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THERMOANALYTICAL INVESTIGATION OF ION EXCHANGE RESINS. THE SWELLING WATER OF ANION EXCHANGE RESINS

J. INCZÉDY

Department of Analytical Chemistry, University of Chemical Engineering, Veszprém, Hungary

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The water uptakes of completely swollen and air dried anion exchange resins were investigated by traditional and also by thermoanalytical measurements. In investigations on the air dried resin samples of HSO_4, H_2PO_4, SO_4, HPO_4 and PO_4 forms, two types of water (strongly and loosely bound) were found. The sequence of water uptake on the resins investigated was compared to the opposite order of the adsorption strengths of the anions and to the entropies of the hydrated anions. A conclusion was made regarding the role of the hydration of the anions in the selectivity sequence of anion exchange.

The operation rate and selectivity of ion exchange resins are strongly correlated with their swelling properties. The water uptake of the swollen resin depends on the one hand on the nature of the counter ion; on its hydration ability and on the nature of the chemical bond existing between the fixed ionic group and the mobile ion. On the other hand, it also depends on the expansibility of the resin matrix, on the density of the ionic groups (capacity) and on the ionic strength and composition of the outer solution.

In the present work the effect of the nature of the counter ion on the water content of a conventional type, strong basic anion exchange resin was investigated using thermoanalytical measurements.

Experimental

Ion exchange resin. Dowex 1 × 8 (Dow Chemical, USA) (100–200 mesh) was used in all experiments. The required form of the resin was made in a column, using the corresponding sodium or potassium salt solution in 1 *M* concentration. After complete saturation, the resin was washed out with water in the case of chloride, nitrate and sulphate form resins. To avoid hydrolytic transformations, the HSO_4, HPO_4, H_2PO_4 and PO_4 form resins were quickly rinsed with the diluted ($- 10^{-2}$ *M*) salt solution only. It must be stressed that the composition of the PO_4 form resin can not be assumed to be uniform. On the use of trisodium phosphate solution for the preparation of the resin sample, hydroxyl or HPO_4^{2-} ions may also bound by the resin. The total capacity of the resin investigated was in chloride form: 3.49 mval/g (dry resin).

Thermoanalytical measurements were carried out with ground air dried resin samples (500 mg) using a derivatograph (System: Paulik – Paulik – Erdey, MOM, Hungary) with a heating rate of 3°/min. TG, DTG, DTA and T curves were recorded. From the TG and DTG curves the amounts of water lost and the related peak temperatures were evaluated. In Figs 1 and 2 typical thermal curves are presented. The results of the evaluated measurements are summarized in

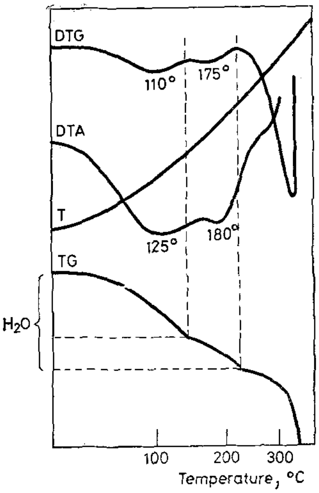

Fig. 1. Thermoanalytical curves of SO_4 form of air dried Dowex 1×8 resin

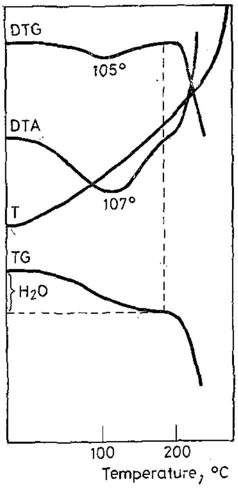

Fig. 2. Thermoanalytical curves of NO_3 form of air dried Dowex 1×8 resin

Table 1

Specific water contents of air dried Dowex 1×8 resin samples of different forms, and some thermodynamic data on the anions.

Ion	NO_3^-	Cl^-	HSO_4^-	$H_2PO_4^-$	SO_4^{2-}	HPO_4^{2-}	PO_4^{3-}
Loosely bound H_2O (120°) mole/equiv. resin	1.64	2.90	2.4	3.3	3.0	3.1	3.0
Strongly bound H_2O (175°) mole/equiv. resin	—	—	0.8	0.4	1.1	1.7	2.0
Total water uptake mole/equiv. resin	1.64	2.90	3.2	3.7	4.1	4.8	5.0
Ion exchange constant (ref. Cl ion)	3.8	1	4.1	0.16	0.06	0.09	0.002
Entropy of hydrated ion (e.u.)	40.3	18.5	35.6	26.6	14.7	2.0	−36.1
Partial molar volume (25°) cm^3/mole	34.3	23.2	41.1	34.5	24.8	18.5	
Hydrated radius (Å)	3.35	3.32			3.7		

Ion exchange constants from [1—3]; entropy and partial molar volumes [4]; hydrated radius [5]

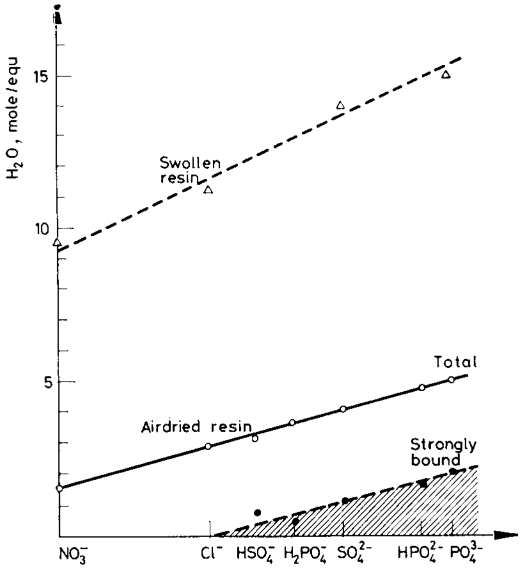

Fig. 3. Water uptakes of anion-exchange resin in different forms (Dowex 1×8; 22°); o-o-o- total bound water; —x—x— strongly bound water

Table 1. Before the measurements all resin samples were conditioned in the same way (22°, 50% rel. humidity).

Swelling measurements. For determination of the water uptake of the swollen resin samples from pure water at different temperatures, a wider-jacketed column was used. After equilibration the water was sucked off quickly and the swollen resin sample weighed. The total water content was calculated from the weights of the swollen and of the in vacuo dried (60°) resin. As a check on the results, the water contents were also determined by the Karl Fischer titration method. The data found are depicted in Figs 3 and 4.

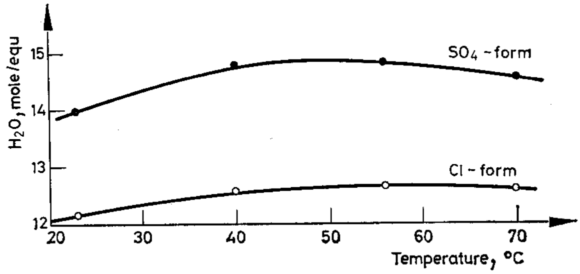

Fig. 4. Water-uptakes of SO_4 and Cl-form anion exchange resins at different temperatures (Dowex 1×8)

Discussion

Under carefully selected conditions (low heating rate, open plate sample holder, etc.), two steps of water loss were observed in the thermoanalytical curves of those air dried resin samples which had high hydration ability. The peak temperatures were found at about 120 and 170°, respectively. Hence, two types of absorbed water could be distinguished: loosely and strongly bound.

In Fig. 3 the anions investigated are arranged according to their water absorption tendency in air dried forms. The water uptakes of the completely swollen NO_3, Cl, SO_4 and PO_4-form resins are also presented. It can be seen that the water uptake of the swollen resin and the strongly bound water increases in a very similar fashion.

The water uptake of the swollen resin changes a little with temperature. This change, with a maximum, is pronounced in the case of the SO_4-form resin sample.

In order to find a correlation between the hydration tendencies of the resin samples of different forms and the thermodynamic properties of the anions, some data were collected and are presented in Table 1.

The data reveal that the hydration tendency sequence of the different forms of resin samples is the opposite of the ion exchange constant (i.e. adsorption strength of the ion) sequence, except for the data on the HSO_4 and SO_4-form resins. More interesting is that the entropy of the hydrated ion also exhibits an opposite sequence, except for the Cl-form resin, where the structure of the ion is markedly different from those of the other anions. Because the oxo-anions investigated are to a first approximation of similar structure, and the entropies of the ions in the gas phase are also near to each other, one can assume that the order of the hydration entropy follows the order of the entropy of the hydrated ions. Unfortunately, there are very few thermodynamic data on the hydration of anions, but one may assume that, as regards the adsorption strengths of the simple anions on the anion exchange resin, besides other effects (polarization, H-bonding, etc.) the free energy of hydration plays an important role. Between the electrostatic attraction and the hydration forces a competition may be assumed. Nevertheless, the radii of the hydrated ions have no significance whatsoever as regards the adsorption strengths of the anions (see also [6]).

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Résumé — On a étudié par des mesures traditionnelles et par analyse thermique l'absorption d'eau par des résines échangeuses anioniques totalement gonflées et séchées à l'air. Lors de l'étude des échantillons de résines séchées à l'air, de formes HSO_4, H_2PO_4, SO_4, HPO_4 et PO_4, on a trouvé deux types d'eau: de l'eau fortement liée et de l'eau faiblement liée. On a comparé l'ordre de l'absorption d'eau des résines étudiées à l'ordre inverse des forces d'adsorption des anions et à l'entropie des anions hydratés. On en tire des conclusions sur le rôle de l'hydratation des anions sur la sélectivité de l'échange anionique.

Zusammenfassung — Die Wasseraufnahme vollständig angequollener und lufttrockener Anionenaustauscherharze wurde mittels herkömmlicher sowie auch thermoanalytischer Messungen untersucht. Bei den Prüfungen der lufttrockenen Harzproben in den HSO_4-, H_2PO_4-, SO_4-, HPO_4-, und PO_4-Formen wurden zwei Arten von Wasser gefunden: stark und schwach gebundenes. Die Reihenfolge der Wasseraufnahme wurde mit der umgekehrten Reihenfolge der Adsorptionsstärke der Anionen und mit der Entropie der hydratisierten Anionen verglichen. Schlüsse bezüglich der Rolle der Hydratisierung der Anionen bei der Selektvititätsreihenfolge des Anionenaustausch wurden gezogen.

Резюме — Поглощение воды полностью набухшили и воздушносухими анионно-обменными смолами было исследовано традиционными методами, а также термоаналитическими. При исследовании воздушно-сухих образцов смол HSO_4-, H_2PO_4-, SO_4-, HPO_4-, PO_4-форм было найдено два типа воды: сильно и слабо связанной воды. Степень поглощения воды исследованными смолами была сопоставлена с обратной степенью адсорбционных сил анионов и с энтропией гидратации анионов. Сделано заключение о роли гидратации анионов на степень селективности анионообменника.