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Abstract

Full Text

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THERMODYNAMICS OF HYDRATION OF ION EXCHANGERS

Synthetic ion-exchange resins are a convenient model object for studying the process of interaction of hydrophilic substances with water. The study of the hydration of ion exchangers also has important independent significance. Knowledge of its nature and mechanism broadens the understanding of the properties of ion exchangers that determine their practical value.

The most theoretically substantiated method for quantitatively evaluating hydrophilicity is the method of heats of wetting ([1]). From the values of the heats of wetting of a hydrophilic substance with water, the amount of bound water, the number of free hydrophilic groups, and the number of hydration groups of various functional groups and cations are determined ([2]). In combination with sorption measurements, this method makes it possible to study the nature of changes in thermodynamic functions during hydration ([3]). Differential enthalpy and entropy prove to be especially indicative functions; from their change as a function of moisture content one can judge the state of the sorbed water up to saturation humidity ([4]). In works devoted to ion exchange, comparatively little attention is paid to the thermodynamics of hydration, and the calculation of thermodynamic functions is usually carried out on the basis of experiments on sorption of water vapor ([5]). Comprehensive studies using sorption and thermochemical data for these purposes have not been carried out, although their relevance has been noted ([6]).

Fig. 1. Isotherms of sorption of water vapor by KU-2 sulfonic cation exchanger. 1 –H^+ form, 2 –K^+ form, 3 –Na^+ form, 4 –Ca^{2+} form

In the present work, the isotherms of sorption of water vapor, the heats of wetting with water, and the thermodynamic functions of water sorbed by various forms of KU-2 sulfonic cation exchanger have been investigated. Two series of experiments were carried out with the H^+-, K^+-, Na^+- and Ca^{2+}-forms of the cation exchanger. In the first of them

samples of resin with a nominal divinylbenzene (DVB) content of 4%; in the second, with 20%. With an increase in the amount of DVB, the number of cross-links in the ion-exchanger matrix increases and, as a result, the degree of swelling decreases. For example, for the H^+- and Ca^{2+}-forms of the KU-2 cation exchanger with 4% DVB it is equal to 237 and 196%, and with 20% DVB to 160 and 130%, respectively. The preparation of resin samples of different forms, their preparation for experiments, and the performance of sorption and calorimetric measurements have been described earlier (5, 7). The results of the experiments are presented graphically in Figs. 1 and 2.

Table 1

Monolayer capacity and energy of adsorption of water by the KU-2 sulfocation exchanger

Cations	4% DVB, v_m, mmol/g	4% DVB, $\Delta\varepsilon$, cal/mol	20% DVB, v_m, mmol/g	20% DVB, $\Delta\varepsilon$, cal/mol
H^+	11.10	1830	12.00	1830
K^+	4.46	1890	5.88	1930
Na^+	6.58	1690	6.86	1850
Ca^{2+}	6.46	1890	7.75	1990

Table 2

Amounts of bound water for the KU-2 sulfocation exchanger

Cations	4% DVB, mmol/g	4% DVB, g-mol/g-equiv	20% DVB, mmol/g	20% DVB, g-mol/g-equiv
H^+	34.0	6.28	37.0	6.82
K^+	13.8	3.06	13.0	2.89
Na^+	19.6	4.03	21.8	4.49
Ca^{2+}	27.7	5.63	27.4	5.56

Figure labels and visible plot text: vertical axes, “cal/g” ; left plot, “4% DVB” ; right plot, “20% DVB” ; horizontal axes, “mmol H_2O/g” ; curves numbered 1–4.

Fig. 2. Heats of wetting with water of the KU-2 sulfocation exchanger. Designations as in Fig. 1

Fig. 3

Figure 2: Fig. 3

In Fig. 1 are shown the sorption isotherms of water vapor by the studied samples of sulfocation exchanger. For all forms the overall sorption capacity proves to be very high. In the interval p/p_0 from 0 to 0.6–0.7 it increases in the series $\mathrm{K}^+ < \mathrm{Na}^+ \approx \mathrm{Ca}^{2+} < \mathrm{H}^+$; near $p/p_0 = 1.0$ the sequence changes: $\mathrm{Ca}^{2+} < \mathrm{K}^+ < \mathrm{Na}^+ < \mathrm{H}^+$. The influence of the number of cross-links is manifested at values $p/p_0 > 0.90$—samples of the cation exchanger with 4% DVB sorb appreciably more vapor than those with 20% DVB.

If it is assumed that on the section of the isotherms from the origin to the first inflection a monolayer is formed, then by the Brunauer, Emmett, and Teller equation (8) one can calculate its capacity v_m and the energy of formation $\Delta\varepsilon$ (Table 1). From the data in Table 1 it follows that both quantities change little with the density of the spatial structure of the matrix. As for

influence of the nature of the counterions, then here an increase in v_m is observed in the series $K^+ < Na^+ \approx Ca^{2+} < H^+$. The closeness of the values of $\Delta\varepsilon$ and their independence of the kind of exchange ions make it possible to assume an identical mechanism of water binding in the initial region of the isotherms.

The course of the curves for the dependence of the heats of wetting on the moisture content of KU-2 sulfocationite samples, $q = f(x)$, indicates a different character

Fig. 3. Differential entropy of water bound by KU-2 sulfocationite. Designations as in Fig. 1

of water binding at different stages of its absorption (Fig. 2). In the moisture-content interval corresponding to the capacity of the monolayer, hydration of the sulfo groups apparently occurs. Upon further moistening, the cations and new active centers formed upon rupture of cross-links between the polymer chains are hydrated (^{9}). Here secondary factors may be superimposed on the hydration energy. For example, in samples of the K^+- and Na^+-forms

Table 3

Binding energy of water molecules

Cations	% DVB	1st mol.	2nd mol.	3rd mol.	4th mol.	5th mol.	6th mol.	7th mol.
		$-\Delta H$, kcal/g-equiv	$-\Delta H$, kcal/g-equiv	$-\Delta H$, kcal/g-equiv	$-\Delta H$, kcal/g-equiv	$-\Delta H$, kcal/g-equiv	$-\Delta H$, kcal/g-equiv	$-\Delta H$, kcal/g-equiv
H^+	4	4.06	2.06	1.20	0.75	0.49	0.21	–
H^+	20	4.80	2.18	1.18	0.50	0.40	0.24	0.15

Cations	% DVB	1st mol.	2nd mol.	3rd mol.	4th mol.	5th mol.	6th mol.	7th mol.
K^+	4	3.90	0.60	0.24	0.12	–	–	–
K^+	20	3.20	1.00	0.34	0.04	–	–	–
Na^+	4	3.34	1.47	0.91	0.30	0.14	0.08	–
Na^+	20	3.64	1.49	0.85	0.46	0.16	0.06	–
Ca^{2+}	4	4.17	1.74	1.00	0.54	0.22	0.12	–
Ca^{2+}	20	3.86	1.87	1.06	0.55	0.28	0.14	0.10

of the resin, the influence of the effect of chain rupture and stretching of the spatial network upon swelling is clearly revealed. In this case, the energy of bond rupture and the work of volume increase are not fully compensated, since the K^+- and Na-ions cannot form bonds between neighboring chains, and the observed heats of wetting become negative after a certain moisture-content limit has been reached.

Table 2 gives the amounts of bound water for the investigated forms of the sulfocationite, calculated from the integral heats of wetting according to the equation of A. V. Dumanskii ([10]).

From the data of Table 2 it is seen that the order of increase of the hydration numbers is the same as in the case of sorption of water vapor at low and medium values of p/p_0, and that the amount of bound water does not depend on the density

of the spatial structure of the ion-exchanger matrix. This confirms the assumption that, in this range of moisture content, water is bound predominantly through hydration of the sulfo groups and of the exchange cations.

From the heats of wetting, the energies of the successive interaction of water molecules with a gram-equivalent of resin were also calculated (Table 3).

The data in Table 3 show that in all cases the first water molecule is bound with an energy close to that of a hydrogen bond and does not depend on the nature of the counterion or on the density of the spatial structure. The subsequent water molecules are attached with a lower energy, the magnitude of which, within a certain interval, is influenced by the type of exchange ion. After a certain limit is reached, different for the different forms of the resin, the bond energies become small in magnitude and again almost identical for all samples. This gives grounds to suppose that the first water molecule is bound to the sulfo groups of the resin, several of the following ones to the exchange cations, and that swelling then takes place. The hydration numbers obtained in this way are close to values reported in the literature ([11]).

Figure 3 shows the curves $-\Delta\overline{S} = f(x)$. The graphs for all forms of the sulfocation exchanger are characterized by two distinct minima. The deeper of these corresponds to the formation of a layer of water molecules with the most ordered structure. Apparently, hydration of the sulfo groups takes place here. The second minimum may be explained by preferential hydration of the cations. Further absorption of moisture proceeds with only a slight change in entropy. In this region, up to the saturation humidity, the state of the molecules of sorbed water differs little from their state in the bulk. Clear differences between the entropy curves of sulfocation-exchanger samples with 4 to 20% DVB are not observed. Similar curves for certain monovalent forms of the KU-2 sulfocation exchanger were also obtained by calculation from sorption isotherms at two temperatures (12). However, the second minimum in them is not as sharply expressed as in our case.

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Note: Figure translations are in progress. See original paper for figures.