Ion Exchange in Concentrated Solutions II. Beryllium Chloride-Hydrochloric Acid System*

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Although the ion-exchange in concentrated solutions has been applied successfully by several investigators to the separation of transuranic elements from rare earths[1] and the mutual separation of transition metals[2], only a few studies have been reported on ion-exchange equilibria in solutions of large ionic strength[3,4]. We had previously studied the equilibria in sodium chloride-hydrochloric acid and lithium chloride-hydrochloric acid systems[5]. In the present study the equilibrium in beryllium chloride-hydrochloric acid system was investigated.

Experimental

(1) **The Resin.**—The resin used was Dowex 50-X8 (hydrogen form) of mesh size 30~80 obtained by wet screening. It was dried at 40°C. The amount of water adsorbed on the resin was determined from the weight decrease on drying the resin at 110°C. It was 0.20–0.23 ml. per gram of the resin. The amount of resin used in one batch experiment was 3.6 g., i. e., about 15 milliequivalents.

(2) **Reagents.**—Commercial beryllium chloride was converted into beryllium basic acetate, and it was purified by recrystallization from hot glacial acetic acid. Purified beryllium basic acetate was decomposed with hot water and beryllium hydroxide was precipitated with ammonia. Beryllium hydroxide thoroughly washed was dissolved in a calculated amount of hydrochloric acid and thus solutions of beryllium chloride were prepared.

(3) **Procedure.**—A certain amount of the resin (exchange capacity E meq.) was put into a glass-stoppered Erlenmeyer flask containing a known amount ($V=30$ ml.) of 0.1~5 N $BeCl_2$-HCl mixtures. After shaking for 40 minutes in a thermostat at 25°C, the resin was quickly separated from the solution by suction on a glass filter. An aliquot of the filtered solution (external solution at equilibrium) was titrated with 0.1 N barium hydroxide solution, and the hydrogen ion concentration $(H^+)_s$ was determined using methyl yellow (pH of its color change: 2.9—4.0) as indicator, because beryllium chloride was hydrolized in the higher pH range. After the above procedure the chloride ion concentration of the filtrate, $(Cl^-)_s$, was determined by Fajans' argentometric titration, using fluorescein as indicator.

The separated resin was then poured into a column (20 cm.×1 cm. diameter) with water and washed repeatedly with distilled water. The amount of hydrogen ion in these washings, $[H^+]_Q$, was similarly determined by titration. The amount of beryllium ion in these washings,

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1) K. Street, Jr. and G. T. Seaborg, *J. Am. Chem. Soc.*, **72**, 2790 (1950).

2) K. A. Kraus, et al., ibid., **71**, 3263, 3855 (1949); **72**, 4293, 5792 (1950); **73**, 9, 13, 2900 (1951); **74**, 843 (1952); **75**, 1460, 3273 (1953); **76**, 984, 5916 (1954); **77**, 1383 (1955).

3) K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

4) R. M. Diamond, *J. Am. Chem. Sec.*, **77**, 2978 (1955).

5) H. Kakihana, N. Maruichi and K. Yamasaki, *J. Phys. Chem.*, **60**, 36 (1956).

$[Be^{++}]_Q$ was determined colorimetrically by 8-hydroxyquinaldine[6].

Then 0.5 N barium nitrate solution was passed through the resin column, and the effluent was titrated with 0.1 N barium hydroxide. The amount of the hydrogen ion which had been retained in the resin, $[H^+]_R$, was thus determined and the amount of the beryllium ion in the effluent, $[Be^{++}]_R$, was determined by the gravimetric method using hydrazine as the precipitating agent.

Relations between the quantities determined above are

$$[Be^{++}]_Q = [Cl^-]_Q - [H^+]_Q$$
$$[Be^{++}]_S = [Be^{++}]_O - [Be^{++}]_R - [Be^{++}]_Q$$
$$(Be^{++})_S = (Cl^-)_S - (H^+)_S,$$

where parentheses and brackets represent concentration (milliequivalents per ml.) and amounts (milliequivalents) of the ions, respectively. Subscripts O, R, S and Q denote the original solution, the resin phase at equilibrium (the perfect exchange phase), the external solution at equilibrium and the quasi-exchange phase, respectively. The last phase, i. e. the quasi-exchange phase, consists of two kinds of solution. One is the solution which adheres to the surface of resin particles and the other is the solution which penetrates into the resin without being exchanged at the time of the exchange equilibrium.

Results and Discussion

(1) **Adsorbed Water.**—The amount of the water adsorbed by the resin, which is in contact with the external solution, is important in the ion exchange and many authors have tried to determine its amount by various methods[7-10]. However, the methods used by previous investigators in dilute or moderately dilute solutions are considerably complicated. The amount of adsorbed water was, therefore, estimated indirectly by the following calculation as reported in the previous paper[5].

The total amount of hydrogen ion in the solution and the resin is equal to

$$(H^+)_S(V-A') + [H^+]_Q + [H^+]_R, \qquad (1)$$

where A' is the volume of water adsorbed in the resin phase at equilibrium. The first term in (1) denotes the amount of hydrogen ion in the external solution. The total amount of hydrogen ion is also equal to

$$E + [H^+]_O, \qquad (2)$$

where E denotes the total exchange capacity of the resin used. Thus

$$(H^+)_S(V-A') + [H^+]_Q + [H^+]_R = E + [H^+]_O \qquad (3)$$

By arranging the equation,

$$A' = \frac{(H^+)_S V + [H^+]_Q + [H^+]_R - E - [H^+]_O}{(H^+)_S} \qquad (4)$$

As all the terms in (4) are determined experimentally, the amount of adsorbed water A' can be calculated. If the water content of the resin used (weight decrease on drying at 110°C) is denoted by A'', total amount of the water in the resin used (E meq.) at the equilibrium is

$$A = A' + A'' \qquad (5)$$

A part of the data obtained and the amounts of water in the resin thus calculated are given in Tables I and II. Values of A decrease as the concentration of the hydrogen ion increases. These values agree with the data of Pepper et al. and those of Davies et al. determined in hydrochloric acid solution. Quite recently

TABLE I

WATER IN THE RESIN

Total exchange capacity	Original soln.		External soln. at equilibrium		Water in the resin
E meq.	$BeCl_2$ (N)	HCl (N)	$BeCl_2$ (N)	HCl (N)	ml./g. dry resin
16.04	0.1	0.00	0.00_3	0.10	2.21
〃	〃	0.32	0.01	0.43	1.30
〃	〃	0.64	0.01	0.76	1.25
〃	〃	0.96	0.02	1.10	1.15
〃	〃	1.27	0.04	1.40	1.16
15.24	0.5	0.00	0.15	0.30	0.86
〃	〃	0.28	0.18	0.58	1.28
〃	〃	0.57	0.26	0.85	1.28
〃	〃	1.56	0.33	1.76	0.98
〃	〃	2.78	0.45	2.97	0.95
〃	〃	5.21	0.38	5.31	0.67
15.12	1.0	0.00	0.59	0.61	2.62
〃	〃	0.56	0.62	0.93	1.62
〃	〃	1.10	0.65	1.41	1.43
〃	〃	2.28	0.68	2.49	1.00
〃	〃	4.59	0.66	4.80	0.96
〃	〃	7.43	0.83	7.57	0.73
15.12	5.0	1.16	4.27	1.76	2.28
〃	〃	4.17	4.08	4.70	1.40

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6) K. Motojima, This Bulletin, **29**, 71 (1956).

7) K. W. Pepper and D. Reichenberg, *Z. Elekteochem.*, **57**, 183 (1953); B. R. Sundheim, M. H. Waxman and H. P. Gregor, *J. Phys. Chem.*, **57**, 974 (1953).

8) K. W. Pepper, D. Reichenberg and D. K. Hale, *J. Chem. Soc.*, **1952**, 3219.

9) H. P. Gregor, K. M. Held and J. Bellin, *Anal. Chem.*, **23**, 620 (1951).

10) C. W. Davies and G. D. Yeoman, *Trans. Faraday Soc.*, **49**, 968, 975 (1953).

Gupta[11] applied our method of determining the adsorbed water to the study of sodium chloride-hydrochloric acid system and found that the ratio of the amount of water in the resin to the concentration of hydrochloric acid used increased linearly with the latter value.

(2) Concentrations of ions in the quasi-exchange phase.—In Fig. 1, the amount of the beryllium ion in the quasi-exchange phase, $[\mathrm{Be}^{++}]_\mathrm{Q}$, and that of hydrogen ion, $[\mathrm{H}^+]_\mathrm{Q}$, are plotted against hydrogen ion concentration in the solution, $(\mathrm{H}^+)_\mathrm{S}$. If there is any competition between beryllium and hydrogen ions in the adsorption on the resin, it is expected that the amount of beryllium ion in the quasi-exchange phase, $[\mathrm{Be}^{++}]_\mathrm{Q}$, will decrease as hydrogen ion concentration in the external solution, $(\mathrm{H}^+)_\mathrm{S}$, increases. Such a fact is found when $(\mathrm{H}^+)_\mathrm{S}$ is low. But, when it is higher than 1 N, values of $[\mathrm{Be}^{++}]_\mathrm{Q}$ show a minimum and then increase as $(\mathrm{H}^+)_\mathrm{S}$ increases. On the other hand, $[\mathrm{H}^+]_\mathrm{Q}$ increases always as $(\mathrm{H}^+)_\mathrm{S}$ increases. This means that some change in the ionic species takes place in the solution. The results of spectrophotometric studies given in (4) reveal formation of complexes in the solution.

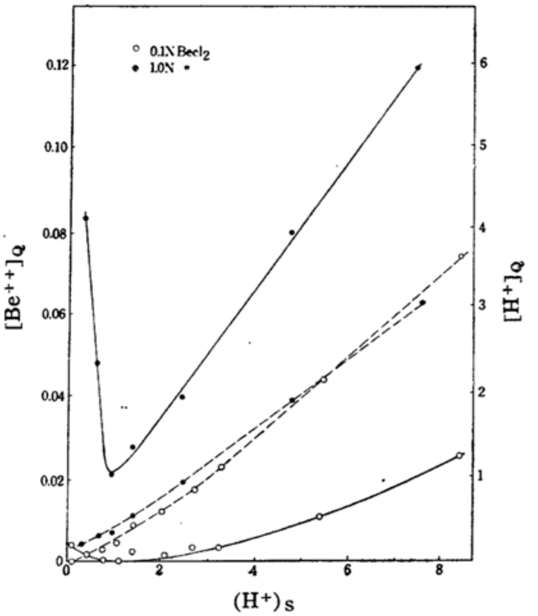

Fig. 1. Amounts of Be and H ions in the quasi-exchange phase. Solid and broken lines denote $[\mathrm{Be}^{++}]_\mathrm{Q}$ and $[\mathrm{H}^+]_\mathrm{Q}$, respectively.

(3) Apparent equilibrium constant.—Apparent equilibrium constant, K, of the exchange reaction between beryllium and hydrogen ions is given by the following equation:

$$K=\frac{(\mathrm{H}^+)_\mathrm{S}^2(\mathrm{Be}^{++})_\mathrm{R}}{(\mathrm{H}^+)_\mathrm{R}^2(\mathrm{Be}^{++})_\mathrm{S}}$$

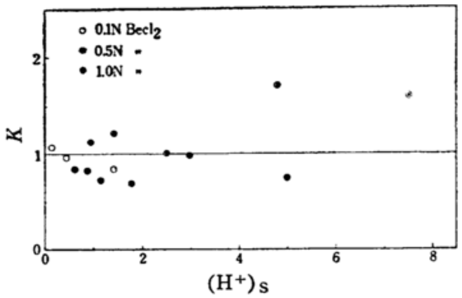

Fig. 2. Relations between apparent equilibrium constant K and the hydrogen ion concentration in the external solution, $(\mathrm{H}^+)_\mathrm{S}$.

where $(\mathrm{H}^+)_\mathrm{R}$ and $(\mathrm{Be}^{++})_\mathrm{R}$ are defined as $[\mathrm{H}^+]_\mathrm{R}/A$ and $[\mathrm{Be}^{++}]_\mathrm{R}/A$ respectively[12]. In Fig. 2 values of K are plotted against the concentration of hydrogen ion in the external solution. When the concentration of beryllium ion is low, K is smaller than 1, but when it is 1.0 N or higher, the value of K is greater than unity. This fact can be explained by the formation of cationic complexes which are more easily captured by the resin than the simple beryllium ion. The formation of such a complex is shown by the spectrophotometric experiments.

(4) Ionic species in the solution.—In Table II values found for $[\mathrm{H}^+]_\mathrm{R}+[\mathrm{Be}^{++}]_\mathrm{R}$, i. e. sums of amounts of ions in the resin phase are always larger than the total equivelent capacities of the resin. This means that two hydrogen ions do not exchange for one beryllium ion and some complexes are formed in the solution.

The formation of complexes is also shown by spectrophotometric evidence. In the region of higher concentrations of hydrochloric acid, mixed solutions of beryllium chloride and hydrochloric acid have a yellow color. In Fig. 3 spectrophotometric curves of beryllium chloride, hydrochloric acid and their mixture are shown. The mixture absorbs more strongly than the components and new absorption bands appear at 265 and 370mμ.

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[11] H. C. Gupta, *Naturwissenschaften*, **43**, 543 (1956).

[12] As the activity coefficients of beryllium and hydrogen ions in the mixtures are not known, neither the rtelaive affinity of the exchange equilibrium of beryllium and hydrogen nor the Donnan equilibrium constant can be calculated.

TABLE II

A PART OF THE DATA OBTAINED

( ): meq./ml., [ ]: meq.

Original soln.		External soln. at equilibrium			Quasi-exchange phase		Resin phase			Total exchange capacity
$(H^+)_O$	$(Be^{++})_O$	$(H^+)_S$	$(Cl^-)_S$	$(Be^{++})_S = (Cl^-)_S - (H^+)_S$	$[H^+]_Q$	$[Be^{++}]_Q$	$[H^+]_R$	$[Be^{++}]_R$	$[H^+]_R + [Be^{++}]_R$	E meq.
1.27	0.10	1.40	1.44	0.04	1.53	0.00_8	15.04	1.14	16.18	16.04
1.56	0.50	1.76	2.09	0.33	1.84	0.00_5	12.18	3.98	16.06	15.24
1.10	1.0	1.41	2.05	0.64	2.11	0.10	9.00	7.63	16.63	15.12
1.16	5.0	1.76	6.03	4.27	4.74	3.10	3.28	13.61	16.89	15.12

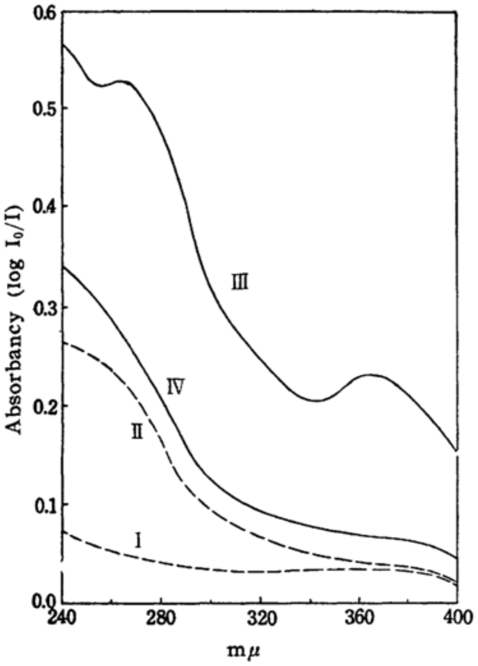

Fig. 3. Absorption curves of beryllium chloride, hydrochloric acid and their mixture.
Curve I: 5 N HCl, II: 3 N $BeCl_2$, III: Mixture of 3 N $BeCl_2$ and 5 N HCl, IV: Sum of I and II.

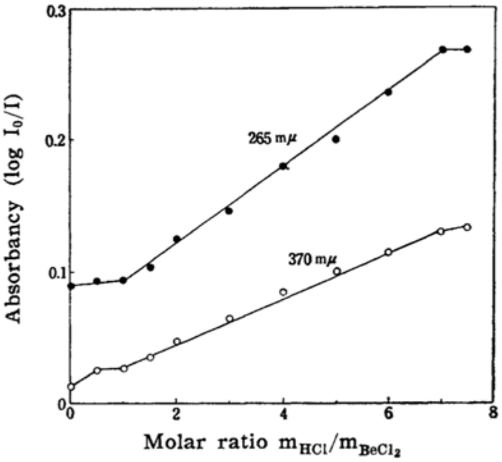

Fig. 4. Relations between absorbancy and molar ratio. Black and white circles denote the absorbancy values at 265 and 370 mμ, respectively.

This supports the view that complexes are formed between beryllium chloride and hydrochloric acid.

An attempt was made to determine the composition of the complexes thus formed by the molar ratio method[13]. The result is shown in Fig. 4. The line has a break at $m_{HCl}/m_{BeCl_2}=1$. This may suggest that the formation of complexes begins at 1 N of hydrochloric acid concentration. Another break seems to be present at $m_{HCl}/m_{BeCl_2}=7$. Since beryllium chloride solution was prepared by dissolving beryllium hydroxide into hydrochloric acid, it was difficult to prepare the mixture of beryllium chloride and hydrochloric acid of larger molar ratio, m_{HCl}/m_{BeCl_2} than 7.5 and to confirm the existence of the second break.

To find out whether the formed complex is cationic or anionic, the solution containing 3 N beryllium chloride and 5 N hydrochloric acid was passed through a column of chloride form of Dowex 1-X8. The ionic species containing beryllium ion was not adsorbed on the resin and the resin and the complex thus formed was found to be cationic.

Kraus et al.[3] reported that the beryllium ion of the tracer scale was not captured by the anion-exchange resin, Dowex 1, in 7 N and 12 N hydrochloric acid. Diamond[4] measured the distribution ratios of the beryllium ion of tracer scale and concluded that the beryllium ion existed as a cationic chloro-complex, probably a polynuclear one. The results of our experiments agree well with their conclusions.

Summary

The ion exchange equilibrium was

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[13] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).

studied in the concentrated solutions of beryllium chloride and hydrochloric acid. The amount of water in the resin was calculated from the difference of hydrogen ion concentration before and after the ion exchange equilibrium. A cationic complex containing beryllium was found to be formed in the solution.

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