrm{Na}}}{x_{\mathrm{NaR}} \cdot f_{\mathrm{NaR}}} \right)^2 \right] \tag{2}$$

where π is the swelling pressure [9], v the partial molar volume, and RT the product of the gas constant and the absolute temperature. Mole fractions and rational activity coefficients are represented by x and f. The subscript R is used for ions belonging to the resin phase.

Combining eqns (1) and (2) and substituting practical (molal) activity coefficients (γ) for rational activity coefficients gives

$$\pi(2v_{\mathrm{Na}} - v_{\mathrm{M}}) / RT = \ln(K_X / n_{\mathrm{r}}) + \ln \gamma_{\mathrm{MR}} / \gamma^2_{\mathrm{NaR}} + \ln \gamma^2_{\mathrm{Na}} / \gamma_{\mathrm{M}}$$

where n_{r} is the total ion concentration in the resin phase in equivalents per 1 000 g water.

The left hand side in this equation contains the pressure-volume term. Data, which permit a calculation of this term, are not available for the resin used in the present investigation, but as the swelling has been shown to be independent of X (Tables 1 and 2) this term may be considered as constant [9,10]. In addition, for the systems investigated n_{r} is independent of X and, as the

Table 3. Ion exchange equilibria Na—Mn in nitrate solution.

Reagents added:

I. 1.000 g Na+ resin (= 2.17 mequiv.)
40 ml 0.100 M $NaNO_3$
a ml 0.0500 M $Mn(NO_3)_2$
10—a ml dist. water

II. 1.000 g Na+ resin (=2.17 mequiv.)
20 ml 0.200 M $NaNO_3$
a ml 0.0490 M $Mn(NO_3)_2$
30—a ml dist. water

	a ml	X	n_{Mn} equiv./l	n_{Na} equiv/l.	K_X
I.	1	0.0429	0.135×10^{-3}	81.8×10^{-3}	2.32
	2	0.0848	0.320	83.8	2.22
	3	0.126	0.547	85.4	2.20
	4	0.165	0.823	87.2	2.19
	5	0.204	1.15	88.8	2.21
	6	0 241	1.55	90.4	2.21
	7	0.277	1.98	92.0	2.27
	8	0.311	2.49	93.5	2.30
	9	0.344	3.07	95.0	2.35
	10	0.376	3.68	96.4	2.44
II.	12	0.429	4.92	98.7	2.61
	14	0.478	6.68	100.8	2.67
	16	0.521	8.75	102.6	2.73
	18	0.558	11.05	104.2	2.81
	20	0.590	13.6	105.6	2.88
	22	0.615	16.4	106.5	2.87
	24	0.641	19.2	107.8	3.01

Table 4. Ion exchange equilibria Na—Mn in nitrate solution.

Reagents added:

I. 1.000 g Na+ resin (= 2.17 mequiv.)
40 ml 0.100 M $NaNO_3$
a ml 0.0500 M $Mn(NO_3)_2$
110—a ml dist. water

II. 1.000 g Na+ resin (= 2.17 mequiv.)
40 ml 0.100 M $NaNO_3$
a ml 0.0490 M $Mn(NO_3)_2$
110—a ml dist. water

	a ml	X	n_{Mn} equiv./l	n_{Na} equiv./l	K_X
I.	1	0.0452	0.0143×10^{-3}	27.3×10^{-3}	2.58
	2	0.0899	0.0344	28.0	2.47
	3	0.134	0.062	28.6	2.36
	4	0.177	0.098	29.3	2.29
	5	0.221	0.141	29.9	2.31
	6	0.263	0.193	30.5	2.33
	7	0.305	0.250	31.1	2 44
	8	0.347	0.321	31.7	2.55
II.	9	0.377	0.420	32.1	2.38
	10	0.415	0.530	32.7	2.45
	12	0.484	0.840	33.7	2.46
	14	0.549	1.21	34.6	2.67
	16	0.604	1.72	35.4	2.81
	18	0.647	2.40	36.0	2.80
	20	0.682	3.20	36.6	2.82
	22	0.712	4.07	37.0	2.89
	24	0.741	4.96	37.4	3.12

Table 5. Ion exchange equilibria Na—Mn in nitrate solution.

Reagents added: 1.000 g Na+ resin (2.17 mequiv.)
40 ml 0.100 M $NaNO_3$
a ml 0.0500 M $Mn(NO_3)_2$
460—a ml dist. water

a ml	X	n_{Mn} equiv./l	n_{Na} equiv./l	K_X
5	0.228	0.0128×10^{-3}	8.98×10^{-3}	2.41
8	0.361	0.0314	9.56	2.57
9	0.405	0.0420	9.76	2.59
10	0.448	0.0550	9.96	2.65
12	0.531	0.093	10.30	2.75
16	0.675	0.269	10.94	2.84
20	0.772	0.675	11.34	2.83
24	0.823	1.23	11.58	2.86

experiments have been performed at a low concentration, the last term on the right hand side can be neglected.

Therefore, it must be concluded that any variations in K_X with varying X must be ascribed to variations in the ratio $\gamma_{MR}/\gamma^2_{NaR}$. A reservation must be made for the intervals in which one of the components is present in very small amounts, since here certain complications may occur [11].

The experiments presented in Tables 3—5 show that for the system Na-Mn the volume of the outer solution, which has been varied between 50 and 500 ml, has no or in any case only a very small influence upon the selectivity coefficient K_X. On the other hand, there is in all experimental series with manganese a significant variation in the selectivity coefficient when the composition changes in the resin phase, K_X being higher for increasing equivalent fraction

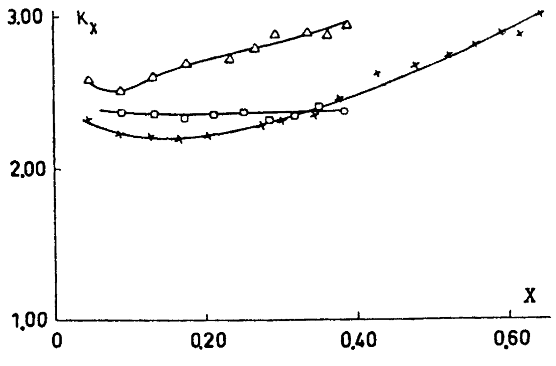

Fig. 1. The selectivity coefficient (K_X) as a function of the equivalent fraction (X) of the bivalent ion in the resin. △ System Na—Cu, □ System Na—Zn, × System Na—Mn.

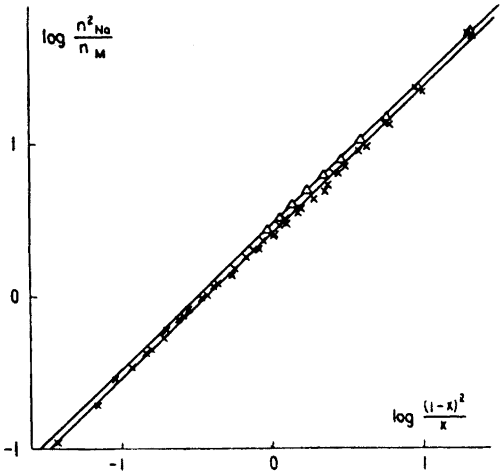

Fig. 2. Log n^2/n_M *versus* log $(1-X)^2/X$. △ System Na—Cu, × System Na—Mn.

(X) of the bivalent ion in the resin phase. As may be seen from Fig. 1 similar variations are obtained also for copper. For zinc the variations in K_X are very small within the interval in X covered in the present investigation. Diagrams of the type given in this figure are useful for calculations of ion exchange equilibria and this type of diagram has been used in the investigations on metaphosphate solutions presented in Part II.

For all three systems the variations in K_X when the equivalent fraction in the resin phase is altered are comparatively small compared with the variations established in other ion exchange reactions. Furthermore the ions studied in the present investigation give remarkably small differences in swelling (Tables 1 and 2). As already mentioned it must be concluded that the variations in K_X arise from variations in the ratio $\gamma_{MR}/\gamma^2_{NaR}$. It may also be pointed out that the differences in K_X for the three systems are comparatively small.

From a practical point of view it may be of interest to find out if the results can be represented by a simple empirical equation. The two-parameter equation proposed by Rothmund and Kornfeld [12] for equilibria in inorganic zeolites has also proved useful to describe the distribution between organic ion exchangers, sulfonated coal [13] as well as resinous exchangers [4,14] and an electrolyte

Table 6. Parameters in Rothmund and Kornfeld's equation

System	k	p
Na—Cu	0.33	1.06
Na—Mn	0.37	1.05

solution. For the exchange between monovalent and bivalent cations the equation can be written:

$$\frac{(1-X)^2}{X} = k \left(\frac{n^2_{\mathrm{Na}}}{n_{\mathrm{M}}}\right)^p \qquad (3)$$

where k and p are empirical parameters. A plot of log $n^2_{\mathrm{Na}}/n_{\mathrm{M}}$ against log $(1-X)^2/X$ is presented in Fig. 2 and as may be seen from the figure a straight line is obtained. From this graph the parameters have been determined. The results are given in Table 6.

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