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Abstract

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INVESTIGATION OF THE ION-EXCHANGE SYSTEM $H^{\cdot}$, $Ca^{\cdot\cdot}$ $\|$ R', Cl'—H_2O BY THE RAY METHOD

The exchange of the calcium ion for the hydrogen ion, which plays an important role in the process of water deionization, has been studied by many authors ($^{1-4}$ and others) for solutions with a low content of calcium salt. However, the study of exchange in the system $Ca^{\cdot\cdot}$—$H^{\cdot}$ for the region of concentrated solutions of HCl and $CaCl_2$ is of considerable theoretical and practical interest. In the present work, by a method of physicochemical analysis that makes it possible to describe the entire system, exchange in the system $Ca^{\cdot\cdot}$—$H^{\cdot}$ on the cation exchanger KU-2 at a temperature of $25 \pm 0.05°$ was investigated. The method for studying ion-exchange systems and the procedure for constructing the diagram are described in work (^{5}). Before the experiments, the ion exchanger, swollen in water, in the H-form was pressed on filter paper. The equilibrium concentration of acid in the solution was determined by titration with NaOH with methyl red as indicator, and the concentration of calcium chloride by complexometric titration with Trilon B. The content of the hydrogen ion and the calcium ion in the smole was determined, as described above, after their desorption in a column with the aid of a 1 N KCl solution. Equilibrium in the system was in the main established within 2-3 h. The actual time of mixing was 8-10 h. From the experimental data (see Table 1) a diagram of the quaternary ion-exchange system $H^{\cdot}$, $Ca^{\cdot\cdot}$ $\|$ R', Cl'—H_2O was constructed, shown in Fig. 1.

The direction of the course of the ion-exchange rays (I—$VIII$) depends on the degree of exchange of the ions and the magnitude of swelling of the ion exchanger (the initial aqueous solutions are denoted by crosses). Let us consider the initial portion of rays I, II, and III in Fig. 1. To determine the concentration of the acid formed during exchange, let us connect by a straight line the composition point of the initial solution (on the concentration axis

Table 1

Fig. 1

Figure 1: Fig. 1

Rays	Conc. in equilibrium aqueous phase, wt. % $CaCl_2$	Conc. in equilibrium aqueous phase, wt. % HCl	Specific volume at 25°	Distribution coefficient $Ca^{\cdot\cdot}$	Distribution coefficient $H^{\cdot}$	Rays	Conc. in equilibrium aqueous phase, wt. % $CaCl_2$	Conc. in equilibrium aqueous phase, wt. % HCl	Specific volume at 25°	Distribution coefficient $Ca^{\cdot\cdot}$	Distribution coefficient $H^{\cdot}$
I	4.09	0.84	1.040	5.83	0.97		12.80	8.89	1.149	1.48	0.46
I	2.41	1.72	1.032	8.64	1.63		9.05	8.88	1.118	1.78	0.67
I	1.32	2.33	1.023	12.48	2.45		3.32	8.46	1.068	3.02	1.17
I	0.50	2.62	1.018	21.63	3.57	VI	27.63	12.97	1.300	0.88	0.03
II	15.10	0.59	1.134	1.66	0.05	VI	25.03	13.02	1.273	0.95	0.06
II	12.67	1.57	1.115	1.97	0.08	VI	20.54	12.78	1.238	1.09	0.14
II	9.41	2.86	1.092	2.37	0.64	VI	13.31	11.83	1.177	1.39	0.37
II	5.32	4.19	1.067	3.46	1.06	VI	9.08	11.23	1.133	1.67	0.58
III	18.08	2.69	1.162	1.37	0.09	VI	5.51	10.41	1.091	2.16	0.84
III	12.86	4.05	1.125	1.75	0.43	VII	1.94	9.02	1.060	3.48	1.34
III	7.18	5.55	1.084	2.44	0.90	VII	20.70	15.60	1.254	1.14	0.06
III	4.09	6.10	1.065	3.35	1.23	VII	17.19	15.36	1.217	1.27	0.14
III	2.12	6.43	1.046	4.62	1.57	VII	13.82	14.65	1.184	1.38	0.27
III	0.89	6.18	1.033	6.92	2.02	VII	8.99	12.92	1.136	1.64	0.53
IV	21.55	5.27	1.212	1.12	0.14	VIII	0.80	17.04	1.166	1.66	0.34
IV	16.89	5.98	1.170	1.32	0.31	VIII	8.67	16.48	1.149	1.69	0.42
IV	11.52	6.79	1.125	1.66	0.58	VIII	6.43	15.14	1.120	1.85	0.57
V	34.09	7.60	1.331	0.73	0.02	VIII	4.79	13.77	1.102	2.07	0.73
V	31.06	7.95	1.325	0.80	0.03	VIII	3.05	12.47	1.085	2.40	0.94
V	25.87	8.38	1.261	0.93	0.08	VIII	1.61	10.66	1.063	3.18	1.23
V	18.74	8.78	1.200	1.18	0.23	VIII	0.44	8.61	1.041	5.16	1.74

$CaCl_2$) with the next one on the ray, and extend the straight line to its intersection with the ordinate axis (HCl). The point of intersection gives the concentration of the acid formed during exchange. By dividing this graphically obtained acid concentration (percent) by the initial concentration of $CaCl_2$ (percent), we obtain a certain ratio, which we compare with the stoichiometric one (for 100% exchange the final concentration of the HCl formed should be approximately 0.66 of the initial concentration of $CaCl_2$).

Fig. 1

Thus, as the initial concentration of $CaCl_2$ decreases, the ratio % HCl/% $CaCl_2$ approaches the theoretical value. Exchange of the hydrogen ion for the calcium ion takes place in accordance with stoichiometry, but instead of the simplest scheme:

$$\mathrm{Ca}^{\bullet\bullet}_{\mathrm{(solution)}} + 2\mathrm{H}^{\bullet}_{\mathrm{(solid)}} \rightleftarrows \mathrm{Ca}^{\bullet\bullet}_{\mathrm{(solid)}} + 2\mathrm{H}^{\bullet}_{\mathrm{(solution)}}$$

a more complex one is realized:

$$\mathrm{Ca}^{\bullet\bullet}_{\mathrm{(solution)}} + [2\mathrm{H}^{\bullet} n\,\mathrm{H_2O}]_{\mathrm{(solid)}} \rightleftarrows \mathrm{Ca}^{\bullet\bullet}_{\mathrm{(solid)}} +$$

$$+ 2\mathrm{H}^{\bullet}_{\mathrm{(solution)}} + n\,\mathrm{H_2O},$$

i.e., the water of the previously swollen cation exchanger passes into the solution and dilutes it.

Table 2

	Ray I	Ray II	Ray III
HCl concentration during exchange, %*	3.00	6.7	8.3
Initial $CaCl_2$ concentration, %	5.5	16.5	27.0
$\frac{\mathrm{HCl}\,(\%)}{\mathrm{CaCl_2}\,(\%)}$	0.55	0.41	0.31

* Determined graphically.

This effect should be especially pronounced at high concentrations of $CaCl_2$.

In the field of unsaturated solutions of the diagram there are various concentrations of acid and calcium chloride; during exchange it is possible to foresee three cases depending on the ratio of the values nH_2O in the cation exchanger and $H_2O/2H^{\bullet}$ in solution: $n < H_2O/2H^{\bullet}$, $n = H_2O/2H^{\bullet}$, and $n > H_2O/2H^{\bullet}$.

In the first case the acidity of the solution will increase; in the second it will remain unchanged; and in the third the acidity will decrease. This is confirmed by the course of the rays: ray *I*—*III*—the acidity increases; ray *V*—the acidity does not change; ray *VI*—*VIII*—the acidity decreases.

The same can be confirmed by graphically determining the acidity obtained as a result of exchange and comparing it with the initial acidity.

Table 3

HCl concentration, %*	8.3	9.2	12.5	13.25	15.2
Initial concentration of $CaCl_2$, %	27.0	24.7	36.5	30.0	23.0
Initial concentration of HCl, %	0	4.7	7.25	13.0	15.75
Change in HCl concentration, times	–	1.9	1.7	1.02	0.96
	The acidity of the solution increases	The acidity of the solution increases	The acidity of the solution increases	The acidity of the solution increases	The acidity of the solution decreased

* Determined graphically.

As exchange proceeds (see the rays in Fig. 1), the amount of water passing into the solution increases, which leads, for rays VI—$VIII$, to even greater dilution than is indicated in Table 3. Hence, in particular, it follows that more or less pure hydrochloric acid (with a small content of $CaCl_2$) cannot be obtained under static conditions on this sample of swollen cation exchanger at a concentration greater than 8-10%. The absence of a convergence point (pole) for the ion-exchange rays indicates that the course of the rays is influenced by the water contained in the ionite ([6]).

The diagram contains isolines of the distribution coefficients of the calcium ion. Each line corresponds to a definite value of K_{dist} (shown by bold numbers in Fig. 1). The course of the isolines is of interest. As the acid concentration increases, there is a monotonic decrease in K_{dist} up to a certain acid concentration; then the distribution coefficient of the calcium ion remains practically constant.

This phenomenon is readily explained with the aid of hydration theory, proceeding from the interactions of the strongly hydrated calcium ion occurring in hydrochloric acid solutions. As is known, the exchange constant of a given metal depends on the degree of its hydration. Its magnitude increases as the degree of hydration of the calcium ion in HCl solutions decreases, since with increasing acid concentration the amount of free water decreases and the effective radius of the calcium ion becomes smaller. Thus, Diamond, Street, and Seaborg (^{2}), studying the distribution of the calcium isotope on the cation exchanger Dowex-50 as a function of hydrochloric acid concentration, indicate a minimum in the calcium distribution coefficient at a 6-molar HCl concentration, followed by its increase when the HCl concentration is raised to 12 M. The calcium ion also becomes increasingly dehydrated as the salt concentration is raised. From the diagram, covering the acid region of approximately 6-molar concentration, it is seen that the cessation of the decrease in the value of K_{dist} as a function of the acid content in the solution shifts toward the abscissa axis as the salt concentration is increased. For solutions with a calcium chloride concentration of 27% and higher, K_{dist} of the calcium ion retains a constant value independently of the acid concentration in the solution; i.e., the hydrogen ions on the ionite are almost entirely replaced by calcium ions (in Fig. 1, the isolines with $K_{\text{dist}} = 0.9$ and to the right). In this case K_{dist} reaches the theoretically possible value. Thus, the decrease in the effective radius of the Ca ion with increasing HCl concentration, as well as the dehydration of the calcium ion with increasing concentration of the salt itself, prove quite sufficient to overcome the opposite influence on the degree of exchange caused by the increase in the concentration of the hydrogen ion in the solution.

Consequently, the actual result of exchange is a consequence of the process of decreasing absorption of the calcium ion as a result of displacement by the hydrogen ion–

of the electrode with increasing acid concentration, and, on the other hand, an increase in the absorption of the Ca ion due to its dehydration and the corresponding increase in the ion-exchange constant. For the region of the diagram adjacent to the origin, where the solutions are weakly concentrated and the dehydration phenomenon is not observed, the isolines are rectilinear in character; here K_{dist} decreases monotonically.

As Diamond indicates (^{1}), complex formation of the Ca ion in HCl solutions is insignificant and has no noticeable effect on the degree of ion exchange up to a concentration of 6 M HCl.

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