Ion Exchange in Concentrated Solutions. III. Magnesium Chloride-Hydrochloric Acid and Aluminum Chloride-Hydrochloric Acid Systems[*]

By Hitoshi OHTAKI and Kazuo YAMASAKI

(Received January 6, 1958)

The ion-exchange equilibria in sodium chloride-hydrochloric acid[1], lithium chloride-hydrochloric acid[1] and beryllium chloride-hydrochloric acid[2] systems were studied in the previous reports. In the present report, the equilibria in magnesium chloride-hydrochloric acid and aluminum chloride-hydrochloric acid systems are investigated.

Experimental

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 water content of the resin used was determined from

---

[*] Read before the 10th Annual Meeting of the Chemical Society of Japan held at Tokyo in April, 1957.

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

[2] H. Ohtaki and K. Yamasaki, This Bulletin, **31**, 6 (1958).

the weight decrease on drying at 110°C. It was about 16.58~20.62%, i. e., 0.20~0.23 ml. per gram resin used for magnesium chloride-hydrochloric acid system and 9.82%, i. e., 0.11 ml. for that used for aluminum chloride-hydrochloric acid system. The amount of the resin used in one batch experiment was 3.6 g. The exchange capacity of the resin used was determined in each series of experiments.

Reagents.—Magnesium chloride of reagent grade was used without purification. Aluminum chloride was dissolved in water to prepare a concentrated solution. After adding hydrochloric acid, the concentrated solution was cooled by the freezing mixture and the stream of dried hydrogen chloride was passed through it. White crystals of aluminum chloride precipitated. After filtration the crystals were washed with cold concentrated hydrochloric acid and then dissolved in water containing a small amount of hydrochloric acid to prevent hydrolysis. This solution was mixed with hydrochloric acid to prepare sample solutions.

Procedure. — All the procedures used for determination of the adsorbed water are similar to those used in the previous studies[1,2]. Mixtures of 0.1~5 N magnesium chloride and 0~11 N hydrochloric acid and those of 0.2~0.9 N aluminum chloride and 0.5~11 N hydrochloric acid were used. In the concentration range lower than 0.5 N of hydrochloric acid the hydrolysis of aluminum chloride occurred, while too much presence of hydrochloric acid caused to crystallize some part of aluminum chloride. Therefore the concentration of hydrochloric acid was maintained lower than 3 N when that of aluminum chloride was 0.9 N.

The concentration of the magnesium ion was determined by titration with 0.02 and 0.001M ethylenediaminetetraacetate solution using Eriochrome Black T as indicator[3]. The concentration of the aluminum ion was titrated by 0.03 M ethylenediaminetetraacetate solution with Chrome Azurol S as indicator[4]. Hydrogen ion concentrations of these solutions were determined by titration with 0.1 N barium hydroxide. Brom Cresol Purple (pH of the color change: 5.2~6.8) was used as indicator for the magnesium chloride-hydrochloric acid system, while Methyl Yellow (pH of the color change: 2.9~4.0) was used for the aluminum chloride-hydrochloric acid system, because aluminum chloride was hydrolyzed in higher pH range.

Results and Discussion

1) Water in the Resin. — The amount of water adsorbed by the resin which was in contact with the external solution was estimated indirectly by measuring the amounts of the hydrogen ion before and after the ion-exchange equilibrium and using the following equation[1,2]:

$$A'=\frac{(\mathrm{H}^+)_\mathrm{S}\cdot V+[\mathrm{H}^+]_\mathrm{Q}+[\mathrm{H}^+]_\mathrm{R}-[\mathrm{H}^+]_\mathrm{O}-E}{(\mathrm{H}^+)_\mathrm{S}} \qquad (1)$$

In equation (1), A' denotes the adsorbed water in the resin at equilibrium and round and square brackets denote the concentration and the amount of ions, respectively. V represents the volume of the original solution taken up in one batch experiment (30 ml.); subscripts S, Q, R and O denote the external solution at equilibrium, the quasi-exchange phase*, the resin phase at equilibrium and the original solution, respectively[1,2]; E represents the total exchange capacity of the resin used. When the original water content of the resin used is represented by A'', the total amount of the water in the resin is

$$A = A' + A''. \qquad (2)$$

Amounts of the water per gram of dried resin thus determined are given in Tables I and II together with other data. As clearly shown in these tables values of the water in the resin for the aluminum chloride-hydrochloric acid system are generally smaller than those for beryllium chloride-hydrochloric acid[2] and magnesium chloride-hydrochloric acid systems. It is known that the larger the charge of the ion exchanged in the resin phase is, the more the resin shrinks. The experimental data shown in Tables I and II are consistent with this fact.

2) Ionic Species in the External Solution and the Resin.—As shown in Tables I and II, the sum of the amounts of hydrogen ion, $[\mathrm{H}^+]_\mathrm{R}$ and metal ion $[\mathrm{Mg}^{2+}]_\mathrm{R}$ or $[\mathrm{Al}^{3+}]_\mathrm{R}$ in the resin phase is larger than the total exchange capacity of the resin used. These discrepancies are supposed to have been caused by the formation of complexes* such as MgCl^+, AlCl^{2+} or $\mathrm{AlCl_2}^+$ which exchange with hydrogen ions. The existence of such complexes containing chlorine in the resin phase is verified by the detection of a minute amount of chloride ion in the solution eluted from the resin by sodium nitrate even after washing the resin thoroughly with water.

---

[3] G. Schwarzenbach, "Die komplexometrische Titration", F. Enke Stuttgart, 2nd Ed. p. 54 (1956).

[4] M. Theis, *Z. anal. Chem.*, **114**, 106 (1955).

* This 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. See References 1 and 2.

TABLE I

A PART OF THE DATA FOR THE $MgCl_2$-HCl SYSTEM.

(1) Concentration of the original solution of $MgCl_2$, $(Mg^{2+})_O=0.11$ N; total exchange capacity of the resin, $E=15.00$ meq.

$(H^+)_O$	0.32	0.65	1.09	1.93	4.31	8.76	N
$(H^+)_S$	0.41	0.75	1.21	2.04	4.44	8.82	N
$(Mg^{2+})_S$	0.00_8	0.02_1	0.04	0.07	0.09	0.09	N
$[H^+]_Q$	0.24	0.56	1.08	1.56	5.11	11.42	meq.
$[Mg^{2+}]_Q$	0.09	0.10	0.04	0.02	0.02	0.06	meq.
$[H^+]_R$	12.89	13.50	13.86	14.30	14.72	14.89	meq.
$[Mg^{2+}]_R$	3.45	2.75	2.37	1.40	0.75	0.43	meq.
$[H^+]_R+[Mg^{2+}]_R$	16.34	16.25	16.23	15.70	15.47	15.32	meq.
water in the resin, *A*.	0.90	1.12	1.13	0.89	0.84	0.69	ml./g. dry resin.

(2) $(Mg^{2+})_O=0.29$ N, $E=15.00$ meq.

$(H^+)_O$	0.00	0.61	2.06	3.09	5.12	8.18	N
$(H^+)_S$	0.20	0.79	2.24	3.23	5.24	8.25	N
$(Mg^{2+})_S$	0.00_9	0.11	0.23	0.26	0.28	0.28	N
$[H^+]_Q$	0.19	0.70	2.06	3.72	5.81	11.96	meq.
$[Mg^{2+}]_Q$	0.01	0.01	0.03	0.02	0.02	0.08	meq.
$[H^+]_R$	9.48	11.08	13.40	14.05	14.37	14.52	meq.
$[Mg^{2+}]_R$	9.03	6.53	2.86	2.01	1.08	0.98	meq.
$[H^+]_R+[Mg^{2+}]_R$	18.51	17.61	16.26	16.06	15.45	15.50	meq.
water in the resin, *A*.	1.27	1.12	1.10	0.93	0.76	0.74	ml./g. dry resin.

(3) $(Mg^{2+})_O=0.50$ N, $E=14.08$ meq.

$(H^+)_O$	0.00	1.02	3.04	5.11	8.17	10.78	N
$(H^+)_S$	0.29	1.21	3.17	5.21	8.15	10.51	N
$(Mg^{2+})_S$	0.07	0.31	0.45	0.48	0.48	0.47	N
$[H^+]_Q$	0.19	1.09	3.44	7.31	10.73	14.01	meq.
$[Mg^{2+}]_Q$	0.01	0.03	0.04	0.11	0.20	0.24	meq.
$[H^+]_R$	5.95	10.15	12.63	13.27	13.60	13.59	meq.
$[Mg^{2+}]_R$	13.13	6.91	2.63	1.86	1.39	1.42	meq.
$[H^+]_R+[Mg^{2+}]_R$	19.08	17.06	15.26	15.13	14.99	15.01	meq.
water in the resin, *A*.	1.05	1.04	0.92	0.91	0.66	0.43	ml./g. dry resin.

(4) $(Mg^{2+})_O=1.00$ N, $E=14.08$ meq.

$(H^+)_O$	0.00	1.02	3.02	5.17	8.24	10.37	N
$(H^+)_S$	0.36	1.29	3.20	5.29	8.25	10.13	N
$(Mg^{2+})_S$	0.48	0.74	0.91	0.96	0.97	0.99	N
$[H^+]_Q$	0.52	1.62	4.37	8.01	13.46	14.01	meq.
$[Mg^{2+}]_Q$	0.05	0.07	0.08	0.30	0.63	0.58	meq.
$[H^+]_R$	3.54	8.11	11.36	12.53	13.02	13.05	meq.
$[Mg^{2+}]$	16.96	10.00	4.90	3.14	2.51	2.51	meq.
$[H^+]_R+[Mg^{2+}]_R$	20.50	18.11	16.26	15.67	15.53	15.56	meq.
water in the resin, *A*.	1.09	1.06	1.01	0.86	0.86	0.46	ml./g. dry resin.

(5) $(Mg^{2+})_O=2.99$ N, $E=14.08$ meq.

$(H^+)_O$	0.27	0.80	2.53	7.09	N
$(H^+)_S$	0.66	1.14	2.77	7.13	N
$(Mg^{2+})_S$	2.55	2.65	2.81	2.90	N
$[H^+]_Q$	1.92	2.80	5.75	13.20	meq.
$[Mg^{2+}]_Q$	1.09	0.69	0.48	1.98	meq.
$[H^+]_R$	2.33	3.96	7.34	10.66	meq.
$[Mg^{2+}]_R$	18.67	16.47	11.36	6.26	meq.
$[H^+]_R+[Mg^{2+}]_R$	21.00	20.43	18.70	16.92	meq.
water in the resin, *A*.	1.16	1.12	1.06	0.79	ml./g. dry resin.

(6) $(\mathrm{Mg^{2+}})_\mathrm{O}=4.96$ N, $E=14.08$ meq.

$(\mathrm{H^+})_\mathrm{O}$	0.00	0.80	5.13	N
$(\mathrm{H^+})_\mathrm{S}$	0.41	1.14	5.26	N
$(\mathrm{Mg^{2+}})_\mathrm{S}$	4.58	4.72	4.92	N
$[\mathrm{H^+}]_\mathrm{Q}$	1.39	3.60	10.69	meq.
$[\mathrm{Mg^{2+}}]_\mathrm{Q}$	3.62	3.15	2.71	meq.
$[\mathrm{H^+}]_\mathrm{R}$	1.30	2.91	8.11	meq.
$[\mathrm{Mg^{2+}}]_\mathrm{R}$	20.48	18.02	9.98	meq.
$[\mathrm{H^+}]_\mathrm{R}+[\mathrm{Mg^{2+}}]_\mathrm{R}$	21.78	20.93	18.09	meq.
water in the resin, *A*.	1.06	1.17	0.82	ml./g. dry resin.

TABLE II

A PART OF THE DATA FOR THE $\mathrm{AlCl_3}$-HCl SYSTEM.*

(1) Concentration of the original solution of $\mathrm{AlCl_3}$, $(\mathrm{Al^{3+}})_\mathrm{O}=0.18$ N; total exchange capacity of the resin, $E=16.69$ meq.

$(\mathrm{H^+})_\mathrm{O}$	1.07	2.17	3.23	5.30	8.47	11.65	N
$(\mathrm{H^+})_\mathrm{S}$	1.25	2.37	3.37	5.44	8.53	11.43	N
$(\mathrm{Al^{3+}})_\mathrm{S}$	0.03	0.07	0.12	0.14	0.14	0.15	N
$[\mathrm{H^+}]_\mathrm{Q}$	1.13	2.84	4.69	8.33	16.19	20.26	meq.
$[\mathrm{H^+}]_\mathrm{R}$	13.49	14.61	15.17	15.54	15.68	15.70	meq.
$[\mathrm{Al^{3+}}]_\mathrm{R}$	3.99	2.66	2.41	1.28	1.33	1.28	meq.
$[\mathrm{H^+}]_\mathrm{R}+[\mathrm{Al^{3+}}]_\mathrm{R}$	17.48	17.27	17.58	16.82	17.01	16.98	meq.
water in the resin, *A*.	0.95	0.85	0.78	0.76	0.72	0.52	ml./g. dry resin.

(2) $(\mathrm{Al^{3+}})_\mathrm{O}=0.52$ N, $E=16.69$ meq.

$(\mathrm{H^+})_\mathrm{O}$	0.38	0.65	1.12	2.17	5.01	10.66	N
$(\mathrm{H^+})_\mathrm{S}$	0.72	0.98	1.41	2.42	5.20	10.59	N
$(\mathrm{Al^{3+}})_\mathrm{S}$	0.12	0.14	0.26	0.39	0.49	0.39	N
$[\mathrm{H^+}]_\mathrm{Q}$	0.74	1.13	1.49	3.38	8.66	18.80	meq.
$[\mathrm{H^+}]_\mathrm{R}$	7.87	8.77	10.30	12.80	14.78	15.19	meq.
$[\mathrm{Al^{3+}}]_\mathrm{R}$	14.23	11.76	9.35	5.18	2.03	1.25	meq.
$[\mathrm{H^+}]_\mathrm{R}+[\mathrm{Al^{3+}}]_\mathrm{R}$	22.10	20.53	19.65	17.98	16.81	16.44	meq.
water in the resin, *A*.	0.89	0.92	0.83	0.86	0.74	0.43	ml./g. dry resin.

(3) $(\mathrm{Al^{3+}})_\mathrm{O}=0.77$ N, $E=16.69$ meq.

$(\mathrm{H^+})_\mathrm{O}$	0.45	1.17	2.16	7.41	N
$(\mathrm{H^+})_\mathrm{S}$	0.82	1.44	2.39	7.64	N
$(\mathrm{Al^{3+}})_\mathrm{S}$	0.29	0.51	0.66	0.68	N
$[\mathrm{H^+}]_\mathrm{Q}$	1.07	2.30	3.87	13.47	meq.
$[\mathrm{H^+}]_\mathrm{R}$	6.62	9.34	11.96	14.80	meq.
$[\mathrm{Al^{3+}}]_\mathrm{R}$	14.59	11.36	7.07	1.59	meq.
$[\mathrm{H^+}]_\mathrm{R}+[\mathrm{Al^{3+}}]_\mathrm{R}$	21.21	20.70	19.03	16.39	meq.
water in the resin, *A*.	1.23	0.73	0.87	0.84	ml./g. dry resin.

(4) $(\mathrm{Al^{3+}})_\mathrm{O}=0.90$ N, $E=16.69$ meq.

$(\mathrm{H^+})_\mathrm{O}$	0.79	1.26	2.21	N
$(\mathrm{H^+})_\mathrm{S}$	1.14	1.58	2.48	N
$(\mathrm{Al^{3+}})_\mathrm{S}$	0.58	0.76	0.78	N
$[\mathrm{H^+}]_\mathrm{Q}$	1.50	2.06	3.39	meq.
$[\mathrm{H^+}]_\mathrm{R}$	6.99	8.89	11.29	meq.
$[\mathrm{Al^{3+}}]_\mathrm{R}$	15.50	12.10	7.88	meq.
$[\mathrm{H^+}]_\mathrm{R}+[\mathrm{Al^{3+}}]_\mathrm{R}$	22.49	20.99	19.17	meq.
water in the resin, *A*.	1.04	0.87	0.88	ml./g. dry resin.

* The amount of $\mathrm{Al^{3+}}$ ion in the quasi-exchange phase is too small to be determined in all cases. Therefore values of $[\mathrm{Al^{3+}}]_\mathrm{Q}$ are not given in this table.

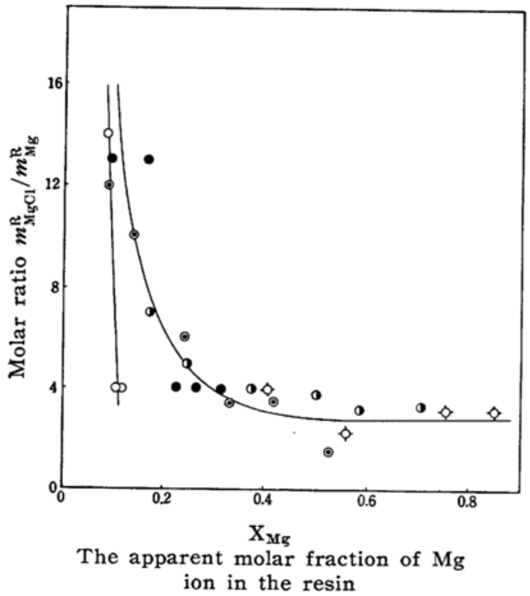

Fig. 1. Relation between molar ratio of $MgCl^+$ to Mg^{2+} in the resin and the apparent molar fraction of Mg ion in the resin.
○ 0.1 ● 0.3 ⊙ 0.5 ◑ 1.0
◇ 5.0 N $MgCl_2$

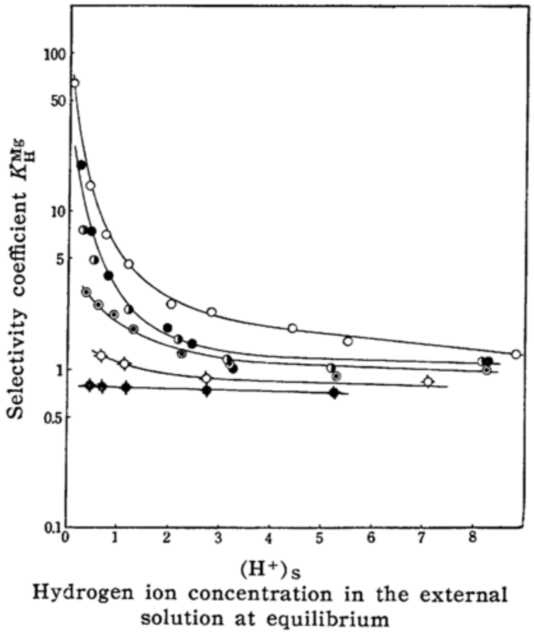

Fig. 2. Selectivity coefficients of $MgCl_2$ $-HCl$ system plotted against $(H^+)_S$.
○ 0.1 ● 0.3 ◑ 0.5 ⊙ 1.0
◇ 3.0 ◆ 5.0 N $MgCl_2$

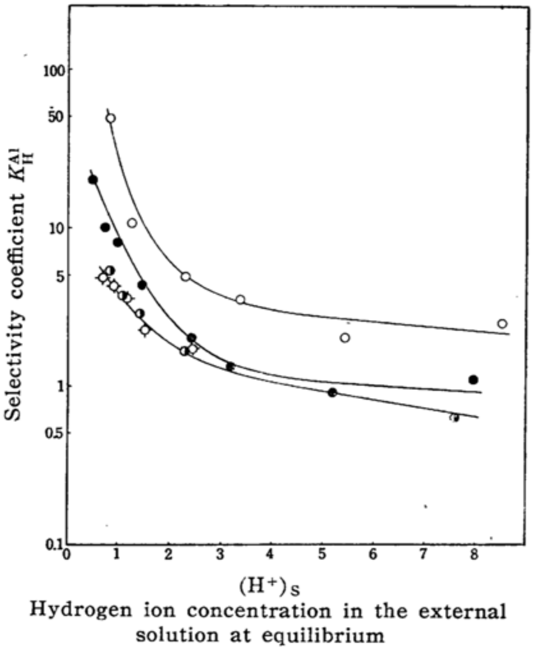

Fig. 3. Selectivity coefficients of $AlCl_3$ $-HCl$ system plotted against $(H^+)_S$.
○ 0.18 ● 0.53 ◑ 0.77
◇ 0.90 N $AlCl_3$

Amounts of Mg^{2+} and $MgCl^+$ ions in the resin phase can be readily calculated from the values of *E*, $[H^+]_R$ and $[Mg^{2+}]_R$ provided that no other complexes are formed. In Fig. 1 values of the molar ratio of $MgCl^+$ to Mg^{2+} ion in the resin m^R_{MgCl}/m^R_{Mg} are plotted against the apparent molar fraction of magnesium ion in the resin, X_{Mg}*. The molar ratio increases as X_{Mg} decreases. Thus, in the range of lower concentration of magnesium chloride and at the same time of higher concentration of hydrochloric acid, magnesium in the resin phase consists almost entirely of $MgCl^+$, and it is possible that a large part of magnesium present in the external solution also forms the chloro-complex $MgCl^+$.

In Fig. 2 values of selectivity coefficient of magnesium calculated after the formula

$$K_H^{Mg}=\frac{(H^+)_S\{[Mg^{2+}]_Q+[Mg^{2+}]_R\}}{(Mg^{2+})_S\{[H^+]_Q+[H^+]_R\}} \quad (3)$$

are plotted against $(H^+)_S$, the hydrogen ion concentration of the external solution. In the range of higher values of $(H^+)_S$, as already described, the ionic species predominant is considered to be $MgCl^+$. Consequently the selectivity coefficient thus calculated represents that of the exchange

---

* Hydroxo-complexes are formed with difficulty in such a strong acidic system as the resin phase concerned. Actually water may be coordinated to these ions in forming $[Mg(OH_2)_5Cl]^{2+}$, $[Al(OH_2)_5Cl]^{2+}$, $[Al(OH_2)_4Cl_2]^+$.

* $X_{Mg}=\frac{1}{2}[Mg^{2+}]_R/\{[H^+]_R+\frac{1}{2}[Mg^{2+}]_R\}$

system of $MgCl^+—H^+$ rather than that of $Mg^{2+}—H^+$ system.

The selectivity coefficient of the aluminum chloride-hydrochloric acid system was calculated by the similar formula as (3):

$$K_{H}^{Al}=\frac{(H^+)_S\{[Al^{3+}]_Q+[Al^{3+}]_R\}}{(Al^{3+})_S\{[H^+]_Q+[H^+]_R\}} \tag{4}$$

These data are plotted against $(H^+)_S$ in Fig. 3. In this system it is difficult to estimate the amount of individual species of aluminum like Al^{3+}, $AlCl^{2+}$ or $AlCl_2^+$ in the similar way as in the magnesium chloride-hydrochloric acid system.

Summary

Ion-exchange equilibria in the concentrated solutions of magnesium chloride-hydrochloric acid and aluminum chloride-hydrochloric acid system were studied. Amounts of the water present in the resin at equilibrium were estimated for these systems. In the magnesium chloride-hydrochloric acid system a large part of magnesium in the resin exists as $MgCl^+$ at equilibrium when the concentration of hydrochloric acid is high. Selectivity coefficients of magnesium chloride-hydrochloric acid and of aluminum cholride-hydrochloric acid systems were calculated.

A part of of the expenses of the present study was defrayed by Grant-in-Aid for Fundamental Scientific Research from Ministry of Education.

Chemical Institute, Faculty of
Science, Nagoya University
Chikusa-ku, Nagoya