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Abstract

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SORPTION OF WATER VAPOR BY SULFONIC-ACID AND CARBOXYLIC CATION EXCHANGERS

Studies of the sorption of water vapor by ion exchangers have been carried out for a number of years. Sulfonic-acid cation exchangers, as well as anion exchangers of the strong-base type, have been studied more fully ([1]-[11]). However, the uptake of water vapor by weak-acid carboxylic cation exchangers has been studied comparatively little ([1], [11]); apart from the hydrogen form, only the Na^+-, K^+-, and NH_4-forms have been investigated. Yet even from the scant information available in the literature it follows that the process of sorption of water vapor on carboxylic cation exchangers apparently differs from the sorption process on sulfonic cation exchangers and cannot be satisfactorily explained on the basis of the concepts ([1], [2], [12], [13]) usually applied to account for the sorption of water by sulfonic-acid cation exchangers.

In the present work we investigated the sorption of water vapor by monofunctional cation exchangers: the sulfonic-acid exchanger KU-2 and the carboxylic exchanger KFU, with the aim of comparing them. To obtain isotherms of water-vapor uptake, the isopiestic method is usually used ([1], [14], [11]). Meanwhile, in the present case, recording isotherms in a vacuum apparatus with the aid of McBain quartz spring balances has the following advantages: 1) a considerable acceleration of the attainment of sorption equilibrium and 2) the possibility of working with small samples. We therefore used this method to obtain the isotherms of water-vapor sorption.

The entire vacuum apparatus was surrounded by an air thermostat with automatic temperature regulation. The isotherms were recorded at 25° simultaneously on eight samples with sample weights of 0.1–0.2 g. Measurements were begun after complete removal of moisture from air-dry samples in the vacuum apparatus at ~40° and a pressure of $\sim 10^{-5}$ mm. Depending on the type and ionic form of the resin, pumping was continued from 1 to 3 days. To check the completeness of pumping, the moisture content of some resin samples was also determined by drying them in an oven at $t \simeq 100–110°$ (KU-2) and by holding them for 3–4 weeks in a desiccator over P_2O_5 (KU-2 and KFU). All three methods gave concordant results.

Figure 1. Water-vapor sorption isotherms by the KU-2 sulfocation exchanger.

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The ion-exchange capacity of the investigated ion exchangers in the hydrogen form was determined potentiometrically. For KU-2 containing 2, 10–12, and 24 divinylbenzene (DVB), it was 4.90, 4.80, and 5.10 meq/g of dry resin, respectively. The capacity of KFU with swelling coefficients K_{swell} in 1N NaOH of 4.5 and 3.8 was equal to 5.70 meq/g of dry resin in the hydrogen form. From these data, capacities were calculated for the other ionic forms.

Under the conditions of our experiments, the equilibrium values of water sorption at p/p_s* up to ~0.8 were reached in no more than 4 hours, whereas at $p/p_s = 1$ a day or more was sometimes required.

The relative error of the measurements in the middle region of the isotherms ($0.4 \lesssim p/p_s \lesssim 0.6$) did not exceed $±$0.5%; as the measured quantities increased it was still smaller; at small p/p_s, in the worst case it amounted to $±$5%.

* p –pressure of saturated water vapor. p_s –pressure of water vapor over the ion exchanger.

Fig. 1. Water-vapor sorption isotherms by the KU-2 sulfocation exchanger.
a –in the H^+ form at DVB content: **1** –2%; **2** –10–12%; **3** –24%;
b –curves for partially neutralized resins: **1** –H^+ form; **2** –65% H^+ + 35% Na^+; **3** –30% H^+ + 70% Na^+; **4** –Na^+ form;
c –various ionic forms: **1** –H^+ form; **2** –Li^+ form; **3** –Na^+ form;
d –**1** –H^+ form; **2** –Mg^{2+} form; **3** –Ba^{2+} form.

Water-vapor sorption isotherms were measured on three samples of the KU-2 sulfocation exchanger in the H^+ form, differing in DVB content (2, 10–12, and 24%), and also isotherms for KU-2 samples with 10-12% DVB in the Na^+, Li^+, Mg^{2+}, and Ba^{2+} forms. In addition, isotherms were obtained for two KU-2 resins (10-12% DVB) with different degrees of replacement of H^+ by Na^+.

For the KFU carboxylic cation exchanger, sorption isotherms were measured for the Na^+ forms of two samples with different swelling coefficients in 1 N NaOH, equal to 4.5 and 3.8. For KFU resin with $K_{\text{sw}} = 3.8$, isotherms were recorded for the Na^+, Li^+, Cs^+, Mg^{2+}, and Ba^{2+} forms. In addition, for this same resin, isotherms were obtained for samples with different degrees of replacement of H^+ by Na^+.

The H^+ forms of the resins were obtained by washing the technical products with 2 N HCl until a negative reaction for the Fe^{3+} ion was obtained, followed by washing out the acid with distilled water.

The other ionic forms, except for the magnesium form, were obtained by treating the H^+ forms of the resins with 1 N solutions of the chlorides of these metals, followed by neutralization of the displaced H^+ ions with hydroxides of the same metals. The Mg^{2+} forms of both cation exchangers were obtained by repeated washing of the hydrogen forms with 1 N $MgCl_2$ solution until the pH values of the equilibrium and initial solutions became identical. KU-2 samples with partial replacement of H^+ by Na^+ were obtained by treating a weighed portion of the H^+ form of the resin with solutions of 0.1 N HCl + 0.1 N NaCl in different ratios. The degree of replacement of H^+ by Na^+ was determined analytically from the change in the concentrations of H^+ and Na^+ in solution. In the case of KFU this was achieved by treating a weighed portion of the resin with a definite volume of 1 N solution containing different amounts of NaOH. The degree of replacement of H^+ by Na^+ was determined potentiometrically. All samples were filtered off from the equilibrium solutions, thoroughly dried with filter paper, and the liquid remaining on the surface of the grains ···

the film of salt solution was removed by rapid washing with distilled water. The samples prepared by these methods were dried in air.

The results of the measurements are presented in Figs. 1 and 2, where only the adsorption branches of the isotherms are shown. It should be noted, however, that for all the samples we studied a distinct, more or less broad hysteresis loop was observed (cf. [2,8,11]). In contrast to sorption on ordinary porous materials, such as, for example, silica gel, the desorption branches for the samples studied do not merge with the adsorption branches down to very small p/p_s.

As can be seen from Fig. 1, all the isotherms for KU-2 have an S-shaped form. At first rapid absorption of water is observed, followed by an almost linear portion of the isotherm, and then, at $p/p_s > 0.6$, a rapid increase in sorption is again observed up to a certain limit. In agreement with the results of studies [1,2,4,9], Fig. 1 shows that the higher the DVB content in the resin, the lower the corresponding isotherm lies. The curves for partially neutralized resins show that the more H^+ is replaced by Na^+, the less water the resin absorbs at identical p/p_s. The relative positions of the isotherms for different ionic forms of KU-2 correspond to the series:

$$H^+ > Li^+ > Na^+ \quad \text{and} \quad H^+ > Mg^{2+} > Ba^{2+}.$$

These series are analogous to the series of hydration of ions in ordinary electrolyte solutions [14]. From these data it follows that a resin containing the ion most highly hydrated in aqueous solution absorbs the greatest amount of water vapor. This is consistent with the results obtained earlier [1,2,4,9]. The different absorption of water by different forms of resins is usually explained [1] on the basis of the analogy between the hydration of cations in solutions and in the resin phase. It was concluded that, in the case of monovalent ions, in these systems there is no interaction between the exchange ions and the resin matrix. But this point of view was disputed by other authors [4,5]. In the case of the Ba^{2+}-form, the possibility of formation of ion pairs was taken into account [1];

this explained the considerably smaller absorption of water by the Ba^{2+}-form than would have been expected from the hydration series.

Fig. 2. Isotherms of sorption of water vapor by the carboxylic cation exchanger KFU: **a**—Na^+-form: 1 $-K$ = 4.5; 2 $-K$ = 3.8. **b**—curves for resins with different degrees of replacement of H^+: 1 $-H^+$-form; 2 -72% H^+ + 28% Na^+; 3 -37% H^+ + 63% Na^+; 4 $-Na^+$-form. **c**—curves for different ionic forms: 1 $-H^+$-form; 2 $-Li^+$-form; 3 $-Cs^+$-form; 4 $-Na^+$-form. **d**—same as **c**: 1 $-H^+$-form; 2 $-Mg^{2+}$-form; 3 $-Ba^{2+}$-form.

Thus, despite certain minor contradictions, the sorption of water by sulfonic-acid cation exchangers was, on the whole, satisfactorily explained by (1) the simple hydration of completely free cations in the resin phase. But the experimentally observed picture changes on going from a sulfonic-acid resin to a carboxylic one.

In Fig. 2 it is seen that the KFU resin with a higher swelling coefficient at high p/p_s sorbs more water. Here the analogy between KU-2 and KFU ends. The curves for carboxylic resins with different degrees of replacement of H^+ by Na^+ show that the more H^+ is replaced by Na^+, the more water the resin absorbs—precisely the opposite of what was observed in the case of KU-2. The sorption curves of KFU do not have the sharp initial rise observed in the case of KU-2.

The arrangement of the water-vapor sorption isotherms for different ionic forms of KFU is completely reversed in comparison with the arrangement of the KU-2 curves. Below the others lies the isotherm for the slightly dissociated H^+-form of the resin. In the case of the other KFU forms, the difference in water sorption can also be explained by the different degree of interaction of the exchange cations with the matrix anion, owing to the different polarizability of the latter in the field of the cations.

It is known that strong acids of the H_2SO_4 type form a poorly polarizable, "hard" anion. Therefore, in the case of the sulfonic cation exchanger KU-2, one may, as was done earlier (1), explain the experimental data on water sorption by differences in the hydratability of the cations, where the formation of ion pairs is unlikely. However, in the case of the carboxylic resin KFU the picture will be different. The carboxyl anion, apparently, is much more easily polarized in the field of cations. Thus, for example, the Li^+ ion, with its smaller radius, should polarize the resin anion more strongly than the larger Cs^+ ion. Consequently, in this case the resin contains fewer "free" cations than in the case of the Cs^+-form; therefore the sorption of water by the Li^+- and Cs^+-forms of KFU will be different. The experimental facts cited are in complete agreement with the viewpoint set forth here. It may further be assumed that, in the present case, the change in the number of "free" ions has a greater effect on water sorption by ion exchangers than do differences in the magnitudes of hydration of each ion.

Similar considerations can also be applied to the divalent ions Ba^{2+} and Mg^{2+}, and thus explain the relative arrangement of the isotherms for the resins in the Ba^{2+}- and Mg^{2+}-forms up to $p/p_s > 0.7$. At higher p/p_s, the curve for Ba^{2+} lies lower than that for Mg^{2+}. The reasons for this are unclear.

The results obtained and their analysis thus show that simple notions about the hydration of completely free cations in the resin phase (1), without allowance for the possible formation of ion pairs between the matrix anion and the exchange cations, probably cannot explain the entire body of experimental facts, especially in the case of carboxylic cation exchangers. Introducing ideas about their different interaction with exchange cations makes it possible to explain all the experimental results obtained in this work.

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