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Abstract

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On the Causes of the Establishment of False-Equilibrium States in the Ion-Exchange Sorption of Large Organic Ions

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One of the features of the ion-exchange sorption of large organic ions is that, as the swelling of ion exchangers decreases or the size of the sorbed ions increases, the amount of ions absorbed by the resin decreases ([1]). A detailed study of such exchange cases showed that the decrease in the sorption capacity of exchangers is associated with a decrease in the permeability of ion exchangers with respect to large ions, leading to false-equilibrium states in ion exchanger—organic electrolyte solution systems ([2]). As exchange proceeds, the sorption rate of large organic ions falls, and the process "comes to a standstill," although the sorbed amount of organic ions has not yet reached the equilibrium value.

In our communication we present the results of studies on the influence of the permeability of ion exchangers on the rate of exchange in which ions of organic compounds participate. The method chosen by us consists in measuring the rate of sorption of an organic ion (the cation of the dye methylene blue) on ion exchangers (sulfonic cation exchangers KU-2 with 2 and 6% divinylbenzene, DVB) at different ratios of the amounts of counterions of hydrogen and methylene blue (MB) in the initial form of the ion exchanger. From these measurements, the differential diffusion coefficients ($\bar{D}_d$) of MB in the ion-exchanger phase were calculated. From data on the dependence of the value $\bar{D}_d$ on temperature, the activation energies of MB diffusion in the ion-exchanger phase were calculated.

The resins we used were spherical grains with a diameter of 0.5–1.0 mm (wet sieving). The number of grains with defects (irregular shape, cracks, vacuoles) in both resin samples did not exceed 5%. The static exchange capacities (s.e.c.), determined with respect to sodium ions, were equal to 5.15 mg-eq/g for the resin with 2% DVB and 4.16 mg-eq/g for the resin with 6% DVB (calculated for the dry H-form). Experiments on sorption of the dye by cation exchangers were carried out under static conditions. The experimental conditions were selected in such a way that the rate of the ion-exchange process was determined by the rate of diffusion of the dye in the ion-exchanger phase. The differential diffusion coefficients of MB in the ion-exchanger phase were calculated by the formula:

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$$F = \frac{6}{r}\left(\frac{\bar{D}_d\, t}{\pi}\right)^{1/2} \quad \text{(for small values of } F\text{)},$$

where r is the particle radius, in centimeters; t is the exchange time, in seconds, during which a certain value of the degree of exchange F is reached, determined by the formula: $F = \Gamma_{\text{MG}}$ (s.e.c. $-\Gamma^0_{\text{MG}}$). In this expression Γ_{MG} is the amount of MB (mg-eq/g H-form) absorbed by the cation exchanger during time t; Γ^0_{MG} is the amount of MB (mg-eq/g H-form) preliminarily sorbed by the ion exchanger.

By studying the statics of exchange of hydrogen ions and MG on the cation exchangers used, it was established that the selectivity coefficient of these ion exchangers with respect to MG ions varies from 500 to 1000, depending

Fig. 1. Sorption curves of MG ions on KU-2 sulfocation exchangers with 2% (a) and with 6% (b) DVB at different temperatures. 1,4 –40°; 2,5 –60°; 3, 6 –75°

Fig. 2. Dependence of the differential diffusion coefficients of MG ions on temperature in KU-2 cation exchangers with 2% (a) and 6% (b) DVB.

Fig. 3. Activation energy of diffusion of MG ions in KU-2 cation exchangers with 2% (a) and with 6% (b) DVB at different degrees of preliminary replacement of hydrogen ions by MG ions in the initial resin

Fig. 4. Temperature dependence of the differential diffusion coefficients of MG ions in KU-2 sulfocation exchangers with 2% (a) and 6% (b) DVB. The numbers beside the straight lines indicate the fraction of hydrogen ions in the resin preliminarily replaced by MG ions

on the degree of exchange and the temperature. Therefore, under the conditions of the experiments reported here, equilibrium in the system H-form of the cation exchanger –solution of the hydrochloride salt of MG corresponds to practically complete replacement of the resin' s hydrogen ions by MG ions.

From the data presented in Fig. 1 it is seen that, during sorption of the dye on KU-2 resin with 2% DVB, thermodynamic equilibrium is established in the system–

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

equilibrium independently of temperature (temperature interval 40–75°). In the case of the KU-2 ion exchanger with 6% DVB, the system reaches equilibrium only at a temperature of 75°. At lower temperatures the system does not reach the state of true equilibrium, although the sorption process practically ceases.

Figure 2 shows the dependence of the differential diffusion coefficients D_d (cm^2/sec) on temperature. In those cases where the ion exchanger–solution system reaches an equilibrium state (on KU-2 resin with 2% DVB at all temperatures and on KU-2 resin with 6% DVB at a temperature of 75°), the value of the differential diffusion coefficient, as the degree of preliminary replacement of the hydrogen ions of the resin by MG ions increases (from 0 to 0.8), decreases by only a factor of 1.5–2. Under conditions in which a state of false equilibrium is established in the system (KU-2 resin with 6% DVB, temperature below 60°), the value of the differential diffusion coefficient decreases by one to two orders of magnitude.

Figure 3 shows the dependence of the activation energy of MG diffusion in the ion-exchanger phase on the degree of preliminary replacement of hydrogen ions in the resin by dye ions. (The activation-energy values were calculated from the data presented in Fig. 4.) From the curves in Fig. 3 it is evident that, for a cation exchanger with a low DVB content, the value of the activation energy does not depend on the amount of sorbed MG ions; whereas in the case of a cation exchanger with a high DVB content, the value of the activation energy of MG diffusion in the ion-exchanger phase increases by a factor of 2.5 as the MG content in the ion exchanger rises from 0 to 80%.

The results presented show that the establishment of false equilibria during sorption of organic ions on ion exchangers is associated with a decrease in the permeability of the ion exchanger with respect to the ion being sorbed. This decrease in permeability is expressed in a decrease in the diffusion coefficients of dye ions in the ion-exchanger phase and in an increase in the activation energy of ion diffusion in the resin as the ion exchanger passes from one form to another.

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