

## SORPTION OF AMMONIA BY ACID MACRORETICULAR ION EXCHANGERS

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The sorption of ammonia was investigated at 150°C on the styrene-divinylbenzene copolymer and the same type of copolymer containing  $-\text{SO}_3\text{H}$ ,  $-\text{P}(\text{OH})_2$ ,  $-\text{PO}(\text{OH})_2$ ,  $-\text{CH}_2\text{PO}(\text{OH})_2$  or  $-\text{PS}(\text{OH})_2$  functional groups, on Amberlyst 15 and on the ion exchangers where hydrogen ions of the  $-\text{SO}_3\text{H}$  group were partially exchanged by potassium. From the linearised form of the Langmuir adsorption isotherms both the values of the monolayer of the irreversibly adsorbed ammonia and the number of the functional groups corresponding to the weight and surface area units were calculated. Although the adsorption isotherm relating to the irreversible sorption satisfies the Langmuir equation it cannot be assumed that the total amount of ammonia is adsorbed in the surface layer. With the partially neutralised ion exchangers containing  $-\text{SO}_3\text{H}$  groups the irreversible sorption is decreased depending on the neutralisation degree.

The measurement of the sorption of ammonia from the gas phase is used for determining the surface acidity of the acid catalyst<sup>1,2</sup>. Some authors investigated this sorption on the acid ion exchangers<sup>3-5</sup> resulting in the ammonia salts formation. For this purpose they used the ion exchangers of the styrene-divinylbenzene type (with 8 and 10% of divinylbenzene) both in the dried state and with some content of moisture. They found that with the increasing amount of moisture also the quantities of adsorbed ammonia were increased till the exchange capacity was almost reached.

In the present study an attempt was made to utilize the sorption of ammonia for determining the number of the surface acid sites of the styrene-divinylbenzene copolymers containing  $-\text{SO}_3\text{H}$ ,  $-\text{P}(\text{OH})_2$ ,  $-\text{PO}(\text{OH})_2$  and  $-\text{PS}(\text{OH})_2$  groups. To this end the macroreticular resin was employed the skeleton of which was cross-linked with 25% of divinylbenzene. Moisture was excluded during the measurement of the ammonia adsorption. In order to follow the adsorption of ammonia on the sorbents with definitely lowered number of the centres the ion exchangers with partially exchanged hydrogen ion were also used.

### EXPERIMENTAL

*Materials.* Gaseous ammonia (Chemické závody ČSSP, Záluží near Most) was dried with the molecular sieve 5A and purified by repeated condensation and expansion in the vacuum apparatus before use. Macroreticular styrene-divinylbenzene copolymer (S) and ion exchangers containing

—SO<sub>3</sub>H(S—S), —P(OH)<sub>2</sub>(S—P), —PO(OH)<sub>2</sub>(S—PO), —CH<sub>2</sub>—PO(OH)<sub>2</sub>(S—CPO) and —PS(OH)<sub>2</sub>(S—PS) functional groups prepared from S were described elsewhere<sup>6,7</sup>. Amberlyst 15, (technical grade) was a commercial product of Serva-Entwicklungslabor (Heidelberg). Sulphonated ion exchangers with partially exchanged proton by the potassium ion S—S<sub>75</sub>, S—S<sub>55</sub>, S—S<sub>35</sub> and S—S<sub>0</sub> were also previously described<sup>6-8</sup>.

### Apparatus and Procedure

The adsorption measurements were performed at 150°C in a standard volumetric apparatus as described before<sup>6</sup>. First of all approximately 1 g of sorbents was outgassed at 150°C for 24 hours. The pressure was checked with McLeod gauge during evacuation. The vacuum amounted to 10<sup>-5</sup> Torr in order of magnitude. When this operation had been finished the B.E.T. — surface areas of the individual sorbents<sup>6</sup> were calculated from N<sub>2</sub> isotherms at -196°C. Nitrogen was removed by pumping at 150°C for 24 hours when the vacuum reached 10<sup>-5</sup> Torr in order of magnitude again. The adsorption of ammonia was measured at 150°C up to the equilibrium pressure of about 550 Torr (Fig. 1, isotherm *I*). Then the sample of the adsorbent was outgassed for 24 hours at 25°C. This temperature was chosen because we had anticipated<sup>9</sup> that all physically adsorbed ammonia would be desorbed under the given conditions. The adsorbent was heated up to 150°C again and a new sorption isotherm of ammonia was taken at this temperature in the same way (Fig. 1, isotherm *II*). The difference<sup>10</sup> between the two isotherms was considered to correspond to a strong adsorption of ammonia (Fig. 1, isotherm *III*). With the ion exchanger S—S this measurement was carried out also at 125°C.

### RESULTS AND DISCUSSION

Three adsorption isotherms were obtained (Fig. 1) by means of the procedure described in the experimental part. The first isotherm represented the total adsorption including both the physical adsorption and chemisorption. Isotherm *II* corresponded

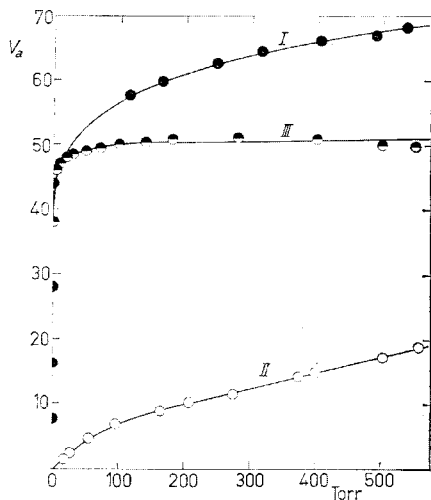


FIG. 1  
Sorption of Ammonia  $V_a$  (cm<sup>3</sup>/g) on the Ion Exchanger S—S at 150°C

● Adsorption isotherm of the total sorption, ○ adsorption isotherm of the physical sorption, ● adsorption isotherm of the irreversible sorption.

to the physical adsorption and isotherm *III* to chemisorption. An attempt was made to use the Langmuir equation for the linearisation of all the three adsorption isotherms. Isotherm *III* was fitted by linear course throughout the whole range of the pressures used. This fact supported our supposition that isotherm *III* corresponded to chemisorption. This correlation for isotherm *I* provided linear dependence only in a limited range of pressures. The deviating points corresponded to the lower pressures. Isotherm *II* did not yield a straight line at all when plotted according to the Langmuir equation. This behaviour was observed with all the investigated ion exchangers. From the linearised forms of the sorption isotherms both the values of the total sorption and irreversibly sorbed ammonia were calculated together with the number of the functional groups corresponding to the ion exchanger weight and surface area units. The results are summarized in Tables I and II.

As it was expected the sorption of ammonia on the resin S was significantly different compared with that on ion exchangers containing the acid groups. By comparison of the total amount of ammonia adsorbed under equivalent conditions both by the primary copolymer and by the resins with acid groups it was immediately evident that the sorption on S was smaller at least by one order of magnitude and the irreversible sorption was never observed. This fact seemed to indicate that the amount of irreversibly sorbed ammonia might become a measure of the number of the surface

TABLE I  
Sorption of Ammonia on the Resin S and on the Acid Ion Exchangers at 150°C

Ion exchanger	Total sorption mmol/g	Irreversible sorption mmol/g	Number of the functional groups		Exchange capacity detn. by titration <sup>8</sup> mmol/g	Number of the functional groups calculated from the elemental analysis <sup>6</sup>
			$\cdot 10^{20}$ corresp. to 1 g	corresp. to 1 Å <sup>2</sup>		
S	0.225	—	—	—	—	—
S—S	3.503	2.561	15.423	0.288	2.40	4.35
S—S at 125°C	4.457	2.522	15.187	0.284	2.40	4.35
S—PO	3.780	2.513	7.569	0.281	3.90	3.90
S—PS	2.492	0.928	2.809	0.031	—	4.30
S—CPO	3.622	2.531	7.622	0.054	—	3.38
S—P	3.275	1.490	8.980	0.094	4.0	4.34
Amberlyst 15	5.500	4.283	25.76	0.604	4.5—4.7 (ref. <sup>14</sup> )	5.21

TABLE II

Sorption of Ammonia on the Ion Exchanger S—S with the Proton Partially Substituted by Potassium Ion at 150°C

Ion exchanger	Total sorption mmol/g	Irreversible sorption mmol/g	Number of the functional groups	
			$\cdot 10^{20}$ corresp. to 1 g	corresp. to 1 Å <sup>2</sup>
S—S	3.503	2.561	15.423	0.288
S—S <sub>75</sub>	3.586	2.331	13.382	0.219
S—S <sub>55</sub>	2.710	1.566	8.293	0.148
S—S <sub>34</sub>	2.318	1.162	5.324	0.087
S—S <sub>0</sub>	1.748	0.412	0	0

acid sites. The ion exchangers S—S, S—PO and S—CPO possessed the highest capacity for the irreversibly sorbed ammonia the value of which was the same for all the three ion exchangers in question. On the contrary, it was lower for the ion exchangers S—P and S—PS. In addition, with the ion exchanger S—S it was found that the amount of strongly adsorbed ammonia was independent of the temperature within the range 125–150°C. The fraction from the total amount adsorbed corresponding to the irreversible sorption is lowered in the order S—S, S—CPO, S—PO,

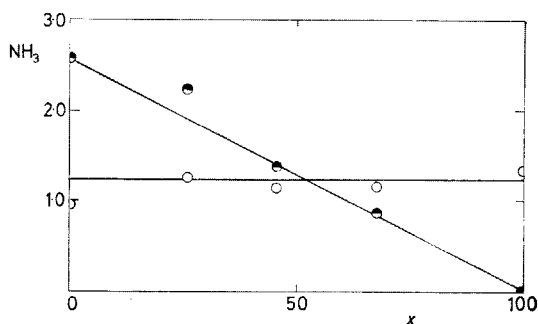


FIG. 2

Plots of the Ammonia Sorption ( $\text{NH}_3$ , mmol/g) upon the Exchange Degree  $\text{H}^+ \rightarrow \text{K}^+$  ( $x$ , %) on the Ion Exchanger S—S

● Irreversible sorption corrected by the sorption on the potassium centres, ○ reversible sorption.

S—P and S—PS. This observation is consistent with the decreasing acid strength of exchangers<sup>7,8</sup> S—S, S—PO and S—P.

From the sorption of ethyl acetate<sup>11</sup> on the ion exchangers mentioned above the area of  $13.8 \text{ \AA}^2$  corresponding to one active site was calculated. Grubhofer<sup>12</sup> asserts that a minimum distance between two sulphur atoms in the model of the sulphonated polystyrene molecule is  $4.4 \text{ \AA}$ . Using this value we can calculate area of  $19.4 \text{ \AA}^2$  corresponding to sulphur atom and forming one active centre (*i.e.* —SO<sub>3</sub>H group). Although both results were obtained by different methods (spectra and sorption) they are within reasonable agreement. Comparing these values with the mean area of NH<sub>3</sub> (ref.<sup>13</sup>) possessing  $14.0 \text{ \AA}^2$  we can observe that ammonium molecule area corresponds to that of one active centre. If the amount of irreversibly sorbed ammonia is expressed by the total area consisting of the individual active sites the specific area of the ion exchanger would have to possess  $193 \text{ m}^2/\text{g}$ . Carrying out a similar calculation also for Amberlyst<sup>15</sup> we find that the surface area should be  $352 \text{ m}^2/\text{g}$ . All ammonia molecules cannot be accommodated on the surface only because the B.E.T. (N<sub>2</sub>) surface areas of S—S and Amberlyst 15 are  $49$  and  $43 \text{ m}^2/\text{g}$  respectively. Therefore, another kind of sorption has to be anticipated. It is conceivable that ammonia molecules penetrate under the ion exchanger surface after the —SO<sub>3</sub>H groups have already been saturated. This phenomenon can be interpreted as swelling whereby the active centres inside the sorbent matrices become accessible to the additional sorbate molecules. Our consideration is consistent with the conclusions drawn by Jeřábek<sup>8</sup> from the investigation of NH<sub>3</sub> sorption on the ion exchangers containing —SO<sub>3</sub>H groups where proton was exchanged by NH<sub>4</sub><sup>+</sup> group. Similar explanation was suggested by Krejcar<sup>3</sup> and Vulich<sup>4,5</sup>. These authors observed that swelling the ion exchanger by water vapors enables greater accessibility of the active centres resulting in a larger uptake of ammonia. With some ion exchangers (S—S) the irreversibly adsorbed amount is closely related to the total exchange capacity determined by titration (comp. Table I, columns 3 and 6.) With the others the total capacity is higher.

On the partially exchanged ion exchangers S—S the total adsorptive capacity for ammonia is decreased depending on the exchange degree (H<sup>+</sup> → K<sup>+</sup>) as it is obvious from Fig. 2. The value of the irreversible sorption falls linearly whereas the reversible sorption remains practically independent of the ion exchange degree. Therefore, the reversible sorption may be considered as a physical sorption because it is not affected by the presence of H<sup>+</sup> or K<sup>+</sup>. The completely exchanged ion exchanger still possesses certain irreversible adsorptive capacity ( $0.412 \text{ mmol/g}$ ) which was never observed with the primary copolymer. This capacity may be ascribed to the surface which contrary to the original copolymer without functional groups is modified with —SO<sub>3</sub>K groups. For this reason the points in Fig. 2 representing the irreversible sorption on S—S<sub>75</sub>, S—S<sub>55</sub> and S—S<sub>34</sub> were corrected by the fraction corresponding to the amount of the ions exchanged. Therefore, the sorption from the gas phase

can be linearly correlated with a number of the groups exchanged. Considering that the parent ion exchanger S—S does not yield the defined number of the surface groups from the  $\text{NH}_3$  sorption the real number of the surface groups cannot be determined even from this correlation. It is evident that such a sorption of ammonia is not capable of providing useful information about the quantity of the surface  $\text{—SO}_3\text{H}$  groups because  $\text{NH}_3$  molecule does not persist on the surface of the ion exchanger only but it very likely forms several layers beneath the surface without penetrating the whole mass of the ion exchanger.

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