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Abstract

Full Text

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HEATS OF INTERACTION OF A SULFOSTYRENE CATION EXCHANGER WITH WATER

Depending on the intended use of an ion exchanger, it is easy to vary the type and number of fixed ions and the number of cross-links in the matrix. This makes synthetic ion-exchange resins a very convenient object for studying the process of binding water by hydrophilic substances. In turn, investigation of the hydration process makes it possible to form a clearer picture of the mechanism of interaction of ion exchangers with aqueous solutions.

One of the most theoretically well-founded methods for the quantitative evaluation of hydrophilicity is the method of heats of wetting ([1]). From experimental values of integral and differential heats, the amount of bound water ([2]), the number of free hydrophilic groups ([3]), the hydration numbers of functional groups ([4]), and other important quantities ([5]) are determined.

Although a large number of works have been devoted to the study of ion exchangers ([6]), the energetic aspect of ion exchange has been studied very little. There are only a few works on heats of wetting ([7]), carried out abroad. The lack of data is holding back the development of the theory of ion-exchange processes; therefore, studies in the field of thermochemistry and thermodynamics are highly relevant ([8]).

The aim of the present work was to study the influence of the nature of the exchange ions on the hydrophilic properties of a strongly acidic cation-exchange resin. The H^+-, K^+-, Na^+- and Ca^{2+}-forms of the sulfocation exchanger KU-2 with a nominal divinylbenzene content of 4% were investigated. Preparation of resin samples of different forms, preparation, and performance of calorimetric measurements of heats of wetting have been described previously ([6,9]). The results of the experiments are shown in Figs. 1 and 2.

As can be seen from the graphs, the nature of the change in the curves $q = f(x)$ as a function of the degree of preliminary moistening indicates a different nature of water binding at different stages of its absorption. At the beginning of the process, a certain amount of water is bound with a considerable thermal effect, apparently by the hydrophilic sulfo groups and exchange cations of the resin.

Fig. 1. Heats of wetting with water. 1 –H^+ form; 2 –K^+ form; 3 –Na^+ form; 4 –Ca^{2+} form

Figure 1: Fig. 1. Heats of wetting with water. 1 –H^+ form; 2 –K^+ form; 3 –Na^+ form; 4 –Ca^{2+} form

Fig. 2. Differential heats of wetting (notations as in Fig. 1)

Figure 2: Fig. 2. Differential heats of wetting (notations as in Fig. 1)

Other processes, for example swelling, here pro–

Table 1

Energy of interaction of H_2O molecules with 1 g-equiv of sulfocation exchanger KU-2

Cations	1st mol.	2nd mol.	3rd mol.	4th mol.	5th mol.	6th mol.
H^+	4.06	2.06	1.20	0.75	0.49	0.21
Ca^{2+}	4.17	1.74	1.00	0.54	0.22	0.12
Na^+	3.34	1.47	0.91	0.30	0.14	0.08
K^+	3.90	0.60	0.24	0.12	0.07	0.05

Energy, kcal (g-equiv)*

* 1 calorie is taken as equal to 4.186 joules.

are weak, but as further moistening proceeds their importance increases and becomes predominant. It is precisely the influence of swelling that can explain the unexpected negative thermal effects of the interaction of the potassium and sodium forms of the resin with water.

If, from the heats of wetting, one calculates the interaction energies of water molecules successively bound by 1 g-equiv of resin, the values given in Table 1 are obtained.

Fig. 1. Heats of wetting with water. 1 –H^+ form; 2 –K^+ form; 3 –Na^+ form; 4 –Ca^{2+} form

Fig. 2. Differential heats of wetting (notations as in Fig. 1)

From the data in Table 1 it follows that in all cases the first water molecule is bound with considerable energy, corresponding to the energy of formation of a hydrogen bond. The nature of the cation is only weakly manifested here. The energies of attachment of subsequent molecules decrease at different rates and, within a certain interval, depend on the type of exchange cations. It may be assumed that the first water molecule is bound by the sulfo groups of the resin, whereas several subsequent ones are bound by cations. After saturation of the resin ions, water is absorbed mainly through swelling. In those cases where no new hydration centers are formed during swelling, the thermal effects become negative (the curves $q = f(x)$ for the Na^+ and K^+ forms, Figs. 1 and 2). During swelling of the Ca^{2+} form of the resin, the appearance of free ions of both signs is possible owing to rupture of transverse bonds formed by the Ca^{2+} ion between two sulfo groups of neighboring chains, followed by their hydration. Evidently, the hydration energy exceeds the negative energy of swelling and bond rupture, and therefore the total value is positive. In the case of swelling of the H^+ form of the cation exchanger the picture is different. Here an oxonium ion is formed, the hydration of which apparently occurs with an energy exceeding the negative swelling energy over the entire length of the curve $q = f(x)$ (10).

As indicated above, from the heats of wetting one can calculate the amount of bound water using the equation of A. V. Dumanskii (11). The corresponding calculations gave the following values for the investigated forms of the cation exchanger (g-mol H_2O/g-equiv): K^+ form –3.06, Na^+ form –4.03, Ca^{2+} form –5.63, and H^+ form –6.28. As can be seen, these values almost coincide with the moisture contents corresponding to the beginning of the horizontal branch of the curves $q = f(x)$

(Fig. 2). If it is assumed that in all cases the first water molecule is bound to the sulfo group of the cation exchanger, then the hydration numbers obtained for the cations are close to the values reported in the literature (12). In particular, the most reliable hydration number of the H^+ ion of a sulfostyrene resin, obtained by Pepper and Reichenberg (13) by three independent methods, is equal to five, i.e., it corresponds exactly to the value obtained by us.

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