well as $\gamma^{r}_{\pm HCl}$, using the activity coefficient $\gamma^{r}_{\pm HCl}$ for the aqueous phase given in the literature.[14] Figure 2 gives a plot of log $\gamma^{r}_{\pm HCl}$ as a function of the molality m^{r}_{H} of hydrogen ions in the resin phase. A similar curve would have been obtained if log $\gamma^{r}_{\pm HCl}$ were plotted as a function of molality m^{r}_{Cl} of chloride ions in the resin phase.

It may be noticed that through most of the range of m^{r}_{H}, log $\gamma^{r}_{\pm HCl}$ varies linearly with m^{r}_{H}, *i.e.*, it follows the equation

$$\log \gamma^{r}_{\pm HCl} = a + bm^{r}_{H} \qquad (3)$$

where $a = -0.43$ and $b = 0.117$. If equation 3 had been given in terms of m^{r}_{Cl}, a would become -1.06 while b would become 0.104. At low concentration of hydrogen ions in the resin phase $\gamma^{r}_{\pm HCl}$ drops rapidly with decreasing m^{r}_{H}. This is the region where, according to Fig. 1, the amount of HCl adsorbed changes only slowly with the HCl concentration of the aqueous phase and where adsorption is dependent on the purification of the resin. In this range, probably some of the adsorption is due to the reaction of HCl with an impurity in the resin, probably an acid–base reaction with tertiary and lower amines,[15] although the rapid decrease in the activity coefficients is not necessarily entirely due to such impurities. The amount of HCl held in this way is very small compared with the total capacity of the resin (<0.3%). This amount was estimated by assuming that $\gamma^{r}_{\pm HCl}$ follows equation 3 to $m^{r}_{H} = 0$, calculating m^{r}_{H} according to equation 1 and comparing these values of m^{r}_{H} with those found experimentally.

For comparison Fig. 2 also contains the activity coefficients $\gamma_{\pm HCl}$ as a function of m_{HCl} for the aqueous phase. It may be noticed that for $m_{HCl} > 1$, *i.e.*, at concentrations where the Debye–Hückel interaction becomes essentially constant, the activity coefficients of HCl in the aqueous and resin phases vary similarly with m_{H} although they are consistently smaller in the resin phase than in the aqueous phase. It thus appears that the resin phase has some properties in common with concentrated aqueous electrolytes and that to a considerable extent the hydrocarbon network of the resin appears to act as a relatively inert diluent in this concentrated electrolyte.

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[14] (a) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933); (b) M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928); (c) G. Åkerlöf and J. W. Teare, *ibid.*, **59**, 1855 (1937).

[15] It was found that in this region the adsorbed HCl is quite difficult to wash out, indicating that some reaction (*e.g.*, neutralization) had occurred. At higher HCl concentrations where the activity coefficients follow Equation 3, no such difficulty was observed.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Anion Exchange Studies. VI.[1,2] The Divalent Transition Elements Manganese to Zinc in Hydrochloric Acid

BY KURT A. KRAUS AND GEORGE E. MOORE

RECEIVED SEPTEMBER 2, 1952

The anion exchange behavior of the divalent transition elements manganese to zinc was studied in hydrochloric acid solutions. The adsorbabilities of the elements differ sufficiently as a function of hydrochloric acid concentration to permit their separation. The hydrochloric acid concentrations where noticeable adsorption occurs increase in the order Zn, Cu, Co, Fe and Mn with no noticeable adsorption for Ni, even in concentrated hydrochloric acid. It appears that the stability of the negatively charged chloride complexes of these divalent elements decreases in this order.

A survey of the anion exchange behavior of the first row transition elements of oxidation number two from Mn(II) to Zn(II) has been carried out in hydrochloric acid solutions. The results for Co(II) and Ni(II) have been given earlier.[3] In the case of these two elements, it was found that they differed greatly in their adsorbability, Ni(II) not being adsorbed from concentrated hydrochloric acid and Co(II) showing strong adsorption. This difference in anion exchange behavior suggested great differences in the stabilities of the negatively charged complexes of the transition elements, and a systematic study of these elements seemed indicated. In addition, there existed the possibility of establishing good separation procedures for these elements by use of anion exchange techniques.

Experimental

The anion exchange behavior of these elements was studied with the quaternary amine polystyrene–divinylbenzene resin Dowex-1 at room temperature, with a column technique.[4] From it the elution constant $E = dA/V$ is obtained where d is the distance an adsorption maximum travels on passage of V cc. of eluent through a column of cross-sectional area A cm.^{2}.

The columns, *ca.* 20 cm. long and of cross-sectional area *ca.* 0.03 sq. cm., were made of Pyrex tubing plugged with glass wool and filled with $-200 + 230$ mesh wet-screened resin in the chloride form. The columns were pretreated with the acid of interest and a small volume (*ca.* 0.025 ml.) of the metal solution containing 1 to 3 mg. of metal in the same acid was placed on the column. After the solutions seeped into the columns, the eluent was added from a buret to permit ready determination of V.

The solutions were prepared from C.P. salts except for the Fe(II) solutions which were prepared by dissolving iron filings in hydrochloric acid. Since Fe(II) and Fe(III)[5] behave very differently on the column and since the two oxidation states can be identified readily analytically, there was no difficulty in the determination of the elution constants of Fe(II). Since copper was found to form a colored band (yellow up to 4 *M* HCl, brown to 9 *M* HCl and orange to 12 *M* HCl) and since the resin is light tan changing to light brown in 12 *M* HCl, d could be determined visually and E obtained from the slope of a straight line plot of d *vs.* V. The elution constants for the weakly colored and colorless ions Mn(II), Fe(II) and Zn(II) were determined by meas-

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper, K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1457 (1953).

[3] G. E. Moore and K. A. Kraus, *ibid.*, **74**, 843 (1952).

[4] K. A. Kraus and G. E. Moore, *ibid.*, **73**, 9 (1951).

[5] G. E. Moore and K. A. Kraus, *ibid.*, **72**, 5792 (1950).

uring the volume necessary to elute the adsorption maximum,[6] noting that d is equal to the length of the column. The eluent was collected in drops on a spot plate, the relative concentrations determined by standard spot tests[7] and the volume noted at which the metal appeared in maximum concentration.

Results and Discussion

1. Elution Constants.—Elution constants were determined in the range 0.5 to 12 M HCl. The results of the experiments are summarized in Fig. 1, where for comparison the earlier data on nickel and cobalt have also been included. For all elements E = *ca.* 2.5 was found at low M HCl. Except for Ni(II), E decreases with increasing M HCl, reaches a minimum or approaches such a minimum. E for Ni(II) is *ca.* 2.5 throughout the experimental range.

Since $E = 1/(i + D)$, where i is the fractional interstitial space and D the volume distribution coefficient (amount per ml. bed/amount per ml. solution) a decrease in E implies an increase in D, *i.e.*, increasing adsorption. For negligible adsorption ($D = 0$) E reaches a maximum value of $1/i$. Apparently $E = 2.5$ represents this maximum value and corresponds to $i = 0.4$.

It is of interest that Ni(II) is the only element of this series which does not show adsorption. Mn(II) and Fe(II) show slight adsorption above *ca.* 5 M HCl. Cu(II) shows some adsorption above *ca.* 1 M HCl, is better adsorbed than Mn(II) and Fe(II) at its maximum, but is never as strongly adsorbed as Co(II) for which appreciable adsorption starts above *ca.* 3 M HCl. Zn(II) shows the strongest adsorption of the series. It is considerably adsorbed in 0.1 M HCl and has an adsorption maximum in *ca.* 2 M HCl; *i.e.*, at an HCl concentration where most of these elements show only small adsorption. In addition the adsorbability of Zn(II) greatly exceeds that of the other elements. From these results it appears that the separation of these transition elements from each other can readily be achieved by anion exchange and this separation will be discussed in the next section.

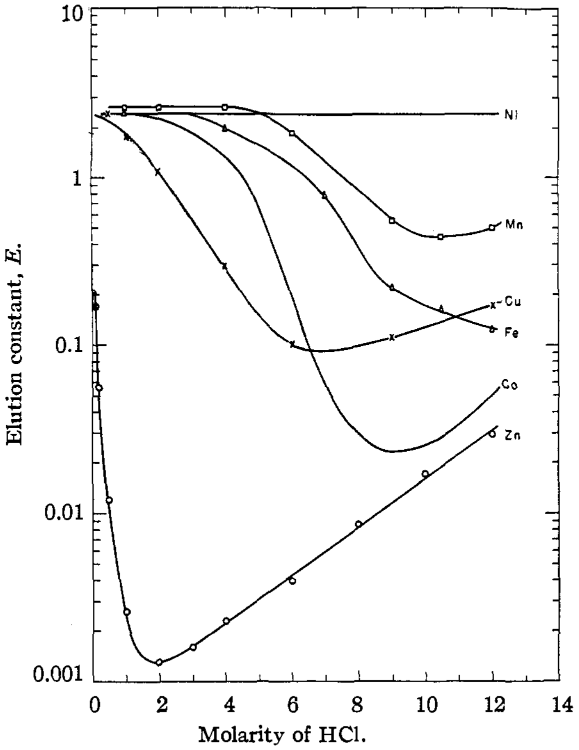

Fig. 1.—Elution constants of some divalent transition elements in hydrochloric acid (data for Zn(II) from unpublished results of F. Nelson).

The large differences in the anion exchange behavior of these elements suggest large differences in their complexing properties and considerable irregularity in the extent of complexing as a function of atomic number. If the hydrochloric acid concentration at which noticeable adsorption first takes place (*e.g.*, $E = 1$) is taken as an index of the strength of complexing, the elements order themselves as shown in Table I, method A.

TABLE I

ORDER OF COMPLEXING OF DIVALENT CHLORIDES

Method	Elements
(A) Anion exchange ($E = 1$)	Zn > Cu > Co > Fe > Mn > Ni
(B) Anion exchange (position of ads. max.)	Zn > Cu > Co > Mn > Fe > Ni
(C) Solubility of MCl_2 in HCl	Zn > Cu > Co > Fe > Ni
(D) Activity coefficients	Zn > Cu > Mn > Fe > Co> Ni
(E) J. Bjerrum	Zn > Fe > Cu > Co

A very similar order of complexing strength is obtained if the hydrochloric acid concentrations are considered at which adsorption reaches a maximum. This order is listed as method B in Table I. The only differences between the order of method A and method B are the relative positions of Mn(II) and Fe(II), which are somewhat uncertain.

As will be discussed in a later paper, method A probably gives the hydrochloric acid concentrations at which these elements form approximately equal (and small) concentrations of the complex ions MCl_4^-. On the other hand, method B probably gives the hydrochloric acid concentrations at which the complexes MCl_4^- become the principal species in the aqueous phase, while the extent of adsorption at the maximum is related to the concentration of the complexes MCl_3^- under these conditions. Although methods A and B measure two different complexing properties of the elements it is of interest that the two methods give very nearly the same order of complexing strength.

Approximately the same order of complexing strength is also obtained from the solubilities of the metal chlorides MCl_2 in HCl[8] (Table I, method C), if the assumption is made that the undissociated compounds MCl_2 have relatively low solubility and that formation of negative complexes is necessary to yield good solubility at high HCl concentration. Thus the solubility of $NiCl_2$ decreases rapidly with

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[6] Some data on the adsorption of Zn using equilibrium experiments with Zn^{65} tracer have been included. These are from unpublished results of F. Nelson.

[7] F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., New York, N. Y., 1946. Fe(II) was determined with dimethylglyoxime and NH_3, Mn(II) by alkaline oxidation to MnO_2, Zn(II) with dithizone and NaOH.

[8] A. Seidell, "Solubility of Inorganic and Metal Organic Compounds," Third Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940.

HCl concentration and that of $FeCl_2$ decreases almost as rapidly. The solubility of $CoCl_2$ decreases less rapidly and shows an increase at high HCl concentration. The solubility of $CuCl_2$ is almost identical with that of $CoCl_2$, but shows a slightly greater increase. The solubility of $ZnCl_2$ shows almost no decrease with HCl concentration. However, in this case the conclusions are more tentative since the solubility of $ZnCl_2$ in water is approximately ten times larger than that of the other metal halides, which have approximately the same solubility in water. There appeared to be no data for the solubility of $MnCl_2$ in HCl.

These results may also be compared with conclusions regarding the complexing strength of these elements taken from the values of the activity coefficients ($\gamma_\pm$) of the metal chlorides. These have been reported to be[9] 0.682, 0.817, 0.884, 0.938, 0.466 and 0.289 for 2 molal solutions of $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$, respectively. In such a closely related series of elements, one might expect that the stoichiometric activity coefficients $\gamma_\pm$ decrease with increasing complexing. Examination of Table I shows that the order of complexing obtained by this method differs greatly from the order obtained from methods A, B and C. Particularly surprising is the close similarity of the activity coefficients of $NiCl_2^-$ and $CoCl_2$ since they differ greatly with respect to the other methods. It is similarly surprising that $MnCl_2$ and $FeCl_2$ have lower activity coefficients than $CoCl_2$ since negatively charged chloride complexes of these elements seem to appear only at very high hydrochloric acid concentrations. The reason for these differences may be that the activity coefficients of the metal halides become low if the complexes MCl^+ and MCl_2 form, while the anion exchange results and solubilities are closely related to the formation of the complexes MCl_3^- and $MCl_4^=$. Comparison of method D with A, B and C, thus indicates that the elements show considerable differences in the relative stability of the various complexes MCl_i^{+2-i}, and that hence the usefulness of the concept of an average stability constant as used by Bjerrum[10] is restricted. The anion exchange results may also be compared with the order of complexing strength suggested by Bjerrum[10] (see Table I, method E). Unfortunately Bjerrum does not include Mn(II) and Ni(II) and a detailed comparison is thus not feasible. However, it should be pointed out that Bjerrum believes that Fe(II) is more strongly complexed than Cu(II). This is in disagreement with method D which we might have expected to yield the same order. Bjerrum's order for Fe(II) is based on the value of the stability constant of $FeCl^+$ determined by Olerup.[11] A check on the value of this constant thus appears desirable.

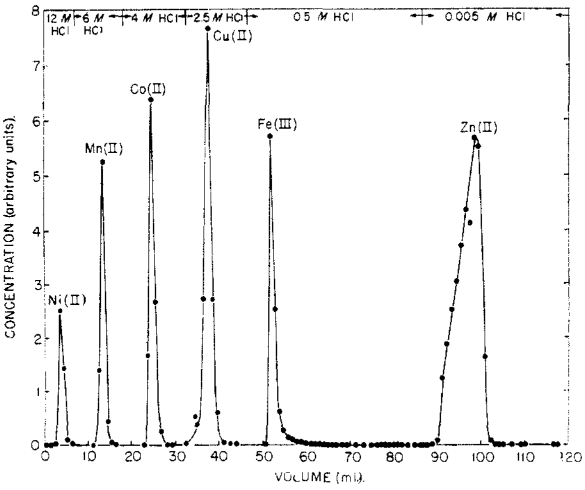

Fig. 2.—Separation of transition elements Mn to Zn (Dowex-1 column; 26 cm. × 0.29 cm.; flowrate = 0.5 cm./min.).

It is of particular interest that none of these methods yields the simple order of complexing strength (increase to Cu and decrease to Zn) which apparently applies with many chelates.[12]

2. Separation of the Transition Elements Mn to Zn.—The considerable difference in the elution constants of these elements implies that their separation on anion exchange columns of moderate length should be possible. To illustrate the technique, the separation of Mn(II), Fe(III),[13] Co(II), Ni(II), Cu(II) and Zn(II) was carried out, and the results are shown in Fig. 2. Approximately 0.85 ml. of a concentrated hydrochloric acid solution containing *ca.* 6 mg. of each of these elements was placed on a 26 cm. × 0.29 cm.^{2} column containing −200 + 230 mesh Dowex-1. Under these conditions Ni(II) is not adsorbed and immediately appears in the eluent. Mn(II) was removed with 6 *M* HCl, Co(II) with 4 *M* HCl, Cu(II) with 2.5 *M* HCl, Fe(III) with 0.5 *M* HCl and Zn(II) with 0.005 *M* HCl. Mn(II) was determined spectrographically.[14] The concentrations of Fe(III) and Zn(II) were determined by tracer techniques using Fe^{59} and Zn^{65}, respectively, while Co(II), Ni(II) and Cu(II) were determined colorimetrically. As shown in Fig. 2, the separation of these elements is quite satisfactory at the flowrate indicated (0.5 cm./min.) and probably would also be satisfactory at considerably higher flowrates.

Acknowledgment.—The authors are indebted to Miss Zella L. Bonner for valuable technical assistance.

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(9) H. S. Harned and B. B. Owen, "Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950, pp. 567, 602.

(10) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(11) H. Olerup, Dissertation, Lund, 1944.

(12) See for example, L. E. Maley and D. P. Mellor (*Australian J. Sci. Res.*, **2**, 92 (1949) (8-hydroxyquinoline, salicylaldehyde, acetylacetone)); Maley and Mellor (*Nature*, **165**, 453 (1950) (amino acids); G. Schwarzenbach and co-workers (*Helv. Chim. Acta*, **33**, 963, 974, 985, 995 (1950) (polyamines)); and M. Calvin and N. C. Melchior (THIS JOURNAL, **70**, 3270 (1948) (5-salicylaldehyde, sulfuric acid)). Calvin and Melchior suggested that the stability of the chelates is related to second ionization potentials of the metals.

(13) In this separation Fe(III) was used rather than Fe(II) since in most practical cases the former would be encountered. Fe(III) is strongly adsorbed by anion exchange resins from concentrated hydrochloric acid solutions (see ref. (5)). It should also be mentioned that the separation of Fe(II) and Fe(III) can readily be carried out in a large range of hydrochloric acid concentrations in view of their large differences in adsorbability.

(14) We are indebted to Mr. C. Feldman and Mr. M. Murray of the Oak Ridge National Laboratory Analytical Division for the spectrographic analyses.