reaction mixture. The equation may be written as

$$x\text{CoCl}_2 + (2x - 4)\text{NaC}_{10}\text{H}_8 = (x - 2)\text{Co} + (2x - 4)\text{-}$$
$$\text{C}_{10}\text{H}_8 + 2\text{Na}_{x-2}\text{CoCl}_x$$

Since the conductance maximum in the titration curve corresponds to the maximum concentration of $\text{Na}_{x-2}\text{CoCl}_x$; the complex formed has the formula NaCoCl_3. On further addition of sodium napthalide, NaCoCl_3 is reduced to colloidal cobalt according to the equation

$$\text{NaCoCl}_3 + 2\text{NaC}_{10}\text{H}_8 = 3\text{NaCl} + 2\text{C}_{10}\text{H}_8 + 2\text{Co}$$
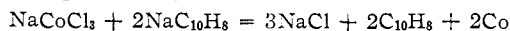
Sodium chloride, because of its insolubility, makes no contribution to the conductance and consequently the conductivity of the reaction mixture decreases to a minimum at a $\text{NaC}_{10}\text{H}_8/\text{CoCl}_2$ mole ratio of 2.0 where the reduction is complete. The conductance then increases rapidly beyond the end point due to the presence of sodium naphthalide.

The conductometric titration of cobalt(II) iodide with sodium naphthalide in tetrahydrofuran solution yielded a similar curve as in the case of cobalt-(II) chloride. However, the end-point is not distinct because sodium iodide is slightly soluble in tetrahydrofuran and makes an appreciable contribution to the conductivity of the reaction mixture.

At the end-point of the titration of cobalt(II) chloride with sodium naphthalide, it was noted that the content of the cell was dark brown and that no precipitate settled on long standing. The dark brown solution was ferromagnetic and showed no characteristic absorption bands in the visible region, indicating the colloidal nature of the reaction product. The stability of colloidal cobalt in tetrahydrofuran is probably due to the presence of naphthalene which is adsorbed by the colloidal particles and lowers the interfacial tension thus preventing coagulation. Colloidal cobalt is relatively unstable on prolonged exposure in air. It coagulates and is rapidly oxidized as is shown by the disappearance of its ferromagnetism. The reactivity of colloidal cobalt may be further illustrated by its reaction with copper(II) chloride in tetrahydrofuran, the latter being reduced immediately to the insoluble copper(I) chloride.

As a conclusion, the process of reduction of metal salts by means of sodium naphthalide in tetrahydrofuran solution consists essentially of the addition of one or more electrons from the naphthalide ion to the metal ion. The sodium ions present and naphthalene formed during the reduction take no part in the reaction and the reduction proceeds quantitatively to completion. In the liquid ammonia system, the reduction of metal ions by alkali metals is frequently incomplete because the metal produced may catalyze the reaction between the alkali metal and the solvent and react with the amide formed.

Anion-exchange Studies. II. The Effect of Cross-linkage on the Elution of Several Transition Elements

BY ROLFE H. HERBER, KAYACAN TONGUC[1] AND JOHN W. IRVINE, JR.

A number of samples of the strongly basic anion–exchange resin Dowex-1 have been studied with reference to their capacity, water content and elution behavior. Column experiments on the elution of Mn(II), Co(II), Cu(II) and Zn(II) with HCl show that in each case retention of the anion complex is dependent on the cross-linkage of the exchanger. While 15 cm. columns of 12% DVB Dowex-1 will effectively separate $\text{Mn}^{52}\text{-Na}^{22}$ mixtures, 2 and 4% DVB resins will not effect this separation even in 12 N HCl. A convenient instrumental arrangement for determining elution behavior of ion-exchange resins is described.

In contrast to the early literature on anion-exchange resins in which scant attention had been paid to the relationship between cross-linkage of the exchanger and other properties such as diffusion, water content, capacity and the elution behavior of different ions, several papers[2] in the recent literature have examined these relationships in detail for the strongly basic anion exchanger, Dowex-2.

Walton[3] has pointed out there is a modest correlation between the ion-exchange equilibrium constant and the ionic radius of the exchanging ion— up to a point, the larger the unsolvated ion, the better it is held by an exchanger.

Kunin and Myers,[4] using both strong-base and weak-base ion exchangers concluded that an increase in the degree of cross-linking is accompanied by a decrease in exchange capacity for both resin series. Using penicillin G, they further note that at high degrees of cross-linking, practically no adsorption of the large penicillin anion can be detected.

The present study is an investigation of the behavior of Mn(II) in hydrochloric acid solutions on several samples of Dowex-1 of varying degrees of cross linkage, and the effect of cross-linkage of the exchanger on the elution behavior of Co(II), Cu(II) and Zn(II).

(1) Technical University of Istanbul. Foreign Student Summer Project participant, Massachusetts Institute of Technology, 1953.

(2) (a) B. A. Soldano and G. E. Boyd, THIS JOURNAL, **75**, 6099 (1953); (b) H. P. Gregor, J. Belle and R. A. Marcus, *ibid.*, **76**, 1984 (1954).

(3) H. F. Walton, *J. Chem. Ed.*, **23**, 454 (1946).

(4) R. Kunin and R. J. Myers, *Disc. Faraday Soc.*, **7**, 114 (1949).

Experimental

A number of samples of the strongly basic anion-exchange resin Dowex-1 were received from different sources, and their properties are tabulated in Table I. The resins were treated several times with 12 N HCl and washed with water, dried at 110° for four hours[5] and then ground and sifted through standard screens. With the exception of samples A and J (Table I), the +100–200 portion was used in each case in the subsequent study.

Table I

Characteristics of Resin Samples

Resin[a]	Nom. DVB	Ca-pacity	Water content, g./g. resin	w_n[b]	Mesh (as received)
G	2	4.159	2.802	1.474	+ 50–100
I	4	3.930	1.351	2.869	+ 50–100
E	7.5	2.524	0.6720	3.655	+ 50–100
H	8	3.654	.6933	5.133	+ 50–100
B	10	3.193	.5865	5.277	+ 50–100
C	10	2.472	.5503	4.345	.....
A	12	3.029	.5699	5.147	+200–400
J	16	1.640	.2627	6.276	+200–400
K	24	...	.2519	...	.....
Scotchlite beads		...	0.0186 ± 0.0002	...	+200–230

[a] The authors are indebted to Drs. K. A. Kraus and W. E. Cohn of ORNL (A,K), J. I. Bregman of the National Aluminate Corporation (E), W. E. Menker of Tracerlab (Berkeley) (C), and R. E. Thiers of Harvard Medical School (J) for supplying samples of these resins.   [b] The weight normality of the resin, w_n, is defined as the

$$\frac{\text{no. of equiv. of ion constituent/kg. dry Cl}^-\text{ resin.}}{\text{kg. H}_2\text{O/kg. dry Cl}^-\text{ resin}}$$

The arrangement for simultaneously recording the radioactivity and volumes of the effluent is a modification of the apparatus used in an earlier study,[6] and is shown schematically in Fig. 1. The resin bed has a diameter of 6 mm. and a length of approximately 15 cm.

The well-type scintillation crystal[7a] inside the lead shield[7b] receives radiation from a small loop of Saran tubing carrying the column effluent. Resolution of the activity peak was improved by shielding all but a short section of the Saran tubing from the detector by means of a cylindrical plug of lead through the long axis of which the tubing entered and emerged from the sensitive volume of the detector.

Pulses from the drop counter are superimposed on the continuous record of the counting rate on an Esterline-Angus Recorder. A mark is made manually on the strip chart record when a known volume of elutriant has passed through the counter arrangement, and subsequent counting of the "pips" during this interval allows a calculation of the volume of elutriant per drop.

The hydrochloric acid used was reagent grade and was standardized against Na₂CO₃. All aqueous solutions were made up with distilled water passed through a bed of Amberlite MB-1 to remove traces of chloride present in the water supply.

The radiotracers were obtained by suitable deuteron bombardments, using the MIT cyclotron, except for Co⁶⁰ which was obtained from Oak Ridge National Laboratory. The radiochemical purities of Mn⁵², Cu⁶⁴ and Zn⁶³ were checked by half-life determinations over at least five half-lives. The specific activities of these tracers were sufficiently high so that not more than 0.06 mg. (~1 μequiv.) of the metal was introduced into the exchanger column in any elution run.

In the column experiments, the resin was pre-treated with at least 10 column volumes of the particular elutriant to be employed in a given run. The adequacy of this pre-
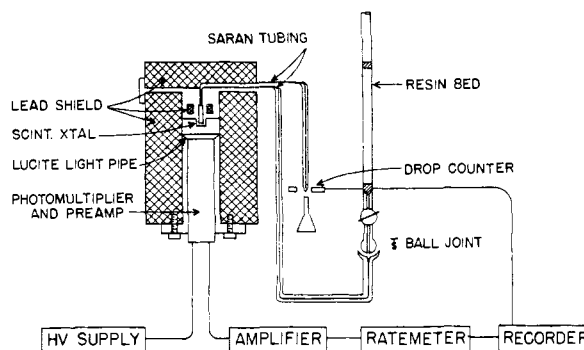

Fig. 1.—Experimental arrangement of apparatus.

treatment was shown by the fact that replicate determinations of the elution position of the concentration maximum of a given ion before and after extensive washing alternately with 12 N HCl and H₂O gave results within 2–3% of the original values observed in that particular column.

The liquid level was then allowed to fall to the top of the resin bed, and the activity introduced as one or two drops of HCl solution by transfer pipet and allowed to seep into the column. The activity lamina was then washed out of the column, the effluent being simultaneously monitored for activity and volume. Flow rates were maintained at 0.3–0.6 cc. min.⁻¹.

The water contents of the resin samples were determined by a modification of the method suggested by Kraus and Moore.[8] Three-gram samples of the resins were treated with 12 N HCl and then thoroughly washed with deionized water. The solid was slurried into a glass chimney fitted with a sintered glass disc. The top of the chimney was covered with aluminum foil to prevent convection current drying of the resin, and the whole assembly centrifuged for a standard time interval in a clinical laboratory centrifuge. The wet resin was promptly transferred in 0.5- to 1.0-g. aliquots to preweighed glass vials and stored in a desiccator partially filled with water until determination of the "wet weight." After weighing the wet resin, the vials were transferred to a vacuum desiccator and dried over Anhydrone under vacuum at 60 ± 5° for at least 15 hr. to constant weight. Spherical glass beads[9] were similarly treated. The water content of the resins given in Table I is the observed water content for the resin minus the water retained by the glass bead standard.

This method of determining the water content gave replicate reproducibility of 1% or better and agreement with the single published value.[8] The results of these determinations are also in general agreement with similar work with the anion exchanger Dowex-2.[10]

The capacities of the resins were determined by neutralizing the hydroxide form of the resin with an excess of standard acid and back titrating the excess acid. The results are given in Table I. This procedure is essentially that of Kunin and McGarvey[11] and Strobel and Gable[12] and gave agreement of ±0.3% for replicate determinations.

Discussion of Results

The comparative retention of a given ion by the exchanger is most conveniently reported in terms of

$$R = V/V_0 \qquad (1)$$

where V is the volume of elutriant necessary to wash out the activity maximum of a given ion band, and V_0 is the volume of distilled water required to wash a band of a standard cation, Na²² in this case,

(5) Although this drying procedure appears drastic in comparison with the treatment recommended for other ion-exchange resins, it has been pointed out by R. E. Anderson (Dow Chemical Co., private communication) that Dowex-1 in the chloride form is ~10 times as stable as Dowex-2, and that Dowex-1 may be dried at 110° for considerable periods of time without discernible decomposition.

(6) R. H. Herber and J. W. Irvine, Jr., This Journal, 76, 987 (1954).

(7) (a) Harshaw Chemical Company, Type No. 22; (b) J. W. Irvine, Jr., Nucleonics, 12, no. 10, 62 (1954).

(8) K. A. Kraus and G. E. Moore, This Journal, 75, 1457 (1953).

(9) −200 + 230 mesh, Minnesota Mining and Mfg. Co., obtained from Dr. K. A. Kraus, ORNL.

(10) B. A. Soldano and G. E. Boyd, This Journal, 75, 6099 (1953).

(11) R. Kunin and F. X. McGarvey, Ind. Eng. Chem., 41, 1265 (1949).

(12) H. A. Stroble and R. W. Gable, This Journal, 76, 5911 (1954).

through the same column. The assumption is made that except for Donnan absorption there is no specific ionic interaction between the sodium ion and the exchanger, and that elution of sodium ion will give reliable values of the void volume of the resin bed and the holdup volume between the bottom of the exchanger bed and the radiation detector. It will be seen that R is also the inverse ratio of the elution constants,[13] $E = Ad/V$, for a given pair of elution runs, and can be calculated for elution data from different columns if the column length (d) and the cross-sectional area of the exchanger bed (A) are known. In determining V from the raw strip chart data, a correction must be made for the small volumes represented by the capillary system from the bottom of the exchanger bed to the center of the scintillation crystal. In the present case this volume was determined experimentally to be 1.75 cc., and the appropriate corrections were made in each case.

The values of R for Mn(II) elution as a function of hydrochloric acid concentration are summarized graphically in Fig. 2. It is seen from this figure that
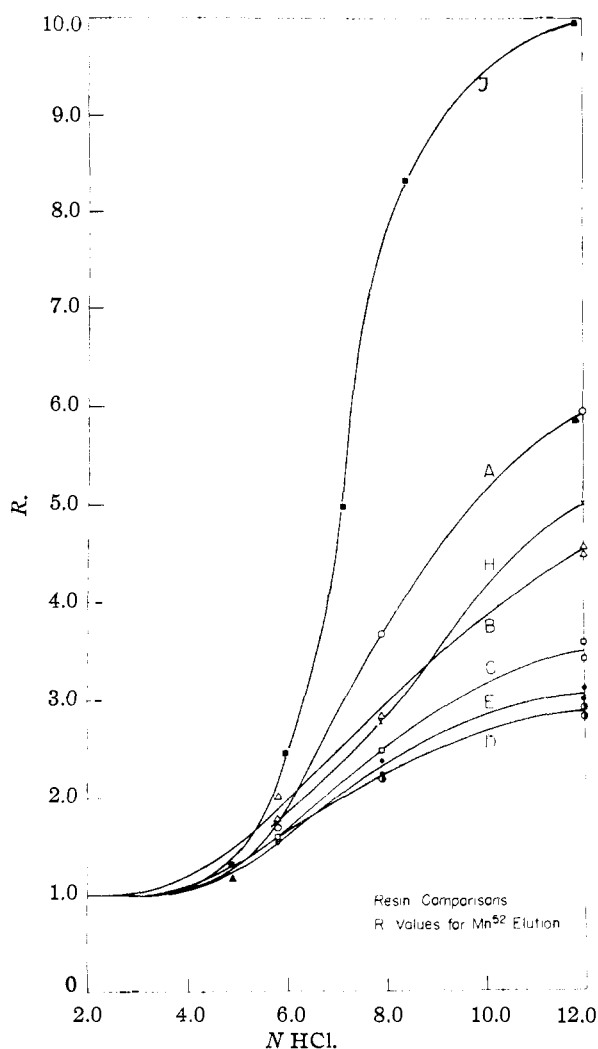
there is a pronounced decrease in R with a decrease in the cross-linkage, although the 8% DVB resin (H) seems to show an anomalously high retention of Mn(II). The 12% DVB sample (A) is from the same batch as that used in an earlier reported separation of Mn(II) from Ni(II),[14] and is seen to be considerably more effective than resins of lower cross-linkage. The 16% resin (I) shows an even greater retention of Mn(II), and has been used quite effectively in the separation of carrier-free Mn(II) from V and Cr.[15]

This difference in the resin performances is further illustrated in Fig. 3 and Fig. 4, which show the degree of separation of a mixture of Na^{22} and Mn^{52} which can be achieved with short column of resins of 12, 7.5, 4 and 2% DVB content. In these experiments, resin beds of ~12–15 cm. length and 7 mm. i.d. were used. With the 12% resin, good separa-
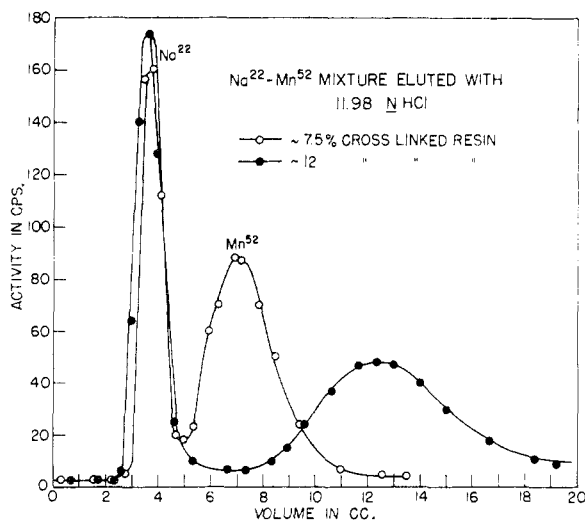
Fig. 2.—R values for Mn^{52} elution. The key to the identification of the various resins is given in Table I.

Fig. 3.—Separation of Na^{22}–Mn^{52} with 11.98 N HCl using 7.5 and 12% DVB Dowex-1.
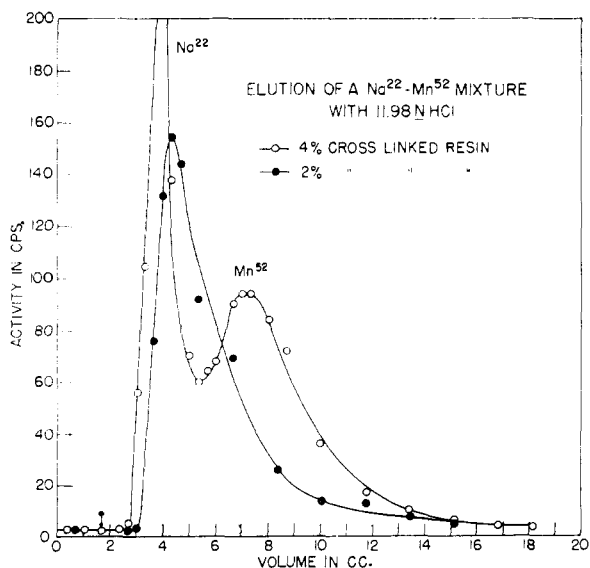
Fig. 4.—Separation of Na^{22}–Mn^{52} with 11.98 N HCl using 2 and 4% DVB Dowex-1.

(13) G. E. Moore and K. A. Kraus, THIS JOURNAL, 72, 5792 (1950).

(14) K. A. Kraus and G. E. Moore, ibid., 75, 1460 (1953).

(15) E. W. Backofen and R. H. Herber. Phys. Rev., 97, 743 (1955).

tion is achieved, the counting rate falling to near background between the two peaks. With the 7.5% resin, slight cross-contamination is seen to occur. This cross-contamination is even more pronounced with the 4% resin, while the elution curve of the activity mixture shows but one peak with the 2% resin. There is a broadening of the elution curve peaks as the cross-linkage of the exchanger is decreased, this phenomenon probably arising from the lowering of the internal chloride ion concentration with lowering of the DVB content.

A similar decrease of retention of a given ion by the exchanger with decrease in the DVB content is shown in the elution of Co(II), Cu(II) and Zn(II).

TABLE II

ELUTION OF Co(II), Cu(II) AND Zn(II) FROM RESINS OF VARYING DVB CONTENT

% DVB	Resin w_n	Zn(II) (0.151 N HCl)	R values Cu(II) (3.02 N HCl)	Co(II) (5.79 N HCl)
2	1.47	5.82	4.80	5.82
7.5	3.66	8.31	5.45	6.77
12	5.15	>15	5.68	14.3

Soldano and Boyd[2a] have pointed out that for Dowex-2, the molality of the exchanger, calculated from experimentally determined capacities, water content and resin weights, increases from 2.3 m for a 1% DVB resin to 10.2 m for a 16% DVB resin. It is evident from Table I that a similar relationship exists for Dowex-1, there being a fourfold increase in weight normality between the 2 and 16% DVB resin.

In connection with their work on Dowex-2, Gregor, et al.,[2b] have suggested that resins, produced by the same manufacturer, and containing the same nominal DVB content, may differ significantly in their exchange properties, and it thus appears necessary to characterize these resins by more than their type (i.e., whether Dowex-1, or 2, etc.) and nominal DVB content. The resins used in the present study have been characterized by the determination of two related properties: (a) the capacity and (b) the water content.

The increase in exchange site concentration with cross-linkage is related to two opposing effects: (a) the decrease in capacity which tends to reduce the weight normality of the exchanger, and (b) the decrease in water content which tends to increase it. A capacity decrease with increasing cross-linkage has been reported by Kunin and Myers[4] for both strongly basic (Amberlite IRA-400) and weakly basic anion exchangers (modified IRA 400), and by Soldano and Boyd[2a] (for Dowex-2).

Table III summarizes the R values with respect to Mn(II) elution as a function of the resin normal-

ity, w_n, at three HCl elutriant concentrations. It is evident from these data that there is a general increase in Mn(II) retention with an increase in w_n. The efficacy of the 12% DVB resin—sample A—appears to be greater than would be predicted from its normality of 5.15. Both the water content and capacity of this resin—identical to that used by Kraus and co-workers[16] in their extensive investigations—have been carefully determined during the course of the present study, and the normality of 5.15 w_n is reported with considerable confidence. Nonetheless it should be pointed out that the performance of resin A is more nearly compatible with a normality of 6.06 (calculated from Kraus' values of the two pertinent parameters) than with the above reported value of 5.15 w_n. This disagreement must remain for the present unanswered.

TABLE III

R VALUES FOR THE SYSTEM Mn(II)–HCl AS A FUNCTION OF EXCHANGER AND ELUTRIANT CONCENTRATION

Resin	D	E	C	B	A	J
Capacity (w_n)	..	3.67	4.35	5.28	5.15	6.28
HCl concn., N						
8	2.24	2.35	2.53	2.96	3.75	7.80
10	2.68	2.83	3.15	3.85	5.10	9.44
12	2.88	3.05	3.49	4.53	5.93	9.96

The performance of the resins of differing DVB content over wide HCl concentration changes seems to indicate that the small decrease in capacity with an increase in cross-linkage is more than offset by the decrease in water absorption by resin which effectively increases the concentration of the exchange sites in the highly cross-linked resins, even in concentrated electrolyte solutions.

The application of these results to the separation of Mn(II) from non-adsorbed cations such as Na, K, as well as Ni, V, etc., has been suggested above. It seems probable that the separations of ions having similar elution behavior, such as Ga(III)–Cu(II),[6] the lanthanide elements, and elements 95–100[17] among others, can be considerably improved by an optimal choice of w_n of the resin type used in the separation.

Acknowledgment.—The authors wish to acknowledge helpful discussions with Dr. K. A. Kraus and Dr. R. M. Diamond, as well as the technical assistance of Mr. E. Rudzitis, in the development of this work. This work was supported in part by the U. S. Atomic Energy Commission.

CAMBRIDGE, MASS.

(16) Paper I in this series is to be found in THIS JOURNAL, 73, 9 (1951), although earlier communications (e.g., ibid., 71, 3263 (1949); 71, 3855 (1949)), etc., reported results with the same resin batch.

(17) S. G. Thompson, B. G. Harvey, G. R. Choppin and G. T. Seaborg, THIS JOURNAL, 76, 6229 (1954).