

ION EXCHANGE IN WATER-ORGANIC SOLUTIONS

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By the process of ion exchange, in a narrow sense, is meant exchange reactions between solution and solid phase, as a result of which ions of definite sign are transferred from the liquid phase to the absorbent, returning an equivalent quantity of different ions to the solution. This reaction is the basis of many laboratory and industrial processes in which synthetic ion exchange resins are used.

The ion exchange phenomenon has been the subject of numerous investigations, in which the leading role belongs to Soviet scientists (K. K. Gedroits, E. N. Gapon, B. P. Nikolsky), who formulated strict quantitative theories of these processes.

Ion exchange is widely used for the analytical purposes of separating and purifying aqueous solutions. There have also been attempts to use exchange processes in non-aqueous and mixed solutions. For example, ion exchange is used for purification of acetone from acid and alkali, for removing calcium and magnesium from kerosene, for dry purification of alcohol, glycerin, ethylene glycol, etc.. However, the phenomenon of ion exchange in non-aqueous and mixed solvents has been insufficiently investigated, which seems to be a deterrent to universal use of ion exchange resins in organic and water-organic media.

Theoretically, ion exchange processes are of interest in the investigation of exchanges involving replacement of water in solution by organic solvents. Such a replacement should lead to a change of ionic distribution between solid phase and solution because of property changes of the ions (hydration, interaction with other ions and solvent) and because of property changes of solid absorbent (swelling).

Wiegner [1], who studied ion exchange in permutite in alcohol-water solutions, attempted to account for the effect of media on exchange reactions. She considered the absorbent as a colloidal system, the particles of which carry a negative charge. Ions entering such a system should be stronger the more dehydrated the ions entering the absorbent and the more hydrated the ions entering the solution. Wiegner investigated the entrance of Na^+ , K^+ and Cs^+ ions into Ca^{++} -permutite and showed that the ionic hydration value decreased with an increase of the per cent of ethyl alcohol in the alcohol-water solutions. The real ionic radii began to play an essential role in exchange, and the order of arrangement of the ions in the lyotropic series changed. Wiegner, assuming that the change of the magnitudes of the cations entering was proportional to the quantity of alcohol in solution, calculated their magnitudes, and they agreed well with experimental data. Wiegner also observed a linear relationship between the quantity of ions absorbed and the alcohol concentration. Ion exchange in soils in alcohol-water solutions was studied by Priyanishnikov [2], and led to a conclusion similar to that of Wiegner.

Of interest, from the point of view of solvents in cationic exchange processes in silicate systems, is the work of Izmailov and Frantsevich-Zabludovskaya [3], who studied the behavior of the glass electrode in alcohol-water solutions. These authors concluded that a change of the exchange constants of the glass during transition from one medium to another depends only on the change of the ratios of the ionic activities in these solutions, which are numerically equal to:

$$\frac{K_I}{K_{II}} = \left(\frac{a_{\text{H}^+}}{a_{\text{Na}^+}} \right)_I : \left(\frac{a_{\text{H}^+}}{a_{\text{Na}^+}} \right)_{II}$$

where K_I and K_{II} are the exchange constants in media I and II, a_i is the corresponding activity of an ion in the solutions.

With ion exchange resins, cation exchange in water-organic media was studied by Kressman and Kitchener [4]. The authors found a whole series of experimental facts, the majority of which were not elucidated. The most essential result of the work seems to be the following: 1) the quantity of absorbed alkali ions increased with an increase in the concentration of the organic solvent, and 2) in alcohol-water solutions the logarithm of the exchange constant changed linearly with the change of alcohol concentration; in acetone-water solutions the magnitude of the constant appears to be a linear function of the acetone concentration. In particular, for exchange of different

TABLE 1

Ionic Exchange of Barium and Sodium on Vofatit C in Aqueous Solutions

Expt. No.	Volume ratio of discharged solutions (V _{Ba} :V _{Na})	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		K _{exptl.}
		C _{Ba}	C _{Na}	G _{Ba}	G _{Na}	
Na-Vofatit						
1	3 : 1	0.05103	0.02398	3.04	0.0465	3.98
2				3.03	0.0561	3.29
3	1 : 1	0.03571	0.04928	2.95	0.121	3.70
4				2.96	0.126	3.52
5	1 : 3	0.01754	0.07476	2.79	0.256	3.69
6				2.81	0.257	3.69
7	1 : 5	0.01206	0.08023	2.73	0.347	3.48
8				2.73	0.340	3.53
9	1 : 10	0.006117	0.09032	2.56	0.501	3.68
10				2.58	0.512	3.62
Average						3.62 ± 0.13
Ba-Vofatit						
11	1 : 10	0.006117	0.09032	2.58	0.519	3.58
12				2.57	0.520	3.53
13	1 : 40	0.001630	0.09758	2.10	0.961	3.65
Average						3.59 ± 0.04

ions in water-organic solvents the authors explained the effect of solvents on the basis of effective ionic diameters, according to Debye (a^0).

Thus, the reports in the literature on ion exchange in non-aqueous and mixed solutions do not give a complete picture of the mechanism of the exchange processes in such media. The difficulty of interpretation of the results obtained in water-organic solutions is accounted for by the meagerness of information on the activity of salts in the presence of non-aqueous solvents.

In the present report cation exchange, with ion exchange resins under dynamic conditions in alcohol-water and acetone-water solutions, was studied for the purpose of examining the applicability of the exchange laws to ion exchange processes in water-organic media, and also to analyses of the operation of a column in such solutions.

EXPERIMENTAL

1. Equilibrium Established During Cation Exchange in Water-Organic Solutions

a) Ion exchange of sodium and barium in alcohol-water solutions. Vofatit C (carboxyl ion exchange) was used as an absorbent for investigating ion exchange in alcohol-water solutions. Barium and sodium served as the exchanging ions. Experiments were carried out principally on the sodium form of Vofatit C, which was obtained by treatment of the initial absorbent with 0.5 N NaCl. Part of the experiment was carried out on the barium form of Vofatit C. The ionic strength of the solutions was kept constant and equal to 0.1. The operating solutions were prepared from 0.0667 N barium chloride solution and 0.1 N sodium chloride solution in the ratios: 3:1, 1:1, 1:3, 1:5, 1:10 and 1:40. The solutions contained 0, 15.5, 30, 50 and 71 weight per cent of ethyl alcohol. The equilibrium ionic concentrations were determined by gravimetric methods: barium as the sulfate and sodium as sodium-zinc uranylacetate. The pH of the active solutions was 6.15-6.40.

The method of conducting the experiments consisted of the following: Into a small weighed column with perforated bottom was placed a weighed portion of cationite (0.3-0.4 g), which was brought into equilibrium with

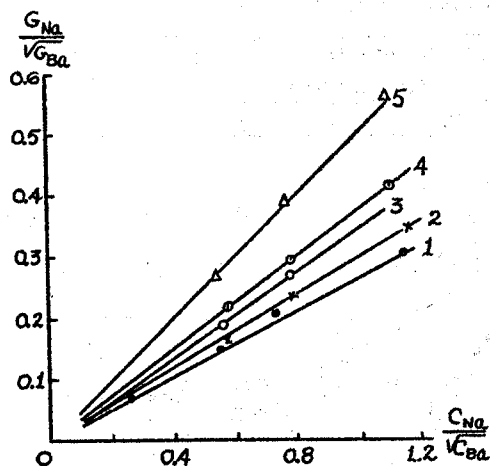


Fig. 1. Isotherms of ionic exchange of sodium and barium for Vofatit C in aqueous and alcoholic-aqueous solutions. 1) 0% C_2H_5OH ; 2) 15.5% C_2H_5OH ; 3) 30% C_2H_5OH ; 4) 50% C_2H_5OH ; 5) 71% C_2H_5OH .

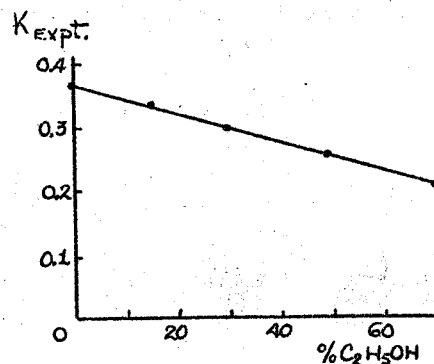


Fig. 2. Relationship of experimental ionic exchange constant of sodium and barium to the per cent content of alcohol in solution.

solutions of barium and sodium ions, taken in different proportions. For this purpose solution was supplied to the column at a rate of 15-20 ml/hr from a bottle with attached tube. Each weighed portion of absorbent was treated with 1 liter of solution. After completion of the operation, the excess of solution was carefully drawn off, and the column was weighed in order to determine the amount of mechanically retained solution, for which a correction was introduced for swelling of the cationite. Then the cationite was washed with 150-200 ml of 0.1 N HCl solution until the absorbed ions were completely displaced. Sodium and barium ions were determined quantitatively in the hydrochloric acid solution obtained. The experimental data served for calculation of the exchange constant, which was calculated from the Nikolsky [5] equation:

$$K = \frac{C_{Na}}{\sqrt{C_{Ba}}} \frac{\sqrt{G_{Ba}}}{G_{Na}}, \quad (1)$$

where C_i is the concentration of an ion in the equilibrium solution (in m equiv/g), G_i is the quantity of absorbed ion (in m equiv/g), K is the exchange constant.

The experimental results for the aqueous solutions are presented in Table 1.

Experiments 1-10 were carried out on the sodium form of Vofatit, and 11-13 — on the barium form, the latter for the purpose of verification of the reversibility of the process. Comparing the exchange constants for experiments on sodium and barium cationites, it is possible to draw conclusions concerning the complete reversibility of the ion exchange of barium and sodium on Vofatit C in aqueous solution.

In Table 2 experimental results for exchange of the same cations in alcohol-water solutions are presented. In Fig. 1 exchange isotherms of sodium and barium on Vofatit C in water and alcohol solutions are represented. From this figure it is seen that the experimental points for all the concentrations of alcohol studied lie on a straight line passing through the origin of the coordinates, and consequently, the cation exchange in synthetic resin absorbent both in aqueous and alcohol solution obeyed equation (1). From Tables 1 and 2 it follows that the exchange constant (will be designated by $K_{\text{exptl.}}$) for sodium Vofatit, calculated from equation (1), appears to be a function of the per cent alcohol content of the solution. The graphical relationship of $K_{\text{exptl.}}$ to the per cent content of alcohol is shown in Fig. 2.

Results of the experiments on barium Vofatit are collected in Table 3. From these data a conclusion can be drawn concerning a certain irreversibility of the process of ion exchange in alcoholic solution ($K'_{\text{exptl.}}$ — the exchange constant for barium Vofatit). An elucidation of these phenomena will be given below.

TABLE 2

Ion Exchange of Barium and Sodium on Vofatit C in Alcohol-Aqueous Solutions

Expt. No.	Volume ratio of discharge solutions (V _{Ba} :V _{Na})	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		K _{exptl.}		
		C _{Ba}	C _{Na}	G _{Ba}	G _{Na}			
15.5% Ethyl Alcohol								
1	1 : 3	0.01673	0.07495	{	2.78	0.262	3.41	
2					2.79	0.270	3.37	
3	1 : 5	0.01123	0.08338	{	2.68	0.384	3.36	
4					2.69	0.376	3.36	
5	1 : 10	0.06105	0.09087	{	2.48	0.549	3.33	
6					2.44	0.561	3.25	
Average						3.37 ± 0.06		
30% Ethyl Alcohol								
7	{	1 : 3	0.01718	0.07440	{	2.78	0.298	3.01
8						2.74	0.293	3.04
9	1 : 5	0.01130	0.08321	2.63	0.442	2.87		
Average						2.97 ± 0.07		
50% Ethyl Alcohol								
10	1 : 3	0.01671	0.07443	{	2.69	0.367	2.57	
11					2.68	0.372	2.54	
12	1 : 5	0.01170	0.08420	{	2.59	0.479	2.62	
13					2.39	0.477	2.62	
14	1 : 10	0.00638	0.09022	{	2.36	0.646	2.68	
15					2.37	0.641	2.69	
Average						2.62 ± 0.04		
71% Ethyl Alcohol								
16	1 : 3	0.01774	0.07317	{	2.60	0.419	2.11	
17					2.62	0.411	2.16	
18	1 : 5	0.01137	0.08214	{	2.48	0.605	2.01	
19					2.42	0.614	1.95	
20	1 : 10	0.00656	0.08929	{	2.23	0.840	1.97	
21					2.24	0.830	1.99	
Average						2.03 ± 0.07		

b) Ion exchange of sodium and ammonium in acetone-water solutions. In this part of the work, the cationic exchange equilibrium in acetone-water solutions was studied. The exchange constant was calculated from the equation

$$K = \frac{G_{Na} C_{NH_4}}{G_{NH_4} C_{Na}} \quad (2)$$

The method of operation was analogous to the preceding. A sample of domestic sulfo-cationite SBS was used as the cationite. Into the column was placed 1 g of SBS resin, which was saturated with ammonium ion, and through

TABLE 3

Ion Exchange of Barium and Sodium on Barium Vofatit in Aqueous and Alcohol-Water Solutions

Expt. No.	Per cent alcohol content	Volume ratio of discharged solutions ($V_{Ba}:V_{Na}$)	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K'_{\text{exptl.}}$	$K_{\text{exptl.}}$	ΔK
			C_{Ba}	C_{Na}	G_{Ba}	G_{Na}			
1	0	1:10	0.006117	0.09032	2.58	0.519	3.59	3.62	-0.03
2					2.57	0.520			
3	15.5	1:10	0.006105	0.09087	2.56	0.503	3.68	3.37	0.31
4					2.56	0.503			
5	30	1:3	0.01718	0.07490	2.79	0.293	3.06	2.97	0.09
6	50	1:10	0.006382	0.09022	2.57	0.558	3.25	2.62	0.63
7	71	1:10	0.006390	0.09103	2.57	0.661	2.76	2.03	0.73

TABLE 4

Ionic Exchange of Sodium and Ammonium in Aqueous Solutions

Expt. No.	Volume ratio of discharged solutions ($V_{Na}:V_{NH_4}$)	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K_{\text{exptl.}}$	
		C_{Na}	C_{NH_4}	G_{Na}	G_{NH_4}		
NH ₄ -Cationite							
1	1 : 3	0.02506	0.07489	{	0.408	1.99	0.612
2					0.413	2.00	0.616
3	1 : 1	0.04996	0.04953	{	0.839	1.49	0.558
4					0.839	1.49	0.553
5	3 : 1	0.07435	0.02491	{	1.46	0.908	0.538
6					1.46	0.91	0.539
Na-Cationite							
7	1 : 3	0.02500	0.07573	{	0.410	1.99	0.623
8					0.411	1.99	0.623
9	1 : 1	0.05014	0.05054	{	0.830	1.49	0.561
10					0.833	1.49	0.564

which was passed a mixture of sodium chloride and ammonium chloride solutions, taken in different ratios (1:3, 3:1, and 1:1). The ionic strength was kept constant and equal to 0.1. The solutions were passed through the column at a rate of 1 ml/min until equilibrium was established. After washing with aqueous solution, the absorbed ions re-

tained in the column were displaced by 0.1 N hydrochloric acid. In the filtrate ammonia was determined by distillation, sodium — by a gravimetric method using zinc uranylacetate. The results of the experiments on the ion exchange of sodium and ammonium in aqueous solutions are presented in Table 4.

The results of Table 4 indicate a regular "rate" of the exchange constant for a change of the solution composition. This phenomenon was observed in a series of cases of ion exchange on resins [6] and, apparently, may be explained by the change of the activity coefficients of the ions in the solid phase. The process of cation exchange of sodium and ammonium in aqueous media seems to be reversible, which can be

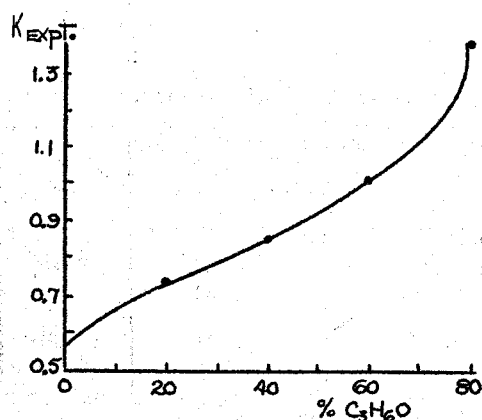


Fig. 3. Relationship of the experimental ionic exchange constant for ammonium and sodium to the percent content of acetone in the solutions.

TABLE 5

Ion Exchange of Sodium and Ammonium in Acetone-Water Solutions with Cationite SBS

Expt. No.	Volume ratio of discharged solution (VNa:VNH ₄)	Ionic concentration in solution (m equiv/g)			Ionic concentration in absorbent (m equiv/g)		K _{exptl.}
		CNa	CNH ₄		GNa	GNH ₄	
20% Acetone							
1	1 : 3	0.02503	0.07494	{	0.484	1.864	0.774
2					0.492	1.872	0.790
3	1 : 1	0.04997	0.04998	{	1.014	1.369	0.733
4					1.001	1.362	0.738
5	3 : 1	0.07509	0.02499	{	1.586	0.761	0.694
6					1.575	0.766	0.682
40% Acetone							
7	1 : 3	0.02540	0.07492	{	0.570	1.860	0.904
8					0.559	1.849	0.892
9	1 : 1	0.05171	0.05008	{	1.120	1.291	0.843
10					1.119	1.285	0.846
11	3 : 1	0.07155	0.02407	{	1.720	0.718	0.801
12					1.730	0.718	0.800
60% Acetone							
13	1 : 3	0.02531	0.07637	{	0.616	1.744	1.070
14					0.614	1.733	1.070
15	1 : 1	0.05062	0.04982	{	1.194	1.185	0.991
16					1.214	1.190	1.000
17	3 : 1	0.07318	0.02454	{	1.761	0.605	0.975
18					1.762	0.610	0.970
80% Acetone							
19	1 : 3	0.02495	0.07491	{	0.827	1.038	1.517
20					0.824	1.651	1.499
21	1 : 1	0.04997	0.04960	{	1.419	1.010	1.388
22					1.394	1.015	1.363
23	3 : 1	0.07440	0.02480	{	1.940	0.505	1.275
24					1.932	0.510	1.263

TABLE 6

Ion Exchange of Sodium and Ammonium on the Sodium Form of Cationite SBS in 40% Acetone

Expt. No.	Volume ratio of discharged solution ($V_{Na}:V_{NH_4}$)	Ionic concentration in solution (m equiv/g)			Ionic concentration in absorbent (m equiv/g)		$K'_{exptl.}^{**}$	$K_{exptl.}^*$
		C_{Na}	C_{NH_4}		G_{Na}	G_{NH_4}		
1	1 : 3	0.02513	0.07504	{	0.552	1.835	0.899	0.898
2					0.552	1.830	0.900	
3	3 : 1	0.07484	0.02505	{	1.710	0.724	0.790	0.800
4					1.714	0.719	0.797	

* $K_{exptl.}$ — the ion exchange constant of sodium and ammonium on ammonium resin.** $K'_{exptl.}$ — the ion exchange constant of sodium and ammonium on sodium resin.

seen from the results of Table 4, comparing the exchange constants for ammonium and sodium resins with similar ratios of ionic concentrations of sodium and ammonium in solution.

In the acetone-water solutions the experiments were carried out with the same ionic ratios and the same ionic strength as were used in the aqueous solutions. The concentrations of acetone in the solutions amounted to 20, 40, 60, 80 weight per cent. Results of the experiments on ion exchange of ammonium and sodium in different acetone-water solutions are presented in Table 5, which shows that for all acetone-water solutions, as also for the aqueous solutions, a "rate" exchange constant for change of the concentration ratios of ammonium and sodium in solution is observed. If one compares the magnitudes of the exchange constants in different acetone-water solutions (Fig. 3) then it can be seen that for increases of the acetone content in solution the exchange constant increases.

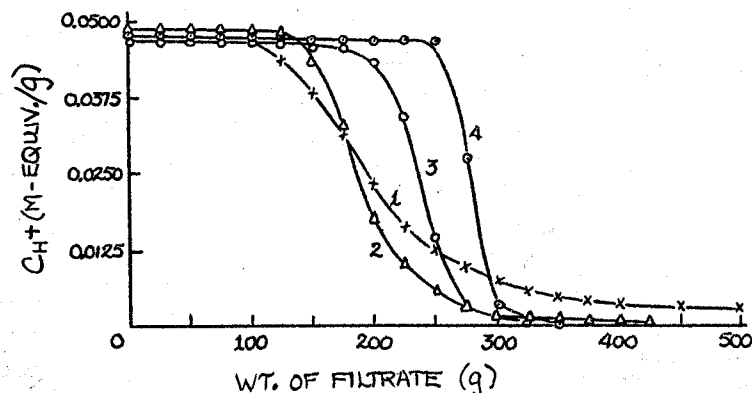


Fig. 4. Discharge curves of the exchange of hydrogen ion for sodium in cationite SBS in different acetone-water solutions. Acetone (in %): 1) 0; 2) 20; 3) 40; 4) 60.

As seen from the data of Table 5, subsequent addition of acetone promotes the absorption of sodium ion and decreases the absorption of ammonium ion.

In order to elucidate the reversibility of the exchange process in acetone-water medium, experiments were made using the sodium form of SBS Resin in a 40% solution of acetone. Results of these experiments are presented in Table 6.

A direct comparison of the exchange constant with the reverse reaction shows that the ion exchange process of sodium and ammonium in acetone-water solutions appears to be completely reversible.

2. Ion Exchange in Water-Organic Solutions Under Dynamic Conditions

Study of the cation exchange in acetone-water and alcohol-water solutions under dynamic conditions was carried out, using the method of discharge curves. The discharge curves, as is well-known, express the relationship of the concentration of the discharging solution to the volume (weight) of the liquid flowing through the column. The method of discharge curves permits the determination of the relative exchange rate, the dynamic exchange capacity and the character of the distribution of ions in the column.

To obtain the discharge curves, the following experiments were planned. A weighed portion of cationite (5-6 g) in the hydrogen form was placed in the column and moistened with the corresponding solvent. A solution of 0.05 N NaCl was passed through the column at a constant rate (1 ml/min). The filtrate was collected in a separate flask. The total fraction of the filtrate amounted to 20-25 g. In each fraction the concentration of the displaced ions was determined.

The results obtained are represented in Fig. 4 in the form of discharge curves, expressing the relation of the hydrogen ion concentration in the displacing solution to the amount of filtrate in grams.

Comparing the discharge curves for different acetone-water solutions, it is possible to point out that the rate of ion exchange of hydrogen ions by sodium ions increases with increase of the per cent content of acetone in the solution. In the aqueous solutions the discharge curves have a more sloping character than in the mixed solutions, i.e., the exchange equilibrium is established more rapidly in the acetone-water solutions than in the aqueous solutions. The length of the horizontal part of the curve, corresponding to a constant concentration of hydrogen ions (until passage of sodium ion), increases with an increase of the acetone concentration in the solution. Consequently, in the acetone-water solutions the exchange proceeds more rapidly than in aqueous solutions; and for the same rate of filtration, for the acetone-water solutions the filtrate may be recovered more completely than for the aqueous solutions.

For elucidating the nature of the changes of the discharge curves with subsequent replacement of water in the mixed solvent by acetone, the effect of the solvents on the swelling of the SBS cationite was investigated. Increase of swelling should promote the progress of the ions into the absorbent and, consequently, should increase the exchange rate. The magnitude of swelling of cationite SBS was determined by a comparison of the volume or weight of solu-

TABLE 7

Relation of Swelling of Cationite SBS to the Concentration of Acetone

Percent content of acetone	Quantity (in g) of absorbed solution per 1 g of resin
0	1.60
20	1.74
40	1.84
60	1.94
80	2.06

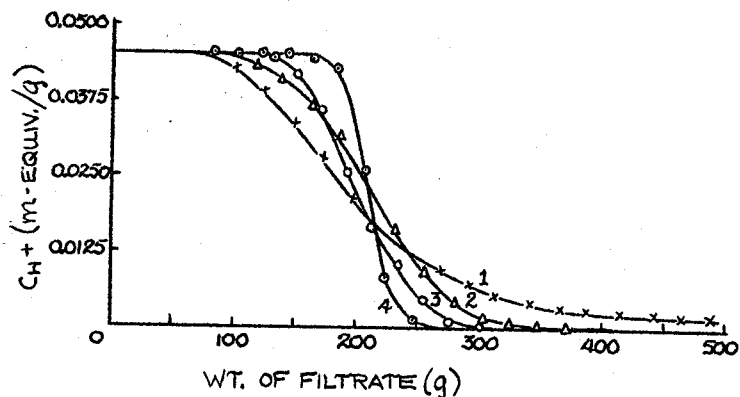


Fig. 5. Discharge curves of hydrogen ion exchange for sodium ion in cationite SBS in different alcohol-water solutions. Alcohol (%): 1) 0; 2) 28; 3) 60; 4) 80.

In direct relation to the increase of the rate of exchange in alcohol-water solutions is the increase of swelling capacity of the SBS resin in mixed solutions, with an increase of alcohol concentration. Results of the swelling of the hydrogen form of the SBS resin in alcohol-water solutions of 0.05 N sodium chloride are presented in Table 8.

DISCUSSION OF RESULTS

Results of the experiments on the ion exchange of barium and sodium in alcohol-water solutions on Vofatit C (Fig. 2) showed that, on replacement of water in the mixed solvent by alcohol, the exchange constant calculated from the Nikolsky Equation decreased with an increase of the alcohol content. In order to account for this fact, it is simple to assume that the change depends on the change of the activity coefficients of the ions in the solution, with an increase of the alcohol content. For verification of this assumption it is necessary to calculate the actual exchange constant, i.e., the value of the constant, expressed by the activity of the ions. Results of such a calculation are presented in Table 9. The ionic activity coefficients of barium and sodium in alcohol-water solutions were calculated from the Vinogradov [7]** nomogram, based on the use of the first approximation of the Debye and Hückel equation.

The actual exchange constant was calculated from the equation

* In these experiments, S. B. Evinina participated.

** Calculation of the activity coefficient values seems to be an approximation, since on the nomogram the individualities of the single ions were not studied, but, in spite of the inaccuracy of the absolute values of the activity coefficients, the character of their changes with decrease of the dielectric constant of the media corresponds to reality.

TABLE 8

Relation of Swelling of Cationite SBS to the Concentration of Alcohol

Percent content of alcohol	Quantity (in g) of the absorbed solution per 1 g of resin
0	0.667
28	0.824
60	0.995
80	1.092

tion before and after swelling. Results of swelling of the hydrogen form of cationite SBS in relation to the concentration of acetone are represented in Table 7. From the data of Table 7 it is seen that the swelling of the SBS resin increases linearly with increase of the acetone concentration.

The discharge curve for hydrogen ions in alcohol-water solution* was obtained under conditions analogous to that for acetone-water medium (Fig. 5). From Fig. 5 it follows that, the greater the concentration of alcohol in the solution, the later the passage of the absorbed ion (sodium) occurs, i.e., the longer the horizontal part of the line, and the steeper the discharge curves. Similarly, acetone-water solutions, to the extent of the increase of the alcohol concentration in mixed solvent, increase the rate of ion exchange.

TABLE 9

Experimental and Actual Values of the Exchange Constant for Different Alcohol-Water Solutions

Percent alcohol content	γ_{Ba}	γ_{Na}	$K_{exptl.}$	K_{actual}
0	0.240	0.705	3.62	5.20
15.5	0.178	0.649	3.38	5.21
30.0	0.100	0.574	2.97	5.39
50.0	0.055	0.490	2.60	5.37
71.0	0.020	0.373	2.03	5.36
Average 5.31 ± 0.08				

TABLE 10

Experimental and Actual Values of the Exchange Constant for Different Acetone-Water Solutions

Percent acetone content	γ_{Na}	γ_{NH_4}	$K_{exptl.}$	K_{actual}
0	0.82	0.75	0.61	0.56
20	0.80	0.68	0.78	0.66
40	0.75	0.60	0.90	0.73
60	0.66	0.47	1.07	0.76

$$K_{actual} = K_{exptl.} \frac{\gamma_{Na}}{\sqrt{\gamma_{Ba}}} \quad (3)$$

Results in Table 9 show that the decrease of the experimental exchange constant with increase of the alcohol concentration in the solution may be accounted for by the change of the relation of the activity coefficients of the barium and sodium ions in the alcohol-water solutions. The stability of the actual exchange constant in the water and alcohol-water solutions may be used for determining the ratio of the activity coefficients

$$\gamma_{M_1}^{1/z_1} : \gamma_{M_2}^{1/z_2}$$

To account for the anomalous behavior of barium Vofatit (Table 3), it is interesting to follow the relation of the absorption capacity of sodium and barium to the concentration of alcohol in the solution. This relationship is represented graphically in Fig. 6, constructed from the data of Tables 1 and 2.

From Fig. 6 it is seen that for sodium Vofatit (continuous curve), with an increase of the quantity of alcohol, G_{Na} increases, but G_{Ba} decreases. For barium Vofatit (dotted curve) something peculiar takes place, explained apparently, by the irreversibility of the exchange process in alcohol-water solutions. The entering of barium ion into the barium Vofatit does not depend on the alcohol concentration, but remains equal to the magnitude of G_{Ba} for the aqueous solution. Such a result was obtained for all concentrations studied.

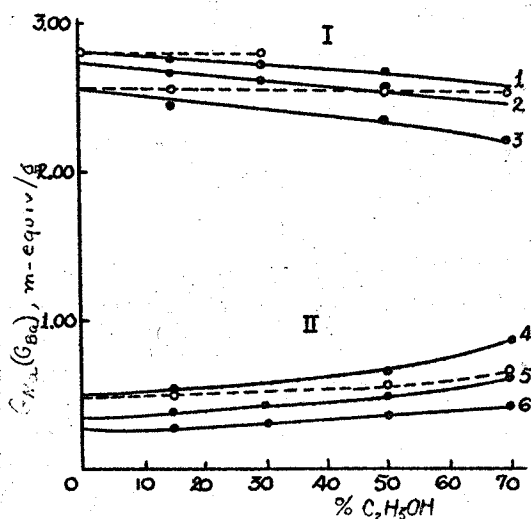


Fig. 6. Relation of G_{Na} and G_{Ba} to the per cent content of alcohol for sodium and barium Vofatit. I) $G_{Ba} = f(\% C_2H_5OH)$; II) $G_{Na} = f(\% C_2H_5OH)$. 1) $C_{Ba} = 0.0175$; 2) $C_{Ba} = 0.0120$; 3) $C_{Ba} = 0.0016$; 4) $C_{Na} = 0.090$; 5) $C_{Na} = 0.083$; 6) $C_{Na} = 0.075$.

The experimental results obtained in the acetone-water solutions (Tables 4, 5, 6 and Fig. 3) showed that, for an increase of the acetone concentration, the value of the exchange constant calculated from Equation (2) increased, since for an increase of the per cent of acetone in the solution, the quantity of absorbed sodium ion increases and the quantity of absorbed ammonium ion decreases. On the part of the curve (Fig. 3) up to an acetone content equal to 60%, $K_{exptl.}$ depends linearly on the acetone concentration. For concentrations of acetone exceeding 60% the curve rises sharply. To account for variance of the exchange constant with an increase of the acetone concentration, the "actual" exchange constant expressed by the activity of the ammonium and sodium ions in the mixed solutions was calculated, just as for the alcohol-water solutions. The activity coefficients in the acetone-water solutions were evaluated from the Vinogradov [7] nomogram. Results of the calculation of the "actual" exchange constants are presented in Table 10; * The calculation is of an extremely approximate character.

* $K_{exptl.}$ was given for a concentration ratio of sodium and ammonium ions in solution, equal to 1:3.

However, a comparison of the experimental and "actual" constants showed that the "actual" exchange constant has a smaller rate than does the experimental constant during transition from aqueous to acetone-water solutions.

The experimental material on cation exchange in water-organic solutions, under dynamic conditions, leads to the conclusion that the rate of the process increases substantially with an increase of the concentration of the organic component in solution. If one compares the discharge curves for different acetone-water and alcohol-water solutions (Figs. 4 and 5), it is easy to see that the initial sloping of the curves from the horizontal, corresponding to the moment of appearance of sodium ion in the filtrate (passage),* occurs earlier in the aqueous solutions and later in the solutions having the largest content of organic component. The effect of the organic component on the kinetics of the ion exchange processes is found to be in direct relation to the change of the swelling capacity of the absorbent.

The results may be of essential practical value for selection of the most favorable conditions of separating and concentrating cations with the help of ion exchange under dynamic conditions.

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SUMMARY

1. The process of ion exchange in alcohol-water and acetone-water solutions was studied.

The applicability of the Nikolsky isotherm equation to the exchange process in water-organic solutions was shown.

2. The relationship of the cations entering the absorbent to the quantity of organic component in solution was studied. An increase of the alcohol content facilitated the absorption of sodium ion and hindered the absorption of barium ion by Vofatit C. Increase of the acetone content promoted the absorption of the sodium ion and decreased the absorption of the ammonium ion by SBS resin.

3. The process of ion exchange was investigated under dynamic conditions in aqueous and water-organic solutions. It was shown that in water-organic medium the exchange process proceeds with a greater rate than in water, in which the rate increased with increase of the content of organic substance in solution.

4. The swelling capacity of cationite SBS in relation to the composition of the solution was determined. It showed that swelling increased linearly with an increase of the content of organic component in solution (acetone or alcohol).

LITERATURE CITED

- [1] Wiegner. Selected Works (1941); Soil Science, No. 3, (1936); Wiegner, Jenny, Koll. Z., 42, 270 (1927).
- [2] Priianishnikova. The Physical Chemistry of Soils. Symposium, Moscow (1935).
- [3] Izmailov and Frantsevish-Zabludovskaya, J. Gen. Chem., 16,501 (1946).
- [4] T. Kressman and J. Kitchener, J. Chem. Soc., 51, 1211 (1949).
- [5] B. P. Nikolsky and V. I. Paramonova, Prog. Chem., 8, 1535 (1939).
- [6] Lowen, Stoenerer, Argersinger, J. Am. Chem. Soc., 73, 2666 (1951).
- [7] G. V. Vinogradov, Prog. Chem., 8, 378 (1939); V. K. Semenchenko. Physical Theory of Solutions (1941).

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* Appearance of sodium ion in the filtrate was controlled by qualitative test.