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APPLICATION OF CONTINUOUS AND SELECTIVE WATER DETECTOR FOR QUANTITATIVE MEASUREMENTS

DETERMINATION OF THE WATER CONTENT OF ANION-EXCHANGE RESINS

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A standard method was developed for investigation of the adsorbed water in ion-exchange resins. The previously-dried anion-exchange resins in Cl, SO_4 and HSO_4 form were investigated by simultaneous TG, DTG and DTA measurements (derivatograph), and the evolved gases were passed through the continuous and selective water detector system developed earlier.

It was found that in the case of SO_4 and HSO_4-form resins two types of water binding (loosely and strongly-bound water) could be distinguished. The second step, the strongly-bound water step, could not be observed in the DTG curves, because the release of the bound water and the decomposition of the fixed ionic group take place simultaneously. As the two types of water peaks strongly overlap, their quantitative evaluation was carried out by graphical analysis.

The water content of an air-dried resin depends on the nature of the counter anion and the chemical bond between the fixed ionic group and the mobile ion.

In the literature a few papers can be found dealing with determination of the water contents of air-dried or swollen ion-exchangers. The methods published involve drying [2, 3], Karl Fischer titration [4, 6], and recently NMR spectroscopy [7]. However, these methods are of no use for the determination of differently bound water in the resin phase, and the results obtained are difficult to compare if air-dried resins are investigated, on account of the uncertainty regarding the initial condition. Special problems arise if not cation, but anion-exchangers are investigated [6].

In the present work a conventional-type polystyrene – divinylbenzene copolymer-based anion-exchange resin was investigated, using thermoanalytical methods. Since the water content of an ion-exchange resin depends strongly on the condition of the surrounding atmosphere, a standardization process was applied before the measurements. From ambient temperature up to 250° the liberation of differently bound water and the partial decomposition of the resin matrix take place simultaneously. The decomposition stages overlap to such an extent that quantitative evaluation of the two types of adsorbed water could only be carried out by using the continuous and selective water detector [1]. The quantitative results of the investigations are given.

Experimental

Ion-exchange resin

Dowex AG 1×8 (Dow Chemical, USA) (100–200 mesh) quaternary ammonium type anion-exchange resin was used.

The required form of the resin was prepared in a column, using the corresponding 1 *M* salt solution. When saturation was completed, the salt-form resin was washed out with water. In order to avoid hydrolysis, the resin in HSO_4-form was washed with gradually diluted $KHSO_4$ solution (down to 10^{-2} *M*).

After formation, the resin samples were powdered in an agate mortar before the experiments. The finely-powdered samples were dried at room temperature. The water content of the air-dried powdered resin at room temperature depends on the humidity of the surrounding air.

To achieve standard conditions, the resin was layered onto the multi-plate sample holder of the derivatograph, and surrounded by a bell-shaped quartz cover. Dry nitrogen carrier gas was passed through the cover at a flow rate of 10 l/h for two hours. In this way, the sample was dried to constant weight by the dry carrier gas stream. It was found that the remaining water content was very reproducible and characteristic of the resin in question. This drying process was used before the measurements in all experiments.

Instrument

Measurements were carried out by a derivatograph (Hungarian Optical Works, Budapest) directly combined with the continuous and selective water detector. The equilibrated sample was heated at a rate of 5°/min. The gases evolved from the sample were collected quantitatively and passed through the detector cell by the nitrogen carrier gas, at a flow rate of 10 l/h.

The trace of the detector and the TG, DTG, DTA and T curves were recorded simultaneously.

The thermogastitrimetric unit of the derivatograph was also used to identify the amine components in the decomposition products.

Procedure used

A known amount of sample was dried to constant weight with the dry carrier gas stream in the furnace chamber of the derivatograph. When the drying process was completed, the sample was reweighed. Then the sample was heated and the thermoanalytical curves, including the trace of the water detector, were recorded.

Thermogastitrimetric measurements were carried out under the same experimental conditions. The decomposition products were collected quantitatively and conducted into an absorber vessel by the carrier gas stream. The changes of the amine concentration in the solution were followed by automatic acid-base titration, using potentiometric end-point indication.

Determination of the total capacity of the resin

The total capacity of the resin was determined in Cl-form. The dried equilibrium weight of the sample was determined above. Then the sample was suspended in 250 ml 1 *M* KNO_3 solution and stirred vigorously with a magnetic stirrer. The amount of chloride ion released into the solution was measured by direct potentiometric titration with 0.05 *M* $AgNO_3$ titrant.

The water content of the dried resin sample was determined as discussed below. It was found that the total capacity of the resin in Cl-form was 3.775 mequiv./g water-free resin.

The capacities in SO_4 and HSO_4-forms were calculated using the following equations:

$$R + Q_{Cl} \cdot M_{Cl} = 1000 \tag{1}$$

$$W = Q_{Cl} \cdot M_X + R \tag{2}$$

where

R is the amount of resin matrix, including the fixed ionic group, in 1000 mg Cl-form, water-free resin,
Q_{Cl} is the capacity of the Cl-form resin in mequiv./g water-free resin,
M_{Cl} is the atomic weight of the chloride ion,
M_X is the molecular weight of the counter anion X
W is the amount of water-free resin in X-form, containing Q_{Cl} mequiv. of anion X.

From Eqs (1) and (2) it follows that

$$Q_X = \frac{Q_{Cl}\,1000}{1000 + Q_{Cl}(M_X - M_{Cl})} \tag{3}$$

where

Q_X is the capacity of the X-form resin in mequiv./g water-free resin units. From Eq. (3) the capacities of the resin in the SO_4 and the HSO_4-form were found to be 3.604 mequiv./g and 3.063 mequiv./g, respectively.

Results and discussion

Figure 1 shows the thermoanalytical curves of the Cl-form resin and the trace of the detector. The recorded curves reveal only one type of bound water. The amount of water was determined in two different ways: from the TG and DTG curves, and from the trace of the water detector after calibration. The crystal water liberated from a known amount of heated $Ca(COO)_2 \cdot H_2O$ was used for calibration.

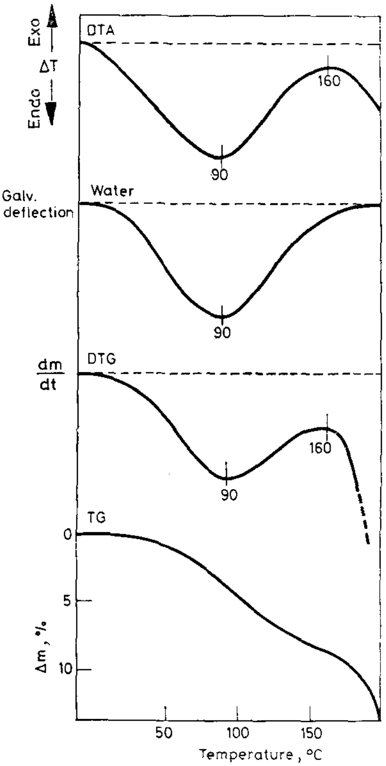

Fig. 1. Thermal decomposition curves of the Cl-form resin, including the signal of the water detector

Table 1

The calculated amount of water in the Cl-form resin

From TG and DTG			From water detector trace		
mol water / equiv. resin	average	deviation from average, %	mol. water / equiv. resin	average	deviation from average, %
1.388		−1.20	1.484		+1.37
1.367	1.400	−2.01	1.475	1.464	+0.75
1.445		+3.58	1.433		−2.12

A comparison of the results obtained by the two methods can be seen in Table 1. The thermoanalytical curves of the SO_4 and HSO_4-form resins and the traces of the water detector are shown in Figs 2 and 3. From comparisons of the corresponding curves the following conclusions can be reached:

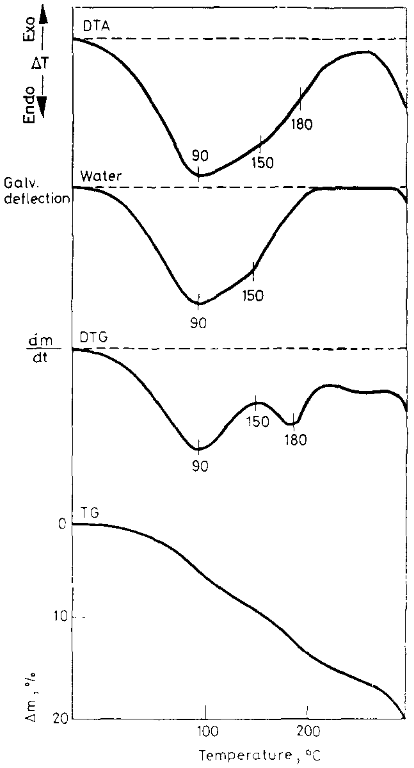

Fig. 2. Thermoanalytical curves of the SO_4-form resin and the trace of the water detector

a) The curves are very similar to each other. Only a slight difference is observed: the shape of the second peak at 180°, is somewhat sharper in the DTG curve of the SO_4-form resin than that for the HSO_4-form resin.

b) The first peak, at 90°, is connected with the release of loosely-bound water, and is indicated by the detector, but the second one at 180°, does not cause a detector response.

c) However, the signal curve produced by the detector does indicate strongly-bound water, with a peak at 150°. The presence of the second type of water is also supported by the DTA curves, with a slight endothermic effect at 150°.

Above 150° the partial decomposition of the resin matrix takes place. The structure of the resin matrix can be characterized by a formula similar to that in Fig. 4.

The evolved gases were absorbed in water by the thermogastitrimetric unit of the derivatograph and tested with Nessler reagent, $BaCl_2$ reagent solution and pH measurements, too.

During the decomposition process no ammonia was identified in the carrier gas, and SO_3 appeared above 230° only. It was found that the decomposition stage at 180° involves release of the methylated amine group, closely overlapping release of

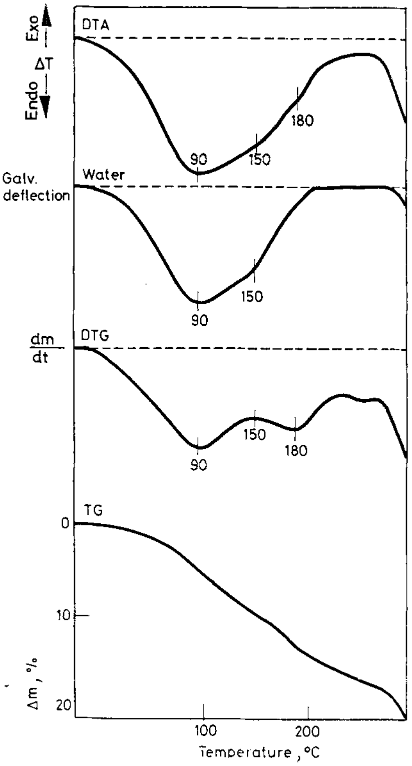

Fig. 3. Thermoanalytical curves of the HSO_4-form resin and the trace of the water detector

the strongly-bound water. According to thermogastitrimetric measurements (0.1 *M* HCl was applied as titrant), the liberation of the amine started at 150°. Unfortunately, complete titration of the amine evolved was not possible, because at ca. 230° the release of SO_3 spoiled the measurements.

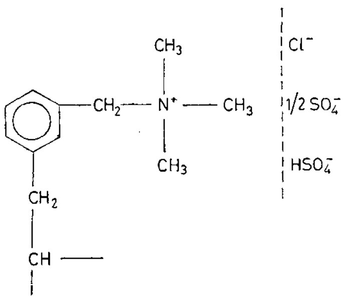

Fig. 4. Structure of the dry resin

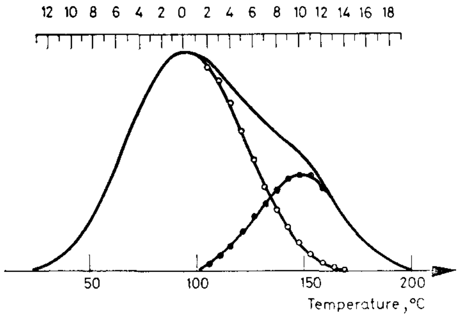

Fig. 5. A graphical separation of the two types of bound water in the case of SO_4-form resin

Quantitative determination of the two types of adsorbed water was carried out by using the signal curves of the water detector. The two strongly-overlapping peaks were separated graphically, as indicated in Fig. 5. In both cases the abscissa was

Table 2

The amount of water in SO_4-form resin

Loosely-bound water			Strongly-bound water		
$\frac{\text{mol. water}}{\text{equiv. resin}}$	average	deviation from average, %	$\frac{\text{mol. water}}{\text{equiv. resin}}$	average	deviation from average, %
1.751		−0.11	0.342		−4.20
1.789		+2.05	0.360		+0.84
1.730	1.753	−1.31	0.354	0.357	−0.84
1.770		+0.97	0.370		+3.64
1.727		−1.48	0.361		+1.12

Table 3

The amount of water in HSO_4-form resin

Loosely-bound water			Strongly-bound water		
$\frac{\text{mol. water}}{\text{equiv. resin}}$	average	deviation from average, %	$\frac{\text{mol. water}}{\text{equiv. resin}}$	average	deviation from average, %
1.974		−5.73	0.443		−1.77
2.210		+5.54	0.443		−2.00
2.206	2.094	+5.35	0.427	0.451	−5.32
2.013		−3.87	0.460		+2.00
2.066		−1.34	0.482		+6.87

divided into equal steps, symmetrically around the peak maximum. The ordinate values of the rising part of the curves were subtracted from the corresponding values over the maximum. Thus, the peaks were separated, and the areas under the curves determined by calibration. From the mass of the sample and the capacity value, the water-free mass and the $\frac{\text{mol. water}}{\text{epuiv. resin}}$ values for both types of water were calculated.

The results are listed in Tables 2 and 3.

Conclusion

With the use of a preliminary dynamic drying process, the determination of the "hydrate water contents" of the ion-exchange resins was possible. The results obtained are reproducible and applicable for comparison of resin samples in different forms (i.e. containing different counter ions). In the SO_4 and HSO_4-form resins, two types of water binding could be distinguished, and their amounts determined; in the Cl-form resin, however, only one type of binding was observed. This is in agreement with the results obtained earlier [8].

That the continuous selectiv ewater detector is an important tool in thermal analysis was supported by the measurements. Both the qualitative and the quantitative information yielded by the detector is indispensable when water is one of the evolved gases and a complicated organic material such as ion-exchange resin is heated.

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Résumé — On a mis au point une méthode type pour étudier l'eau adsorbée sur les résines échangeuses d'ions. On a étudié par TG, TGD et ATD simultanées les résines échangeuses d'anions sous la forme Cl, SO_4 et HSO_4 préalablement séchées et on a fait passer les gaz dégagés dans le système détecteur d'eau continu et sélectif mis au point précédemment.

Dans le cas des résines sous la forme SO_4 et HSO_4, on a trouvé que deux types d'eau (faiblement et fortement liée) pouvai ent être distingués. La deuxième étape, dénommée étape de l'eau fortement liée, ne peut être observée sur les courbes TGD, car le dégagement de l'eau liée et la décomposition du groupe ionique fixé ont lieu simultanément. Comme les deux types de pics dus à l'eau se recouvrent fortement, on a effectué leur évaluation quantitative à l'aide d'une méthode d'analyse graphique. Les données trouvées, exprimées en moles d'H_2O sur résine équivalente, sont les suivantes: pour la résine sous forme Cl 1.464, pour les résines sous formes SO_4 et HSO_4 les types d'eaux faiblement et fortement liées donnent respectivement 1.753, 0.357 et 2.094, 0.451.

ZUSAMMENFASSUNG — Eine Standardmethode wurde zur Untersuchung des absorbierten Wassers in Ionenaustauscherharzen entwickelt. Die vorhergehend getrockneten Anionenaustauscherharze in Cl, SO_4 und HSO_4-Form wurden durch die Methode der simultanen TG, DTG und DTA-Messungen untersucht und die entwickelten Gase das durch früher entwickelte kontinuierliche und selektive Wasserdetektorsystem geleitet.

Es wurde gefunden, daß in dem Falle der Harze der SO_4 und HSO_4-Form zwei Typen von Wasser (lose und stark gebundenes Wasser) unterschieden werden können. Die zweite Stufe, die sogenannte «Stark-gebundenes-Wasser»-Stufe konnte an den DTG-Kurven nicht beobachtet werden, da die Freisetzung des gebundenen Wassers und die Zersetzung der fixierten ionischen Gruppe simultan erfolgt. Da die zwei Typen der Wasser-Peaks stark überlappen, wurde ihre quantitative Auswertung under Anwendung einer graphischen Analysenmethode durchgeführt. Die auf äquivalentes Harz bezogenen Angaben in H_2O-Mol waren wie folgt: für Harz in der Cl-Form, 1.464, für die Harze in SO_4 und HSO_4-Form waren die Werte von lose und stark gebundenem Wasser 1.753 und 0.357, bzw. 2.094 und 0.451.

Резюме — Разработан стандартный метод исследования воды, адсорбированной на ионообменных смолах. Предварительно высушенные анионообменные смолы в Cl, SO_4 и HSO_4 формах исследовались одновременно методами ТГ, ДТГ, ДТА, а выделенные газы были пропущены через систему непрерывного и селективного детектирования воды, ранее разработанную авторами. Найдено, что в случае смол в SO_4 и HSO_4 — формах, можно разделить два вида воды: свободно связанную и сильно связанную. Вторая ступень, так называемая ступень сильно связанной воды, не может проявляться на кривых ДТГ, поскольку одновременно протекает выделение связанной воды и разложение фиксированной ионной группы. Поскольку эти два пиков воды сильно перекрываются, их количественная оценка была проведена методом графического анализа. Полученные данные, выраженные в молях воды на эквивалент смолы, следующие: для смолы в Cl-форме — 1,464, для смол в SO_4 и HSO_4-формах — свободно и сильно связанная вода, соответственно, — 1.753; 0.357 и 2.094; 0.451.