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Fig. 1

Figure 1: Fig. 1

Abstract

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TRUE AND FALSE EQUILIBRIA IN ION-EXCHANGE PROCESSES ON CARBOXYLIC CATION EXCHANGERS WITH THE PARTICIPATION OF THE STREPTOMYCIN ION

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In previous works ([1], [2]) we showed that the rate of ion-exchange processes on carboxylic cation exchangers in which streptomycin ions (Str^{3+}) take part is determined by the rate of its diffusion into the interior of the cation-exchanger grain.

On certain types of cation exchangers the rate of penetration of Str^{3+} into the grain, after the cation exchanger has absorbed a certain amount of it, slows down so much that the course of the reaction practically ceases and an apparent (false) equilibrium is established. This phenomenon occurs in the sorption of Str^{3+} both on the Na form (RNa) and on the H form (RH) of the cation exchanger; moreover, in the latter case the existence of false equilibria is especially strongly expressed. Grinding the cation exchanger in the Na form and increasing the sorption temperature promote a more complete replacement of Na^+ in the ionogenic groups of the resin by Str^{3+} and thereby bring the system closer to the state of true equilibrium. Further study of the sorption of Str^{3+} by carboxylic cation exchangers showed that, in the transition of the cation-exchanger-solution system from false to true equilibria, in addition to temperature and the dispersity of the resin, the concentration of mineral ions in the solution is of very great importance. The present work is devoted to this question.

Fig. 1. Dependence of the magnitude of sorption of Str^{3+} for the Na form of the cation exchanger KB-4 on C_{Na^+} in solution. Temperature 25°; **1**—cation-exchanger grain size 0.25-0.50 mm; **2**—0.08-0.12 mm

The study of the ion-exchange processes was carried out, as in our previous works ([1], [2]), under static conditions with intensive stirring of the solution of the sulfuric-acid salt of streptomycin with the cation exchanger. In sorption on

Fig. 2

Figure 2: Fig. 2

the H form of the cation exchanger, in order to maintain a constant pH value (~7), the anion exchanger (AOH) EDE-10 was introduced into the solution (^{1}). The investigation was carried out on two cation exchangers—KFU and an I-m sample of KB-4 (^{2}).

Figure 1 shows the amounts of Str^{3+} sorbed by the Na form of the KB-4 resin of two grain sizes during 190 hours of contact as a function of C_{Na^+} in solution. The initial concentration of Str^{3+} in all cases remained constant and equal to 0.026 N. The amount of Str^{3+} sorbed during 190 hours of contact is practically limiting.

As is seen from Fig. 1, an increase in the dispersity of the cation exchanger affects the magnitude of sorption of Str^{3+} only at C_{Na^+} within the range from 0 to 0.5 N. Na-

starting with a Na^+ concentration equal to 0.5 N, sorption of Str^{3+} does not depend on the grain size of the cation exchanger. This fact indicates that the nonuniform distribution of Str^{3+} over the grain radius, which determines the difference in the behavior of cation exchangers of different dispersity, practically disappears at higher values of C_{Na^+}. Thus, false equilibria in the Str^{3+}–Na^+–KB-4 cation-exchanger system occur only at C_{Na^+} below 0.5 N.

Very clearly revealed is the influence of the sodium concentration in solution on the transition from false equilibria to true ones during sorption of Str^{3+} by the H-form of the cation exchanger. In the previous work (1) it was already shown that introducing sodium sulfate into a solution of Str that is in contact with the H-form of KFU leads to a sharp increase in sorption of Str^{3+}. At the same time, the limiting sorption of Str^{3+} does not depend on the form of the cation exchanger introduced into the solution (H- or Na-form). This made it possible to suppose that in this case the establishment of true equilibrium in the system takes place.

Fig. 2. Kinetics of sorption of Str^{3+} by the H-form of the KB-4 cation exchanger as a function of C_{Na^+} in solution. Grain size 0.25-0.50 mm. Temperature 29°. C_{Na^+}: **1**–0; **2**–0.03 N; **3**–0.3 N; **4**–1.0 N; **5**–2.0 N.

We investigated the ion-exchange process in the system H-form KB-4—streptomycin sulfate at various concentrations of sodium sulfate in solution. The data obtained are presented in Fig. 2, from which it is seen that in the absence of Na^+ the cation exchanger sorbs only 1 meq/g of Str^{3+}, and the process is completed in 24 hours. Introducing sodium sulfate into the solution, calculated for a concentration of 0.03 N, leads to a strong increase in ion exchange, with an increase in the time over which the limiting sorption value is attained, up to

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

124 hours. An increase of C_{Na^+} to 0.3 N leads to an even greater increase in sorption of Str^{3+}. Further

Fig. 3

Fig. 4

Fig. 3. Dependence of the magnitude of sorption of Str^{3+} for the H-form of the KB-4 cation exchanger on C_{Na^+} in solution. Grain size 0.25-0.50 mm. Temperature 29°. Contact duration: **1**—3 hours, **2**—6 hours, **3**—24 hours, **4**—120 hours, **5**—240 hours.

Fig. 4. Dependence of the magnitude of sorption of Str^{3+} for the H-form of the KFU cation exchanger on C_{Na^+} in solution. Grain size 0.25-0.50 mm. Temperature 29°. Contact duration: **1**—3 hours, **2**—6 hours, **3**—24 hours, **4**—72 hours, **5**—144 hours.

an increase of C_{Na^+} to $1\,N$ and $2\,N$ already causes a decrease in sorption. At the same time, the time required for completion of the ion-exchange process is greatly shortened. These data become still more evident if the amount of sorbed Str^{3+} for different periods of time is plotted on the ordinate axis, and C_{Na^+} on the abscissa axis, as has been done in Fig. 3. The amount of limitingly sorbed Str^{3+}, as is seen from this figure, passes through a maximum, which corresponds to C_{Na^+} close to $0.3\,N$.

The condensation cation exchanger KFU behaves in exactly the same way as the cation exchanger KB-4, as is seen from Fig. 4. In the latter case the maximum of Str^{3+} sorption is shifted somewhat into the region of smaller C_{Na^+}.

From the data presented it is clear that, at small C_{Na^+} in the solution, true equilibrium in the streptomycin salt—cation exchanger system is not attained. In this region of C_{Na^+} only false equilibria occur. At large values of C_{Na^+}, a decrease is observed in the amount of sorbed Str^{3+} with increasing C_{Na^+}, which is what should have been expected in the case of establishment of true equilibrium in the system under study. This explanation is fully consistent with the data shown in Fig. 1, which show, for the KB-4 resin, a dependence of the sorption of Str^{3+} on the grain size at small C_{Na^+} in solution and independence at C_{Na^+} above $0.5\,N$.

Table 1

RH, g	RNa, g	AOH, g	Str^{3+}, mg-eq	Na^+, mg-eq	Sorbed Str^{3+}, mg-eq/g
0.5	–	0.75	5	3.5	3.10
–	0.5	–	5	3.5	4.35
0.5	–	0.75	5	200	2.06
–	0.5	–	5	203.5	1.97

The existence of false and true equilibria in the cation exchanger–streptomycin solution system can also be demonstrated very clearly if one starts from the H- and Na-forms of the cation exchanger and introduces into the system Na_2SO_4 in such an amount as to keep the Na^+ content in it constant. Four such experiments are given in Table 1.

As is seen from Table 1, at small C_{Na^+} in the system the amount of Str^{3+} sorbed by the Na-form is noticeably greater than in the case of the H-form. With a large amount of Na^+ introduced into the system, the final state does not depend on the form of cation exchanger taken. We have, therefore, every reason to consider that in the first case the equilibrium is false, and in the second it is true.

At the present time it is still difficult to give a fully substantiated explanation of the action of Na ions on the transition of cation exchanger–streptomycin systems from states of false equilibria to true ones. On this question one can only put forward certain assumptions. The strong influence of the dispersity of the cation exchanger on the amount of sorbed Str^{3+} at small C_{Na^+} shows that in the present case the exchange of resin Na^+ for Str^{3+} is limited by a small depth from the external surface of the grain. At small values of C_{Na^+}, in the case of true equilibrium there should occur practically complete replacement of resin Na^+ by Str^{3+}. This undoubtedly does take place in the layer of the cation exchanger directly in contact with the solution. The Str-form of the cationite formed is only slightly permeable to Str^{3+} and acts, as it were, as a protective film against its further penetration into the depth of the grain. The introduction into the solution of a considerable amount of Na^+, naturally, will cause partial replacement of Str^{3+} by Na^+ in the outer layer of the cationite particle, which will lead to the formation of a mixed Str–Na-form. In the latter, the diffusion rate of Str^{3+} increases appreciably, which makes it possible for Str^{3+} to be distributed uniformly throughout the entire mass of the cationite grain.

The data presented in the present article are of undoubted interest also for the correct calculation of equilibrium constants of the ion-exchange reaction involving Str^{3+}.

In the works of previous investigators (^{3}), devoted to equilibria in the carboxyl resin–Str^{3+} system, it was assumed that in the cation exchanger there is a certain number of ionogenic groups whose cations are completely incapable of being replaced by Str^{3+}. The untenability of this proposition had already become evident from our data set forth in previous works. The present study has shown that it is not possible to determine the true capacity of the resin for Str^{3+} by lowering C_{Na^+} in solution for cation exchangers with a medium degree of cross-linking (5-10% DVB), since under these conditions, with grain sizes on the order of 0.2-0.5 mm, false equilibrium occurs. The true value of the resin capacity for Str^{3+} for such cation exchangers can be determined only under conditions of their high dispersity. We believe that in this case the resin capacity for Str^{3+} will be equal to the capacity for Na^+. The calculation of the exchange constant (K_{Na}^{Str}), possible only for the descending branch of the curve expressing the dependence of Str^{3+} sorption on C_{Na^+} (Figs. 3 and 4), must be performed on the basis of the total Na^+ introduced into the cation exchanger.

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