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Abstract

Full Text

CHEMISTRY

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INVESTIGATION OF ION-EXCHANGE PROCESSES BY THE METHOD OF PHYSICOCHEMICAL ANALYSIS

The simplest ion-exchange reaction, from the standpoint of the phase rule, is described within the limits of a quaternary reciprocal system. For example, for the case of exchange of hydrogen for a metal,

$$\mathrm{RH} + \mathrm{MA} \rightleftharpoons \mathrm{RM} + \mathrm{HA}$$

we have the system $(\mathrm{H}, \mathrm{M}^{\cdot})$, $(\mathrm{R}^{-}, \mathrm{A}^{-})$, H_2O. If one remains in the region of unsaturated aqueous solutions, then the system will contain one solid phase (the ion exchanger). In this case, to a first approximation, it should be regarded as a phase of variable composition, of the type of a solid solution. Ion-exchange processes can be studied by the method of physicochemical analysis by analogy with extraction processes ($^{1-4}$). In doing so, one may use the method of constructing a diagram (composition—property) proposed by A. V. Nikolaev for extraction systems (^{5}), which makes it possible to describe the entire system both for dilute and for concentrated aqueous solutions, which is convenient for theoretical and technological calculations of ion-exchange processes.

Fig. 1. Diagram of the ion-exchange system NH_4Cl—HCl—RH—H_2O at 25°

We studied the ion-exchange system ammonium chloride—hydrochloric acid—cation exchanger (UK-2 in the H-form)—water at a temperature of 25 ± 0.05°C. The conditioned ion exchanger was first dried in a vacuum oven at a temperature of 110°. Equilibrium during ion exchange was achieved—

Table 1

Compositions of the aqueous and resin phases of the ion-exchange system NH_4Cl—HCl—RH—H_2O at 25°

Rays	Conc. in equilibrium aqueous phase, wt.% NH_4Cl	Conc. in equilibrium aqueous phase, wt.% HCl	Specific gravity at 25°	Distribution coefficient NH_4^+	Distribution coefficient H^+	Rays	Conc. in equilibrium aqueous phase, wt.% NH_4Cl	Conc. in equilibrium aqueous phase, wt.% HCl	Specific gravity at 25°	Distribution coefficient NH_4^+	Distribution coefficient H^+
I	4.89	none	1.018	–	–	III	15.09	none	1.047	–	–
I	4.72	0.01	1.018	5.06	4.23	III	14.48	0.61	1.049	1.57	1.60
I	4.11	0.63	1.019	4.99	4.03	III	11.91	3.73	1.056	1.44	1.29
I	2.92	1.78	1.021	4.86	3.83	III	9.78	7.06	1.065	1.32	1.09
I	2.28	2.88	1.023	4.48	3.32	III	7.84	10.67	1.077	1.18	0.96
I	1.46	4.20	1.028	4.15	2.95	III	6.78	13.58	1.089	1.06	0.85
I	1.21	4.85	1.029	4.02	2.72	III	6.12	15.93	1.094	0.96	0.76
I	0.73	6.80	1.036	3.02	2.20	III	5.64	17.96	1.099	0.88	0.74
I	0.51	8.66	1.043	2.49	1.81	III	5.35	19.61	1.107	0.83	0.70
I	0.36	11.03	1.055	1.84	1.46	IV	19.39	none	1.062	–	–
I	0.19	13.20	1.062	1.60	1.20	IV	18.59	0.81	1.060	1.22	1.27
II	9.85	none	1.034	–	–	IV	15.69	4.60	1.072	1.11	1.01
II	9.74	0.06	1.033	2.48	2.20	IV	13.52	8.12	1.084	1.03	0.86
II	9.19	0.62	1.035	2.41	2.29	IV	11.68	11.52	1.089	0.94	0.78
II	6.68	3.60	1.039	2.19	1.81	IV	10.23	14.27	1.099	0.87	0.73
II	4.58	7.15	1.050	1.94	1.46	IV	9.80	15.22	1.112	0.84	0.72
II	3.56	9.65	1.058	1.70	1.28	V	24.74	none	1.074	–	–
II	2.71	12.06	1.070	1.56	1.13	V	24.21	0.56	1.073	0.97	0.86
II	2.34	14.10	1.076	1.36	1.02	V	23.21	1.65	1.076	0.94	0.85
II	2.01	15.98	1.079	1.19	0.93	V	21.02	4.52	1.085	0.88	0.86
II	1.80	17.79	1.084	1.13	0.86	V	20.46	5.24	1.091	0.87	0.77
II	1.57	19.36	1.088	1.01	0.76						

is achieved by shaking the resin and solution in test tubes (with ground-in stoppers) for twenty-four hours. The actual mixing time in the study of the system was two days. The acid in a weighed portion of the aqueous phase was determined by titration with NaOH using methyl red; ammonium was determined by the formaldehyde method, by titration with phenolphthalein.

The resin phase was thoroughly pressed out on filter paper and the electrolyte was washed out with water; the content of hydrogen ion and ammonium ion was determined, as described above, after desorption in a column with a KCl solution. The distribution coefficient (K_{dist}) was calculated as the ratio of the ion content in the solid phase (resin), in mg-eq per 1 g of dry ion exchanger in the H-form, to its content in the aqueous phase (in mg-eq per 1 g of solution). Table 1 gives

Fig. 2. Sections at isoconcentrates of hydrochloric acid

Figure 2: Fig. 2. Sections at isoconcentrates of hydrochloric acid

Fig. 3. Sections along lines A—D

Figure 3: Fig. 3. Sections along lines A—D

the data from which the diagram of the system was constructed (Fig. 1), where in ordinary rectangular coordinates the composition of the aqueous solutions of the system is shown, bounded by the saturation line of NH_4Cl in HCl solutions, while the solid (resin) phase is represented by plotting the equilibrium values of the distribution coefficients (properties) at the point of composition of the liquid phase (respectively). I—V are ion-exchange rays, i.e., lines along which the composition of the aqueous phase changes in the course of the ion-exchange process. The ion-exchange ray begins at the composition point corresponding to the concentration of the initial solution and ends at the point corresponding to one of the compositions of the equilibrium aqueous phase. Owing to the small value of the exchange constant of ammonium ion for hydrogen ion and, because of the large volume of cation exchanger associated with this, movement along the ion-exchange ray had to be carried out by preparing a new solution exactly corresponding in composition to the last equilibrium stage, with the addition to it of a fresh portion of resin (one or several). Points with the same value of K_{dist} were connected into isolines. In the system studied, the isolines of K_{dist} for ammonium (in Fig. 1 indicated by bold numerals) and, analogously, for the hydrogen ion have a rectilinear character, cutting off approximately equal segments on the coordinate axes. The course of the isolines in the field of unsaturated solutions depends on a number of factors, such as, for example, hydration of the ions in solution, the phenomenon of complex formation, the nature of the ion exchanger, etc. The course of K_{dist} for ammonium as a function of the concentration of NH_4Cl at constant acid content (sections of the diagram by horizontal planes) is shown in Fig. 2. Isoconcentrates with respect to the acid are expressed by smooth curves, showing that K_{dist} of ammonium decreases toward the region of concentrated solutions. This is especially clearly seen in sections taken along diagonal planes (Fig. 3). The presence of isolines of K_{dist} and ion-exchange rays makes it possible, without carrying out an experiment, to represent the course of the process for any initial solution of the given system.

Fig. 2. Sections at isoconcentrates of hydrochloric acid

Fig. 3. Sections along lines A—D

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