HEAT EFFECTS AND RATES AND MOLECULAR MECHANISMS OF WATER SORPTION BY PERFLUORINATED POLYMER MATERIALS BEARING FUNCTIONAL GROUPS

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Abstract

The heat effects and the rates and equilibrium quantities of H_2O vapour sorbed and desorbed on polymeric perfluorinated materials (functional groups $-SO_3H$, $-SO_3Na$, $-SO_3K$) and on material treated with $FeCl_3$ solution as sorbent were investigated.

Sorbed H_2O may be completely desorbed in vacuum at 443 K. The material bearing $-SO_3H$ has maximum sorption affinity: the molar heat of $-SO_3H$ wetting is close to that of H_2SO_4 wetting. The differential heat of sorption decreases from 68 kJ mol^{-1} at $n \cong 0$ ($n = H_2O/-SO_3H$) to 45 kJ mol^{-1} at $n \cong 5$, but not below the heat of H_2O condensation. The $-SO_3H$ samples sorb H_2O vapour in the presence of liquid H_2O at 293 K up to $n = 17$. The $-SO_3K$ material has minimum affinity for H_2O: the equilibrium quantity sorbed in room air is less by a factor of 4 than that for the $-SO_3H$ material. The spatial arrangement of H_2O molecules near the sulpho groups is considered.

Keywords: polymeric perfluorinated materials

Introduction

Calorimetric investigations complemented by stoichiometry measurements may serve as the basis for elucidation of some of the important details of molecular mechanisms of heterogeneous processes [e.g. 1–3]. We investigated the material 'Nafion'. In the source material, the main polymer chains consist of perfluoroethylene units, while the side-chains contain $-SO_3M$ functional groups and have the following composition:

$$-[O-CF_2-CF(CF_3)]_m-O-CF_2-CF_2-SO_3M \tag{1}$$
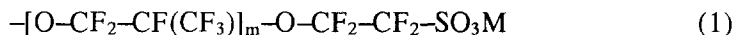
where M is H or a metal atom. Materials analogous with 'Nafion' [4] are used in the fabrication of cell membranes for the electrolysis of NaCl. The chemical properties and structure of 'Nafion' have been studied [e.g. 5–11], and the results have been reviewed [4, 12].

The present paper reports and discusses data on H_2O vapour sorption by materials with $M = H$ [13] and by such materials treated with $FeCl_3$ solution, and new data are also presented on H_2O sorption by materials with $M = Na$.

The sorption measurement procedure allows measurement of the differential enthalpy of hydration of the substrate, beginning with the lowest degree of wetting. Such measurements are important for elucidation of the molecular mechanisms of hydration processes.

The sorption and desorption of H_2O vapour in vacuum (closed system) and in humid room air (open system) were investigated.

Experimental

Materials

The samples for investigation were obtained by using the source polymer material with $M = H$ in the form of 0.25 mm thick films. The polymer mass on a $-SO_3H$ group basis (equivalent mass) is about 2000, i.e. the $-SO_3H$ group mass comprised 4.05% of the sample mass. The dehumidified polymer density is about 0.95 g cm^{-3}; in humid room air, the density is about 1.0 g cm^{-3}.

The source material was purified from iron ion impurities by exposure for 1 day to 17% HCl solution. The samples were then decanted many times with distilled water to wash out Cl^- ions. They were next exposed to air at room temperature for no less than 4 days until equilibrium with the room air had been reached (this interval was determined experimentally; see Fig. 4, curve OH). In this way, the $M = H$ samples for investigations were obtained.

To obtain the $M = Na$ (K) samples, the $M = H$ samples were exposed for 1 day to a 0.5 N solution of NaOH or KOH. The excess of $Na^+(K^+)$ ions was then washed out with distilled H_2O. The samples were next exposed to room air as described above. To obtain the samples with iron ions, the $M = H$ samples were exposed for 1 day to a 0.5 N solution of $FeCl_3$, then washed with distilled H_2O and exposed to room air.

For each experiment, accurate weights of samples were used (4–5 g). Noncalorimetric measurements were performed with pieces measuring $10 \times 3 \times 0.25$ mm (samples 1–8). Calorimetric measurements were made on samples of 20 mm wide ribbon (samples 9–12).

Reagents of grade p.f.a. ('pure for analysis') were used. For the experiments in the closed system, distilled H_2O vapour was used.

Sorption apparatus and noncalorimetric procedures

Noncalorimetric measurements were performed in a closed system and an open one (see Table). For the experiments in the open system, the samples were placed in a glass test-tube about 5 cm high. Noncalorimetric experiments in the

Table 1 Preliminary treatment of samples and nature of experiments

No.	M	Preliminary treatment of smples for investigations	Experiments	System
1	H	Humidified for 7 days at 293 K over liquid H_2O inside a desiccator	Desorption under room air conditions	Open
2	H	Held in room air at 293 K and 80–85% humidity for 30 days	H_2O vapour sorption from room air	Open
			Desorption under vacuum	Closed
3	H	Pumped out for several min to $1 \cdot 10^{-3}$ hPa with the trap (6, Fig. 1,a) cooled to 77 K; the tap (7) was then turned off and the trap was heated to 273 K	Desorption under vacuum at 273 K and above	Closed
4	H	As sample 3	Desorption under vacuum at 293 K and above	Closed
5	H	Held under vacuum for 24 h at 273 K and 4 h at 293 K with condensation of H_2O in the trap; the sample was then cut off with the tap (11) and the trap was pumped out	Desorption under vacuum at 333 K and above	Closed
6	Na	As sample 3	Desorption under vacuum at 273 K and above	Closed
7	K	As sample 3	Desorption under vacuum at 273 K and above	Closed
8	H(FeCl$_3$)	As sample 3	Desorption under vacuum at 273 K and above	Closed
9	H	Heated under vacuum for 6 h at 408 K with pumping out of desorbed H_2O	Calorimetric studies of H_2O vapour sorption	Closed
10	Na	As sample 9	Calorimetric studies of H_2O vapour sorption	Closed
11	H(FeCl$_3$)	As sample 9, but at 443 K	Calorimetric studies of H_2O vapour sorption	Closed
12	H(FeCl$_3$)	As sample 9	Calorimetric studies of H_2O vapour sorption	Closed

closed system were carried out in a sealed glass apparatus (Fig. 1,a). The sample for investigation was placed into the ampoule (3); the ampoule was sealed in the apparatus. Before experiments, the samples for investigations were treated as described in the Table.
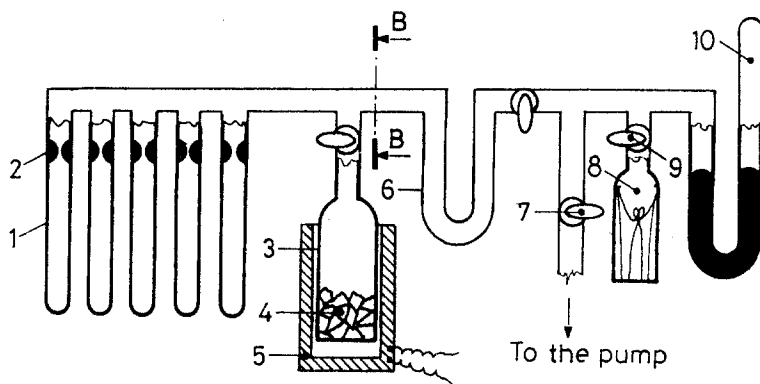
Fig. 1a Glass apparatus: (1) test-tube; (2) neck; (3) ampoule; (4) sample; (5) furnace; (6) trap; (7) tap; (8) thermocouple manometer; (9) tap; (10) mercury manometer

The experiments with samples 3–8 were carried out as follows. The ampoule with the sample was sealed into the apparatus (Fig. 1a) and was subjected to preliminary treatment (see Table). The ampoule was next connected to the degassed test-tube (1) with a neck (2); the test-tube was cooled to 77 K and the experiments on H_2O desorption under vacuum were performed. The test-tube with desorbed H_2O was then sealed and cut off across the neck, weighed and cut in two. The H_2O was evaporated at 380 K and the empty tubes were weighed. The mass of desorbed H_2O was calculated.

After the first test-tube was unsealed, the next desorption experiment at the same temperature was carried out, and so on until the desorption ceased. The desorption temperature was raised stepwise. The experiments with each sample were finished once a further rise in temperature did not result in any additional desorption.

Under the test conditions, the samples evolved nothing but H_2O vapour. It was established beforehand that in the test-tube cooled to 77 K the desorbed H_2O was not adsorbed by the glass walls, but was entirely frozen out. When the samples were heated over 478 K, small oily droplets were observed on the glass tube near the heated ampoule containing the sample.

For sample 5, the desorption at 333, 378, 408 and 443 K was performed for a longer time than for samples 3, 4, 6 and 8.

The experiments with sample 2 were performed in the following way. After the preliminary treatment, when the equilibrium with room air had been established, the ampoule with the sample was kept in room air for 3 h at 438 K, cooled to room temperature and maintained under these conditions for 220 h. The changes in sample mass were determined. Next, the ampoule with the sample was sealed into the apparatus and desorption under vacuum was measured under stepwise heating from 293 to 408 K as described above. At each temperature, the H_2O was condensed inside the cooled trap until desorption ceased.

Microcalorimeter and calorimetric procedure

We used a 'FOSKA' differential microcalorimeter [14, 15] with resistance thermometers.

The ribbon sample was rolled up and pushed into the ampoule (1, Fig. 1b) through section A – A. In the wide section of the ampoule, the ribbon slightly unrolled because of its elasticity; the distance between the spirals ranged from several tenths to 1 mm. The ampoule was then sealed into the apparatus (Fig. 1b), at section A – A. The apparatus was sealed to the vacuum set at section C – C.
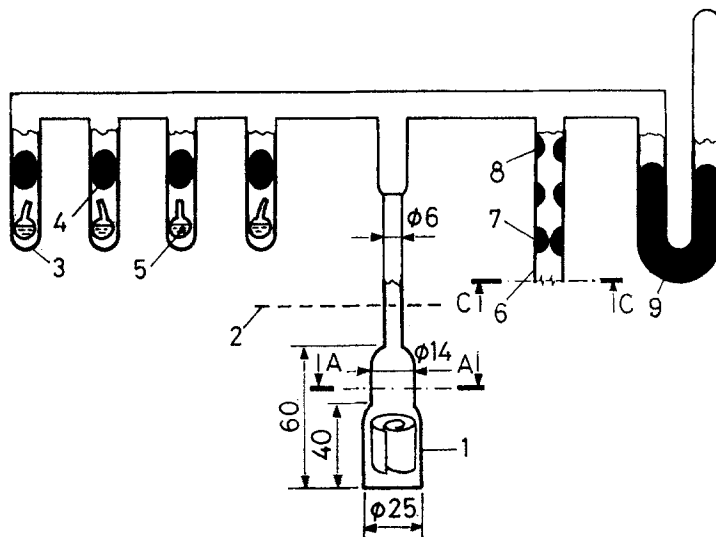

Fig. 1b Portable glass apparatus: (1) ampoule; (2) top of calorimeter; (3) test-tube; (4) magnetic cylinder; (5) thin-walled glass sphere; (6) site of sealing to vacuum set; (7), (8) necks; (9) mercury manometer

The preliminary treatment of the samples before the calorimetric studies is detailed in the Table. It was found (see below) that after such treatment the H_2O had already been fully removed from the samples, whereas the polymer was not destructured, was unblackened and had not lost its capability of reversible H_2O sorption. After preliminary treatment, the glass apparatus with sample 9, 10, 11 or 12 was sealed and cut off across the neck from the vacuum set, and the ampoule with the sample was lowered into the calorimeter.

The portable glass apparatus (Fig. 1b) with the ampoule (1) had a volume of 105 ± 5 cm^3, the inner surface area of the apparatus walls being 430 ± 20 cm^2. Inside the test-tubes (3), accurate amounts of distilled H_2O (from 9 to 130 mg) and magnetic cylinders (4) were placed. The water was hermetically sealed in the thin-walled glass spheres (5) and the magnetic cylinders were covered with glass.

The experiments were performed as follows. After thermal equilibrium in the calorimeter had been established, we broke one of the spheres with the magnetic cylinder via the outside magnet. H_2O was evaporated, the vapour being sorbed by the sample. The thermokinetic curve was recorded as the thermal power *vs.* time diagram. The completeness of H_2O sorption was controlled with a mercury manometer (9). The H_2O vapour pressure decrease, together with the excess heat flux cessation, indicated that the sorption was finished. The heat quantity evolved was calculated from the area under the thermokinetic curve. After one experiment was finished, the next sphere containing H_2O was broken, the heat of sorption was measured, and so on.

The apparatus was then resealed to the vacuum set at section C – C, and the unused 'comb' with the test-tubes, supplied with the H_2O-containing spheres and magnetic cylinders, was sealed to it; the sample was dried by vacuum heating, as described above, the next series of calorimetric sorption experiments was carried out, and so on.

Experimental errors

The absolute error of weighing was $0.025 \cdot 10^{-3}$ g, independently of the mass.

In noncalorimetric experiments, the errors were characterized by the following data. The desorbed H_2O mass was determined with an absolute error not exceeding $0.16 \cdot 10^{-3}$ g, i.e. about $0.03 \cdot 10^{-3}$ g per g of sample. To estimate the reproducibility of the noncalorimetric measurements, it is sufficient to compare the curves OB (sample 3), OB' (sample 4) and OB'' (sample 5) in Fig. 2. The samples were treated separately before the experiments. Nevertheless, the discrepancies between the quantities desorbed at each temperature are within the limits of 5%.

In calorimetric experiments, the errors are characterized by the following data. The maximum relative error in the H_2O sample weighing was 0.3%. The relative H_2O vapour pressure towards the end of each sorption experiment, P/P_o (where P is the experimental pressure, and P_o is the equilibrium vapour pressure over liquid H_2O), did not exceed 0.5. At such relative pressure, H_2O vapour could not condense on the apparatus walls. The mass of the unsorbed residual vapour in each experiment did not exceed $0.28 \cdot 10^{-3}$ g. In most experiments, it was less than 1% of the H_2O mass and never exceeded 2%. The H_2O vapour adsorption on the glass walls could not introduce any noticeable error into the results, as a H_2O monolayer on the glass was not more than $0.02 \cdot 10^{-3}$ g H_2O (0.24% of H_2O sorbed in an experiment). The relative error in the sorbed H_2O mass determination did exceed 2%.

The sensitivity of the flux measurements was about $2.3 \cdot 10^{-5}$ W. The error in the evolved heat determination was within 1%. The microcalorimeter was cali-
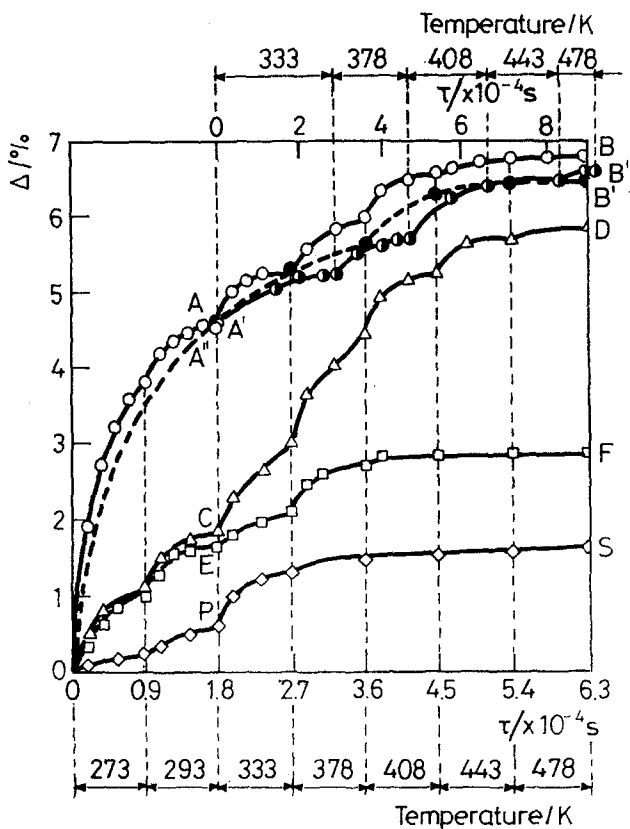
Fig. 2 Water vapour desorption under vacuum: curve OB, sample 3; curve OB', sample 4; curve OB'', sample 5; curve OF, sample 6; curve OS, sample 7; curve OD, sample 8; (for curve OB'', sample 5, the abscissa is at the top)

brated with the Joule heat evolution in the calibrating ampoule. The calibrating ampoule was identical to the calorimetric sorption ampoules in size, mass and specific heat; it contained the wire heater situated inside the ampoule geometrically identical to the sorbent in the sorption ampoule. As a result of the calibration, the constant of the calorimeter was obtained in terms of mJ cm^{-2} (ratio of flux to area under the thermokinetic curve). The scales of recording corresponded to 32.84, 82.1 or 328.4 ($\pm 1\%$) mJ cm^{-2}. Verification of the calibration was carried out as follows.

We used the calibrating ampoule with the wire heater. To verify the results of calibration, we fixed the Joule heat evolving conditions (current intensity and duty cycle) so that the calibrating thermokinetic curve was close to the experimental one. After the fixed heat flux was recorded, the area under the thermokinetic curve was determined. The heat quantity was calculated by using the constant of the calorimeter, and it was compared with the heat quantity known

from measurements of electrical parameters. The difference was within the limit of 1.5%. This verification was supplemented by reproduction of the known heat effect of ethylene polymerization. The latter was carried out on solid catalyst without resort to any solvent [16]. In most experiments, the error in the molar heat of H_2O vapour sorption was not more than 2% and was never above 3%.

The degree of reproducibility of the heat effect is seen in the most generalized form from the following comparison. We compared the integral molar heats of H_2O vapour sorption, measured in two independent sets, 3 and 4 (Fig. 3), up to $\Delta = 3.81\%$(mass). Values of 57.84 (set 3) and 59.28 (set 4) kJ mol^{-1} were obtained. The difference is 2.5% only, and thus the results reproduced rather well.

The reproducibility of the noncalorimetric results is seen from the following comparison. Samples 3–5 were pretreated independently and then the isothermal H_2O vapour desorption was measured (Fig. 2) at the different temperatures. At each temperature, the average deviations of the integral quantities of H_2O desorbed from the samples were as little as 3.5%.

Results

It was established in a separate experiment that perfluoroethylene free of ionic groups did not sorb H_2O vapour under our test conditions.

In all Figures in this part of the article, data on the relative sample mass change on H_2O vapour sorption (Δ, %) or desorption ($-\Delta$, %) are given; Δ, $\% = 100(m_w/m_p)$, , where m_w is the sample mass change over the period of the measurements, and m_p is the sample mass before the measurements. In some Figures, the n values are given too, n being the number of sorbed H_2O molecules in the sample, related to the number of $-SO_3M$ groups in it, $n = 1.11\Delta$.

Figure 2 presents data on vacuum desorption from three $M = H$ samples, an $M = Na$ sample, an $M = K$ sample and a sample pretreated with FeCl$_3$ solution. The desorption at 333, 378, 408 and 478 K from sample 5 was carried out for a longer time than that from samples 3 and 4 (see the top abscissa). These results make it possible to relate the $M = H$, K, Na samples and the sample pretreated with FeCl$_3$ solution as concerns their sorption characteristics.

Figure 4 presents results on H_2O sorption and desorption in room air by $M = H$ samples 1 (curve OH) and 2 (curve OJKP). The time interval required for equilibrium of the humidified sample with room air to be established was measured on sample 1. The experiments on sample 2 were performed to obtain data on the reversibility of the H_2O sorption – desorption process and to determine the time interval necessary for equilibrium of the dried sample with room air to be established.

H_2O desorption under vacuum practically ceased at 443 K from the $M = H$ samples and the sample pretreated with FeCl$_3$ solution, and at 408 K from the $M = Na(K)$ samples.
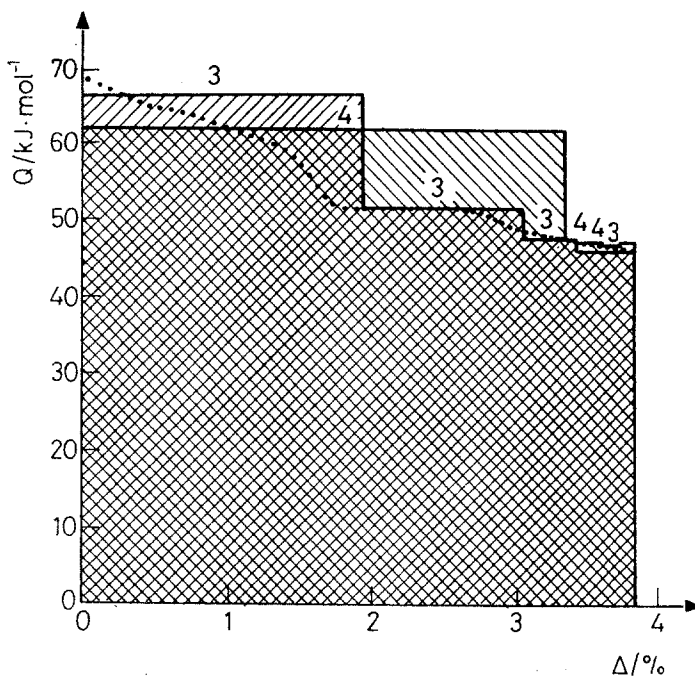
Fig. 3 A comparison of the integral heat effects measured in sets 3(H) and 4(H) up to $\Delta=3.81$
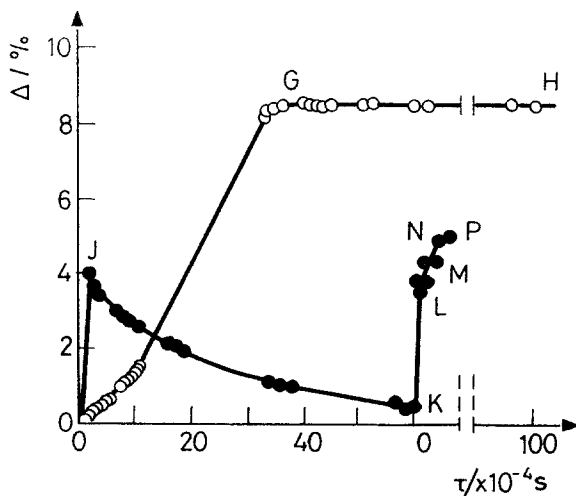

Fig. 4 Sorption and desorption of H_2O vapour by the $M = H$ polymer: curve OGH – sample 1, open system; curve OJKZMP – sample 2, OJK – open system, KZMP – closed system

Figures 5 and 6 present results of measurements of molar heats of H_2O vapour sorption. Figure 5 gives the heats of sorption by sample 9 with $M = H$ (sets 1(H)–4(H)), and Fig. 6 the heats of sorption by sample 10 with $M = Na$ (set 1(Na)) and by samples 11 and 12, pretreated with $FeCl_3$ solution (sets 1(Fe) and 2(Fe), respectively). $Q_L = 44.13$ kJ mol^{-1}, shown by the dash and dot lines, are the heat of H_2O vapour condensation on the liquid H_2O surface. The lengths of the segments in Figs 5 and 6 correspond to the H_2O vapour quantity sorbed in each experiment. Small masses of H_2O (as a rule 9–14 mg) were used in sets 1(H) and 2(H) and in most experiments with sets 1(Na), 1(Fe) and 2(Fe). In most experiments with sets 3(H) and 4(H), the sorbed H_2O mass was much greater, up to 130.6 mg. The dotted curve in Fig. 5 is plotted on the basis of the results of those experiments in which the mass of H_2O was small. The Q vs. n(or Δ) dependence described by this curve is close to the dependence of the
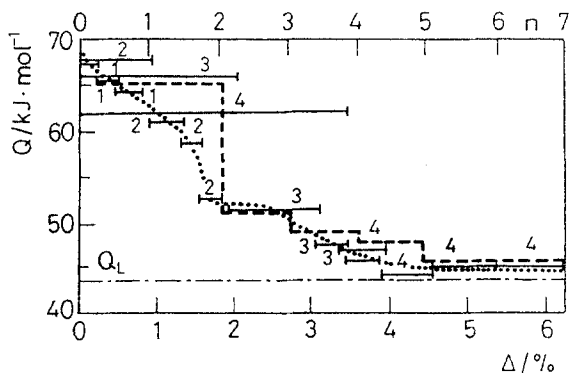

Fig. 5 Calorimetric results on $M = H$ polymer, sample 9. Figures over the sections of a line correspond to experimental set numbers. Dashed broken line corresponds to heats of H_2SO_4 dilution by H_2O vapour
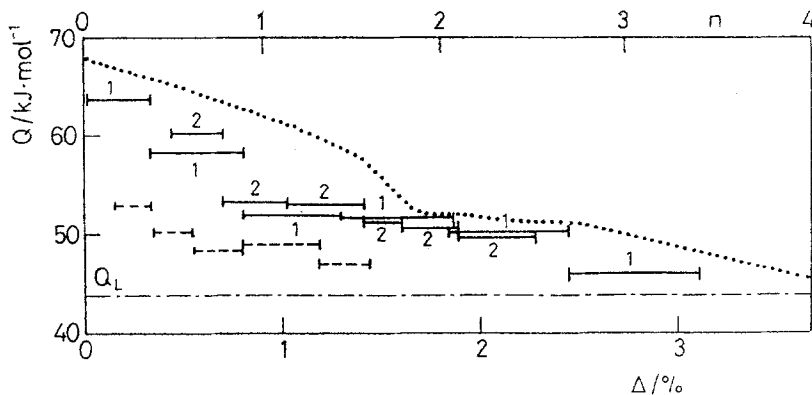

Fig. 6 Calorimetric results on $M = Na$ polymer, sample 10 (without figures over the sections) and on the polymers pretreated with $FeCl_3$ samples 11 (figures '1' over the sections) and 12 (figures '2' over the sections)

differential heat of H_2O sorption on the sorbed H_2O quantity. The same dotted curve is reproduced in Fig. 6.

The dashed broken line in Figs 5 and 6 is plotted on the basis of data [17] relating to the molar heats of H_2SO_4 dilution. In Fig. 5, the upper step of the broken line corresponds to the heat of mixing of H_2SO_4 (1 mole) with H_2O (2 moles); the next step corresponds to the heat of mixing of the above solution with 1 mole of H_2O; the third step corresponds to the heat of mixing of the second solution with 1 mole of H_2O, and so on. In the dashed curve in Fig. 6, the steps correspond to the heats of formation of $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$ and $H_2SO_4 \cdot 3H_2O$ solutions as a result of the successive addition of H_2O.

The purpose of the experiments depicted in Figs 5 and 6 was to obtain data on the chemical state of wetted polymers containing the functional groups $-SO_3M$. The results in Figs 5 and 6 allow us to relate the molecular mechanisms of H_2O interaction with H_2SO_4 and with the $-SO_3M$ groups of the polymer.

After the set 2(H) experiments on the heats of H_2O sorption, the experiment on the heat of H_2O desorption was carried out. For this purpose, we cooled the glass tube above the neck (7, Fig. 1b) to 77 K, sealed and cut off the tube across the neck (8), and weighed the desorbed H_2O as described above. The molar heat of H_2O desorption was found to be 52.38 kJ mol^{-1} (the molar heat of sorption in the preceding experiment of set 2(H) had been 52.48 kJ mol^{-1}).

After the desorption of several mg of H_2O, the desorption rate fell so much that further measurements of the heat effects were impossible.

The results show that the $M = H$ polymer has the highest chemical affinity for H_2O. About 15% of H_2O on a dry sample mass basis may be sorbed by this polymer at room temperature and 100% humidity (Figs 2 and 4). H_2O amounting to 8.4% of the fully humidified sample mass (curve OGH, Fig. 4) was desorbed in room air at 80–85% humidity; on the other hand, H_2O amounting to about 4% (curve OJ) or about 5% (curve KP) of the wetted sample mass was desorbed from sample 2 wetted in room air, when it was heated in room air or under vacuum, respectively. About 6.5% of H_2O by mass was desorbed from wetted samples 3–5. That is, the fully humidified sample contains about 14% of H_2O relative to the humidified sample mass, or 15–16% of H_2O relative to the dry sample mass. The formal calculations show that the fully humidified $M = H$ polymer contains about 17 molecules of H_2O on a sulpho group basis. However, it is not reasonable to state that all this H_2O is bonded with the sulpho groups.

About 65% of the above-mentioned H_2O quantity is desorbed from the humidified sample during the stabilization of its mass in room air. Six H_2O molecules on a sulpho group basis are contained in the polymer at equilibrium with room air and $2H_2O$ molecules remain after exposure of the polymer to vacuum at 293 K (Fig. 2, curves AB, AB' and AB''). Under the above-mentioned conditions, the polymer contains 2.37 (2.14), 2.04 (1.85) and 2.17 (1.96) H_2O

molecules in samples 3, 4 and 5, respectively (the values of $\Delta, \%$ are given in brackets). This result is close to that in [7]. Hence, it is possible to distinguish conventionally 'strongly bonded' and 'weakly bonded' H_2O in the polymer. 'Weakly bonded' H_2O may be desorbed under vacuum at room temperature; the H_2O which remains in the polymer after such treatment is 'strongly bonded'. 'Strongly bonded' H_2O may be fully desorbed under vacuum at 443 K.

Calorimetric measurements (Fig. 5) show that first $2H_2O$ molecules on a $-SO_3H$ group basis are sorbed more strongly than the following ones. The mean molar heat of sorption of first $2H_2O$ molecules is about 66 kJ mol^{-1} (experiment 1, set 3(H), Fig. 5). This heat quantity is very close to the heat of the reaction $0.5H_2SO_{4(l)} + H_2O_{(g)} = 0.5(H_2SO_4 \cdot 2H_2O)_{(l)}$, i.e. 64.93 kJ mol^{-1} [17].

As n increases, the molar heat of sorption decreases to almost the heat of H_2O evaporation Q_L. However, up to $n = 7$, the former is above the latter. In the experiments illustrated in Fig. 5, the H_2O sorption rate decreases by a factor of several hundred as the sample fills with H_2O.

The dashed curve in Fig. 5 has a step near $n = 2$, and a second one, not so deep, near $n = 3$.

To desorb the H_2O entirely, it would suffice to heat the polymer in vacuum at 443 K. The sorption – desorption process is reversible when the temperature or H_2O vapour pressure is varied. In vacuum under isothermal conditions, desorption ceases after 3–4 h. In room air, the equilibrium H_2O content in the polymer is established slowly: for the prewetted polymer the process lasts for about 4 days, while for the predried polymer it lasts for about 7 days (Fig. 4).

The initial rate of H_2O sorption by the dried sample is characterized by the following data. The sorbed quantity in mass % is: 0.22 for 0.4 h (about $5 \cdot 10^{16}$ molec/s·g), 0.47 for 1.5 h and 0.53 for 3.0 h. The same order of initial rate was observed in the calorimetric experiments, H_2O sorption proceeding under vacuum. In these experiments, the sorption rate was estimated by using the power of the heat evolution and the predetermined value of the molar heat of sorption. In the experiments outlined in Fig. 5, the sorption rate decreased as the sorbed quantity increased: in set 1(H) by a factor of 2, in set 2(H) by a factor of 8.5, in set 3(H) by a factor of 50 and in set 4(H) by a factor of 300. The polymer pretreated with alkaline solution and then brought to equilibrium with humid room air contains much less H_2O than the wetted $M = H$ polymers (Fig. 2). The H_2O quantity in the polymer with $M = K$ is less than in that with $M = Na$. The quantities of 'strongly bonded' H_2O in the wetted polymers with $M = K$ and $M = Na$ are close in magnitude; the sorbed quantities correspond approximately to $1H_2O$ molecules per $-SO_3M$ group. The $M = K$ polymer sorbs much less 'weakly bonded' H_2O (about 0.5 molecule per $-SO_3K$ group) than the $M = Na$ polymer (about 1.7 molecule per $-SO_3Na$ group). The wetted polymers with $M = K(Na)$ desorb H_2O practically totally under vacuum at 378 K.

The heat of H_2O sorption by the polymer with M = Na (Fig. 6) is much less than for that with M = H. The initial heat of sorption is about 53 kJ mol^{-1}; even at n = 1.5 it falls to about 74.5 kJ mol^{-1}, exceeding the heat of H_2O evaporation by as little as 3.5 kJ mol^{-1}.

The H_2O sorption rate by the polymer with M = Na at n = 1.5 is less than that for the dry polymer by a factor of 18.

At equilibrium with room air, the polymer pretreated with $FeCl_3$ solution sorbs only a little less H_2O than the M = H polymer (Fig. 6): approximately $6H_2O$ molecules per $-SO_3H$ group. When this polymer is heated under vacuum, the H_2O is desorbed much more slowly than for the M = H polymer (Fig. 2). This feature is particularly pronounced at 333, 378 and 408 K. The isothermal H_2O desorption from the sample pretreated with $FeCl_3$ solution (curve OD) does not cease for 2.5 h, in contrast with the M = H polymer.

The heat of H_2O sorption by the polymer pretreated with $FeCl_3$ solution was measured in two sets of experiments, the results being reproduced (Fig. 6). The heat of sorption for the sample pretreated with $FeCl_3$ is intermediate between those for the M = H and M = Na samples, the comparison being carried out at the same sorbed quantities. The initial heat of sorption is 63.6 kJ mol^{-1}. As H_2O is sorbed up to n = 1, the heat of sorption decreases to about 50 kJ mol^{-1} and remains at this level until n = 3. The fourth H_2O molecule is sorbed with a heat effect differing from the heat of H_2O condensation by not more than about 2 kJ mol^{-1}. The sorption rate decreases as H_2O is sorbed. In the last experiment, it is less by a factor of 35 than that for the dry sample. The mean molar integral heat of sorption up to n = 3 is 53.5 kJ mol^{-1} (for comparison: the mean heat of H_2SO_4 dilution by H_2O vapour is 60.5 kJ mol^{-1}; the mean heat of H_2O sorption by the M = H sample (in set 3H) is 61.8 kJ mol^{-1}). A comparison of the 'pure' integral heat effects (the excess of the heat effect over the heat of vapour condensation) is most illustrative. They are 16.3, 17.7 and 9.4 kJ mol^{-1} for H_2SO_4, the M = H polymer and the polymer pretreated with $FeCl_3$ solution, respectively.

Discussion

Throughout the entire experimental range of n values up to n = 7, the heat of H_2O vapour sorption exceeds the heat of condensation on the liquid H_2O surface.

The results show that the main cause of the excess of the heat of sorption over the heat of condensation is the presence of the $-SO_3H$ groups in the polymer, rather than sorption inside the micropores.

Let us assume that H_2O is sorbed mainly inside the micropores. The replacement of H in the $-SO_3H$ group by Na should then not decrease the differential heat of H_2O sorption, comparison being made at the same n value. The dis-
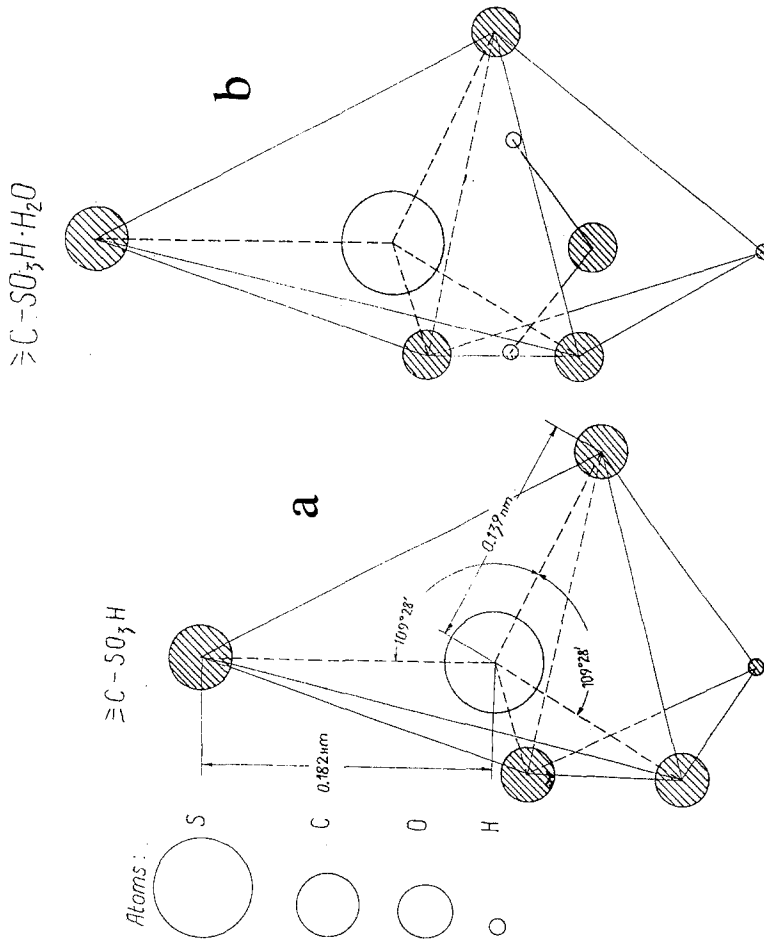
Fig. 7 Structure of sulpho group (a) and hypothetical hydrate structures of $M = H$ polymer: $-SO_3H \cdot H_2O$ (b)
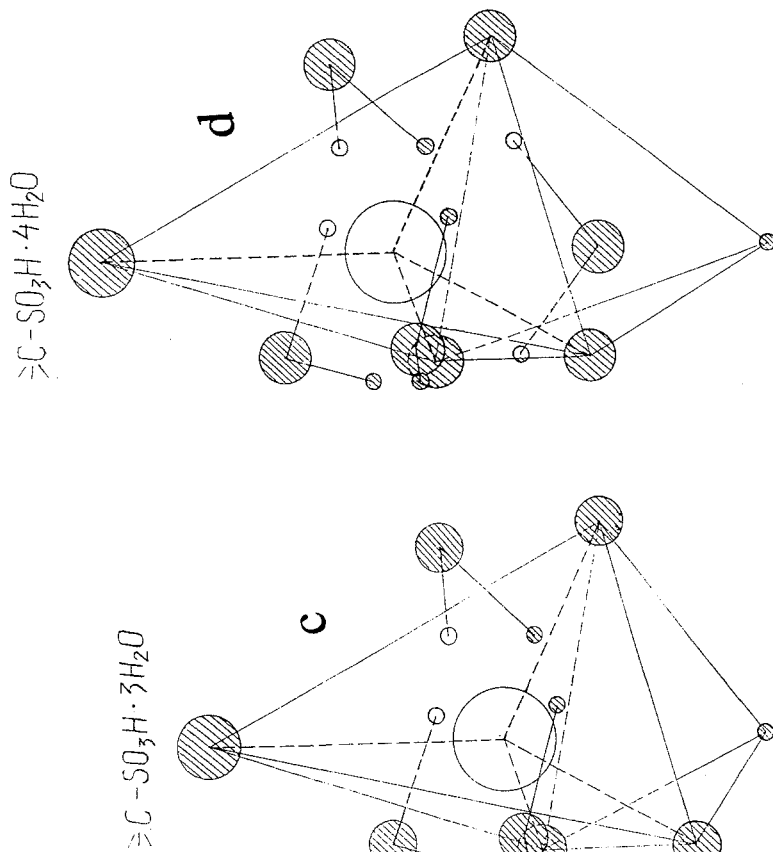
Fig. 7 Continued: hypothetical hydrate structures of M =H polymer: $- SO_3H \cdot 3H_2O$ (c), $- SO_3H \cdot 4H_2O$ (d)

tances between the $-SO_3M$ groups in the polymer are too great for a significant influence of the ion-exchange on the sample structure as a whole. The mean distance between the $-SO_3H$ groups is about 1.55 nm, with the mean volume of one $-SO_3H$ group 3.6 nm^3. However, the results in Fig. 3 show that the initial heat of sorption by the $M = Na$ sample decreases to 47 kJ mol^{-1} as n increases to about 1.5, whereas such a small sorption heat is observed for the $M = H$ sample only near $n = 4$. That is, at least up to $n = 4$, the main cause of the increased heat of sorption by the $M = H$ samples is not the micropore structure, but the presence of the $-SO_3H$ groups.

Similarly, replacement of the $-SO_3H$ group by the $-SO_3Na(K)$ group should not affect the sorption rate if the sorption proceeds mainly inside the micropores. However, the experiments show that, at the same n (or Δ) values, the rate of H_2O sorption by the $M = Na$ polymer is significantly lower than that by the $M = H$ polymer. For example, at $n = 1.5$ ($\Delta = 1.35$) the rate of sorption by the $M = Na$ sample is 100 times smaller than that by the $M = H$ polymer; the rate of sorption by the $M = H$ sample at $n = 7$ is equal to that by the $M = Na$ sample at $n = 1.5$. The observed sorption rate is the difference between the rates of the elementary processes of sorption and desorption. However, the desorption from the samples with the lowered heats of sorption (i.e. from the $M = Na(K)$ samples) proceeds with enhanced rate, as the desorption rate depends exponentially on the sorption bond energy.

The correlation between the heats of H_2O vapour sorption by the $M = H$ polymer and of H_2SO_4 dilution by H_2O vapour condensed in it [17] (Fig. 5) shows the following. The replacement of the $-OH$ group in H_2SO_4 by the monovalent organic radical does not affect the energy of H_2O bonding significantly. This means that the effective positive charge of the central S atom is of decisive importance for H_2O bonding. The multicentral 'smeared-out' negative charge of the O atoms is of less importance. Therefore, it is reasonable to conclude that the sorbed H_2O molecules are coordinated in the vicinity of the central S atom rather than away from it. Let us consider the known data on the structures of H_2SO_4 and organic sulphoacids before discussing the possible structure of the hydrated $-SO_3H$ group in the polymer. The H_2SO_4 molecule contains a symmetric tetrahedral ion.

The $-SO_3M$ group in the salts RSO_3M (R is an organic radical) has a tetrahedral structure, the tetrahedron being extended along the S–R bond, the S–O bonds being alike and close to an ethylene bond; if $M = H$, the H atom is coordinated near the O atom. The structure of the sulpho group (of phenylsulpho acid) is shown in Fig. 7a [18].

Since the H_2O molecule must be bonded with the S atom, and from a consideration of symmetry, we believe that the energy-favourable position of the H_2O molecule in $RSO_3H \cdot H_2O$ corresponds to that shown in Fig. 7b: the O atom of the H_2O molecule is situated on the axis of the tetrahedron connecting the C and S atoms, where it experiences the attraction of the positively charged H and

S atoms. The H atoms of the H_2O molecule are coordinated relative to the plane of the negatively charged O atoms.

The H_2O molecule in the hydrate $H_2SO_4 \cdot H_2O$ is most probably coordinated in a similar way. The hydrate in the $H_2SO_4 \cdot H_2O$ composition gives a clear extremum in the melting temperature vs. composition diagram [19], the melting point being 283.53 K.

For $n = 3$, the H_2O molecules are probably arranged in the following way (Fig. 7c). The O atom of each of $3H_2O$ molecules is embedded at the intersection of one side of the tetrahedron with two planes: the axial plane of the tetrahedron passing through the median of the tetrahedron base, and the plane perpendicular to the axis of the tetrahedron and intersecting it in the vicinity of the S atom. The H atoms of each H_2O molecule are coordinated in the direction of the O atoms of the sulpho group nearest to them.

For $n = 4$ (Fig. 7d), the H_2O molecules are probably arranged so that their O atoms from an irregular tetrahedron. Thus, the spatial arrangement of 4 H_2O molecules is close to the combination of two structures shown in Figs 7b and 7c.

Evidently, the tetrahedra of H_2O molecules around the $-SO_3H$ group are the centres of further H_2O condensation. Due to the additional polarization of the tetrahedrally situated H_2O molecules by the S atom, the heat of water condensation during this process remains higher than that on the liquid H_2O surface. At $n > 4$, the excess of the heat sorption over the heat of condensation is not great. Accordingly, this excess could not be measured accurately in our experiments. For more accurate measurements of this value, experiments on the interaction of liquid H_2O with polymer are necessary. Such experiments must elucidate the specificity of the $M = H$ polymer in comparison with H_2SO_4 in the region $n > 4$.

The spatial structure of the $-SO_3H$ group in the polymer is such that, when $n = 2$, it is less fixed than at $n = 1$, $n = 3$ and $n = 4$. In other words, in the case with $n = 2$, several spatial positions of the sorbed H_2O molecules are possible. These positions may be characterized by slightly different energies.

The crystal hydrates $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, $H_2SO_4 \cdot 3H_2O$, $H_2SO_4 \cdot 4H_2O$ and $H_2SO_4 \cdot 6H_2O$ are known [19]. All these hydrates are well-defined in the melting temperature vs. composition curve. Clearly, the process of H_2O sorption by the $M = H$ polymer is nothing but the totality of the successive changes in state in the substrate, each change being characterized by its own heat effect.

At room temperature in the series of hydrates $-SO_3H \cdot H_2O$, $-SO_3H \cdot 2H_2O$, $-SO_3H \cdot 3H_2O$ and $-SO_3H \cdot 4H_2O$, the energy of transformation from some hydrate into the adjacent one (without evolution of H_2O vapour) differs from the molecular heat movement energy RT by as little as a factor of several units. Therefore, as H_2O is sorbed, each next hydrate in the above-mentioned series begins to appear before the formation of the preceding one is completed. The

steps in the plot in Fig. 5 are not well-defined, obviously as a result of the above-mentioned features of the H_2O sorption kinetics.

Nevertheless, Fig. 5 indicates convincingly that at $n > 2H_2O$ sorption by the $M = H$ polymer is proceeding with much lower heat effects than those at $n < 2$. On the other hand, as may be seen in Fig. 2, 2 moles of H_2O are desorbed from the moistened $M = H$ samples under vacuum at above room temperature, this value being well reproduced. These 2 moles are 'strongly bonded' H_2O. It is now seen that 'strongly bonded' H_2O is the H_2O sorbed in the phase $-HSO_3 \cdot 2H_2O$ with significantly higher heat effect in comparison with that of further H_2O sorption.

As mentioned earlier, the $M = Na(K)$ polymers sorb much less H_2O than the $M = H$ polymers. Figure 2 shows that smaller amounts of 'weakly bonded' and 'strongly bonded' H_2O are desorbed from the wetted samples with $M = Na(K)$. It follows from Fig. 6 that even at a very small sorbed amount ($n = 0.6$) the heat of sorption by the $M = Na$ sample is below 50 kJ mol^{-1}. We have already pointed out the low rates of H_2O sorption by the $M = H$ samples.

These observations correlate well with the above-developed concept concerning H_2O sorption by the $M = H$ samples.

The Na atom in the $-SO_3Na$ group is embedded on the tetrahedron axis near the site occupied in Fig. 7a by the H atom of the $-SO_3H$ group, but nearer to the central S atom. The radius of a Na atom[*] (0.154 nm) is much more than that of a H atom (0.031 nm). The replacement of H by Na in the $-SO_3M$ group therefore excludes the possibility of the H_2O molecule being located on the axis of the tetrahedron near the S atom, where the heat of sorption for the $M = H$ polymer is maximum. Besides, the Na atom depolarizes the positive effective charge of the S atom to a significantly greater extent than does the H atom in the $M = H$ polymer. Therefore, the $M = Na$ polymer sorbs a small amount of 'strongly bonded' H_2O, the sorbed quantity corresponding to $n < 1$. As a result, the quantity of 'weakly bonded' H_2O is sharply decreased. 'Weakly bonded' H_2O, as stated above, is sorbed by the $M = H$ polymer in consequence of the induction effect caused by the presence of the additionally polarized 'strongly bonded' H_2O molecules oriented in the vicinity of the S atom.

The $M = K$ polymer sorbs even less H_2O since the K atom radius is larger than that of Na, and the former depolarizes the central S atom to an even greater extent than the latter.

It is obvious from the given data that the polymer pretreated with $FeCl_3$ solution sorbs H_2O more strongly (and in greater quantity) than the $M = Na$ polymer, but less strongly (and in smaller quantity) than the $M = H$ polymer. The mean molar heat of sorption by the sample pretreated with $FeCl_3$ solution

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* Different methods are used in the literature for atom and ion radius determination. They lead to different results.

(Fig. 6) is slightly less than that for the $M = H$ sample. Therefore, the equilibrium sorption in room air by the former sample (Fig. 2) (i.e. the total H_2O quantity desorbed on heating) is less than for the latter.

The decreased rate of H_2O desorption from the sample pretreated with $FeCl_3$ solution relative to that from the $M = H$ polymer at low temperatures can evidently be explained by the lower rate of diffusion in the pores of the sorbent.

According to [11, 21], pretreatment of material such as 'Nafion' with $FeCl_3$ solution leads to the deposition of structured microparticles consisting of Fe, O and H in the pores of the polymer material. The filling of the pores by such microparticles makes H_2O diffusion difficult and decreases the rate of vacuum H_2O vapour desorption. As diffusion proceeds with activation energy at such low temperatures, the rate of H_2O desorption from the polymer pretreated with $FeCl_3$ solution is lower than that from the $M = H$ polymer. At higher temperatures (333 and 378 K), the rate of H_2O desorption is increased, and thus H_2O not desorbed at lower temperatures is now desorbed.

Conclusion

H_2O is sorbed reversibly by aliphatic fluorinated polymers such as 'Nafion', the main cause of sorption being specific interaction with the $-SO_3M$ groups rather than interaction with the polymer inside the micropores.

The $M = H$ polymer at equilibrium with humid room air at 293 K contains H_2O in a quantity corresponding to about $n = 7$; at equilibrium with saturated H_2O vapour, the H_2O content corresponds to about $n = 17$. Under vacuum at a residual pressure of about 10^{-3} hectoPa, the H_2O content in the polymer at 293 K corresponds to $n \sim 2$, while at 443 K the H_2O is desorbed entirely. The integral molar heat of H_2O sorption by the polymer up to $n = 7$ is very nearly equal to the heat of H_2SO_4 dilution by H_2O vapour. Up to $n = 4$, the differential heats of H_2O sorption by polymer and by H_2SO_4 are also close. The H_2O molecules are structured in the polymer in the vicinity of the S atom of the sulpho group, the hydrates $-HSO_3 \cdot H_2O$, $-HSO_3 \cdot 2H_2O$, $-HSO_3 \cdot 3H_2O$, $-HSO_3 \cdot 4H_2O$, etc. being formed successively in the process of H_2O sorption.

The $M = Na(K)$ polymer at equilibrium with humid room air at 293 K contains H_2O in a quantity corresponding to about $n = 3$ ($n = 2$). Under vacuum at a residual pressure of about 10^{-3} hectoPa, the H_2O content in the polymer at 293 K corresponds to $n = 1.3$ ($n = 1.1$), while at 378 K the H_2O is desorbed practically entirely. The heat of H_2O vapour sorption by the Na(K) polymer is much lower than that by the $M = H$ polymer; the initial heat of H_2O sorption by the $M = Na$ polymer is about 53 kJ mol^{-1}, while at $n = 1.5$ it exceeds the heat of H_2O condensation on the liquid H_2O surface by as little as 3.5 kJ mol^{-1}. The Na(K) atom is structured in the sulpho group along the axis of there tetrahedron near the plane of the O atoms and near the S atom. It screens the S atom and sharply diminishes its affinity for H_2O.

The polymer with the sulpho groups pretreated with $FeCl_3$ solution is characterized in its H_2O sorption capacity by properties intermediate between those of the $M = H$ polymer and those of the $M = Na(K)$ polymer. At equilibrium with humid room air at 293 K, such a polymer contains H_2O in a quantity corresponding to about $n = 6$. Under vacuum at 273 and 293 K, it desorbs H_2O significantly more slowly than the $M = H$ polymer; at 443 K, it may be dehumidified entirely. The mean integral molar heat of H_2O vapour sorption by such a polymer is 53.5 kJ mol^{-1} up to $n = 3$; this is about 15% less than the molar heat of H_2O vapour sorption by the $M = H$ polymer. Fe^{3+} is smaller than Na^+ and K^+, and screens the S atom of the sulpho group to a lesser degree. This determines the fact that it influences the polymer affinity for H_2O more weakly than the alkali metal ion.

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