CHEMISORPTION PROPERTIES AND CATALYTIC ACTIVITY OF ORGANIC CATION EXCHANGE RESINS

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Sorption of organic bases from a gaseous phase on sulphonated styrene–divinylbenzene resins with varying porosity and degree of cross-linking was studied. Experiments with a series of bases differing in the size of their molecule showed that the amount sorbed is dependent on the size of the molecule of a sorbate and on the structure of resin macromolecule. Sorption of the compounds with different basicity was found to be influenced only by their basicity. Changes in the degree of cross-linking did not exert a clear-cut effect. It was found that strongly basic compounds occupy along with surface acidic groups also the majority of the groups located within the polymer mass of ion exchanger. The effect of polymer structure of the resin on catalytic activity was studied with dehydrations of methanol and tert-butanol in a gaseous phase. Results showed that the course of the catalytic reaction is influenced similarly as sorption. In all cases a fundamental difference was found between the properties of macroreticular and standard ion exchangers.

Of few studies dealing with adsorption on organic ion exchangers from a gaseous phase, the most are concerned with adsorption of water or ammonia. Sorption of organic compounds on the ion exchangers has usually been studied in conjuction with their catalytic activity[1-5]. These works showed that a measure of sorption properties is the affinity of active groups of an ion exchanger to a sorbate, which is given by the acidity or basicity of the sorbate. The adsorbed amount is, of course, also affected by the surface area of the sorbent. In some cases sorbate not only occupies surface active groups but also penetrates into polymer mass. In studies on the effect of the amount of cross-linking agent (divinylbenzene)[6,7] and of the size of the molecule of a sorbate[8] it was established that these two parameters do influence the amount adsorbed.

In this work a set of sulphonated styrene–divinylbenzene copolymers differing in their porosity and in the structure of their macromolecule was chosen. With these models, the sorption, from a gaseous phase, of a series of organic compounds differing in their basicity and in their size was studied. The aim of this study was to ascertain how these factors influence the extent of adsorption. The attempt was also made to find whether and how the above factors affect the course of heterogeneous catalytic reactions of these models.

EXPERIMENTAL

Sorbents. A series of sulphonated macroporous styrene–divinylbenzene copolymers with 10, 15, 25, 50, and 70% of divinylbenzene (denoted as MS-10, MS-15, MS-25, MS-50, and MS-70) and a series of sulphonated standard styrene–divinylbenzene copolymers with 8, 15, 25, and 50% of divinylbenzene (denoted as SS-8, SS-15, SS-25, and SS-50) were used. All resins were produced by Výzkumný ústav synthetických pryskyřic a laků, Pardubice. The resins were shattered prior to using and sorted out to 0·20—0·315 mm particles. All ion exchangers were converted to the H-form with 1M-HCl by a flow method and washed with distilled water until negative test on the presence of chloride ions. Then the resins were predried in air and dried in a vacuum drying oven under a pressure of 1 Torr and at a temperature of 105°C for 3 h. The samples were stored in a dessicator over phosphorus pentoxide. Their properties are in Table I.

Sorbates. Methylamine (Fluka) and trimethylamine (Fluka) were used without further purification. Piperidine (Lachema) was distilled through a 10 TP column, b.p. 106°C. Tetrahydrofuran (Laborchemie, Apolda, GDR) was dried over sodium bis(2-methoxyethoxy)aluminium hydride and distilled. Tert-Butylamine was prepared by reported procedure[9], b.p. 44—45°C. Thiophene (Reachim, U.S.S.R.) was dried over sodium and distilled. n-Hexane (Lachema) was purified chromatographically with 5 A molecular sieve. The purity of all compounds was checked by gas-liquid chromatography.

Other substances. Nitrogen, for electric lamps, and electrolytic hydrogen were dried with 5 A molecular sieve. Tert-butanol (Reanal, Budapest) was predried with sodium hydroxide and distilled through a column with sodium, b.p. 82·5°C, m.p. 25·5°C. Methanol (Lachema) was dried with magnesium sulphate and distilled through a 10 TP column.

Pulse sorption apparatus. The apparatus was equipped with a thermal conductivity detector (Fig. 1) and consisted of a mercury manometer 1, containers of sorbates 2, a six-way feeding valve (Zimmermann, GDR) with feeding loop 3, valves 4, a thermal conductivity detector, type C 8 (Chemoprojekt, Satalice) connected *via* bridge with an EZ 3 recorder (Laboratorní přístroje, Prague). Sorbent was placed in a short glass column provided with a temperature-controlled heating jacket 6. The carrier gas hydrogen, was introduced through a drying column and a flow regulator into a reference cell of the detector and *via* feeding valve and a sorption column into a measuring cell of the detector. The base which was not sorbed by the sorbent was trapped by absorption in a washing bottle 8 containing 0·01N-H_2SO_4. All experiments were carried out with a 75 ml per min hydrogen flow rate and at a 150°C sorption column temperature. The sorption
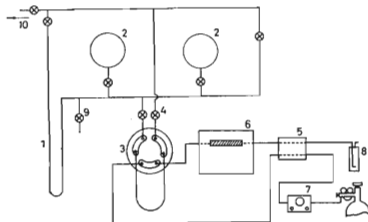

FIG. 1

Scheme of Pulse Sorption Apparatus
For description see Experimental.

column was charged with 0·2—0·3 g of ion exchanger which was then stabilised in a stream of hydrogen at a temperature of 150°C over a period of 1 h. By filling valve 9, the container 2 was charged with the sorbate and degassed by repeated cooling with liquid nitrogen and evacuation 10. Feeding loop 3 of a volume of 3·17 ml (calibrated by mercury) was evacuated and filled with the sorbate under the pressure which was read on manometer 1. The loop was inserted into a stream of carrier gas by turning feeding valve 3. The frequency of feeding was 1 pulse per 7·5 min. In initial pulses the organic base was completely sorbed on the sorbent. The experiment was finished when last three pulses had the same response on the recorder. The amount sorbed was calculated as the difference between the total fed amount of the base (determined as the number of pulses multiplied by their volume) and the amount of the base which passed through the sorption column (determined by retitration of the acid in the washing bottle).

Sorption balances. The McBain balances were used in a modification suggested by Rubin-štejn[10]. The instrument used made it possible to sorb simultaneously six samples. The container of sorbate was separated from the apparatus by mercury valves. The parts of the apparatus in which balance pans with samples were moving were maintained at a required temperature by means of a silicon oil bath, the temperature of which was controlled by a thermostat. The samples (0·1—0·2 g) were first desorbed at 150°C for 24 h. Initial pressure in the apparatus was in each experiment $1 . 10^{-3}$ Torr. Measurements of the surface area and pore distribution were performed

TABLE I

Characteristics of Ion Exchangers Used

Ion Exchanger	MS-10	MS-15	MS-25	MS-50	MS-70	SS-8	SS-16	SS-25	SS-50
Titration exchange capacity, mequiv/g	5·34	5·28	3·43	2·68	2·22	5·45	5·22	4·58	2·72
Specific surface area m²/g	< 0·1	43·0	77·5	263·2	266·3	< 0·1	< 0·1	< 0·1	< 0·1
Pore volume at saturation by n-hexane cm³/g	—	0·318	0·568	1·33	0·987	—	—	—	—
Helium density g/cm³	1·44	1·43	1·40	1·33	1·31	1·45	1·45	1·38	1·45
Mercury density g/cm³	1·38	0·96	0·86	0·49	0·48	1·43	1·39	1·35	1·39
Average pore radius Å	—	148	147	101	77	—	—	—	—
Porosity, ml/ml	0·042	0·329	0·386	0·632	0·634	0·014	0·041	0·022	0·041
Calculated thickness of pore wall, Å	—	110	89	26	19	—	—	—	—

at 20°C, using n-hexane which does not cause swelling of the ion exchangers under study. Sorption of organic bases was carried out at 150°C in a similar way. Because of the higher boiling points of some substances the measurements were performed only with low relative pressures.

Other methods. Mercury and helium densities of ion exchangers were determined in the usual way. Titration exchange capacity of ion exchangers was determined with 0·1—0·2 g samples of an ion-exchanger, which was allowed to swell in 10 ml 0·1M-KCl for 24 h, by titration with 0·1M-NaOH on bromothymol blue as an indicator. Catalytic experiments were carried out in a glass flow reactor maintained at the reaction temperature by a heated glycerol bath. The reaction mixture was prepared in an evaporator, by injecting an alcohol with a feeding device into a stream of nitrogen, which served as an inert gas. Reaction products were fed directly into a gas chromatograph equipped with an ionisation detector and a column (2 m by 3 mm) filled with 15 wt. % poly(ethylene glycol) 300 on Cellite (BDH, 30—80 mesh). An oven temperature was 120°C and nitrogen was used as a carrier gas.

RESULTS AND DISCUSSION

Before commencing this work we had assumed that fundamental difference in texture would be observed only between unporous gel-like resins and the substances with artificially formed porous structure (macroreticular). This assumption was verified, but it was also found that the texture of macroreticular resins depends on the amount of cross-linking agent (divinylbenzene) (Fig. 2). From the data on pore volume at saturation, on the mercury and helium density (Table I), and under the very simplified assumption that the pores are cylindrical we calculated the average thickness of the wall of the pore with mean radius for a given ion exchanger. The values so obtained are presented in the last column of Table I. It is seen that in
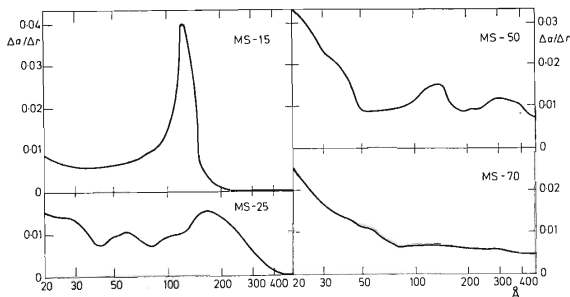

Fig. 2
Pore Size Distribution Curves Obtained from n-Hexane Isotherms

MS-15 the average distance between two pores is 220 Å, which represents approximately $10-15$ "layers" of polymeric chains, whereas in MS-70 this distance is only about 38 Å, *i.e.* approximately two layers of polymeric chains. More cross-linked copolymers retain well their spatial structure. This holds especially for MS-70 and MS-50, while in the case of MS-25 and MS-15 the resins can be partially deformed due to rotation of aliphatic chains, as found with the aid of Stuart models. Copolymers containing 10% of divinylbenzene and less retain no more their spatial structure. This is evidenced by the fact that after first soaking in water (or in other liquid in which the copolymer swells) it looses its porosity and acquires the properties of standard gel. More cross-linked ion exchangers retain its porous structure even after repeated soaking or after exchange of hydrogen ion for a cation.

The aim of this work was to examine the influence of four parameters: the degree of cross-linking of the copolymers of the ion exchangers used, their texture, the size of sorbate molecule, and the basicity of the sorbate. Apart from these parameters, the amount sorbed depends also on exchange capacity of ion exchangers. Although it would in principle be possible to prepare the resins with the same exchange capacity, a practical realization of this intention is, however, difficult. In a study of the effect of size of the molecule of a sorbate on sorbed amount we used methylamine, trimethylamine, and tert-butylamine. The basicities of these amines are expressed in Table II by logarithms of their dissociation constants for the equilibrium between the protonated forms of a given base and the solvated proton in an aqueous medium. For purposes of this study the difference of one order of magnitude can be neglected and the bases employed may be regarded as equal. Dimensions of molecules were measured with the aid of Stuart models and are expressed by two greatest dimensions

Table II

Some Properties of Sorbates Used

Sorbate	B. p. °C/760 Torr	Basic size of molecule[a] Å	pK (ref.[11])	Cross-section surface area, Å²	$\Delta\nu$ cm^{-1}
Methylamine	−6·5	3·6 . 4·3	10·66	19	—
Trimethylamine	3·5	6·3 . 6·3	9·75	30	—
tert-Butylamine	45·2	6·8 . 6·4	10·68	34	—
Piperidine	106	6·9 . 6·9	11·1	32	≫ 500
Tetrahydrofuran[c]	65·5	6·2 . 6·5	−2·08	28	296
Thiophene[d]	84	7·2 . 6·2	−4·08[b]	28	55

[a] Determined with Stuart models; [b] for tetrahydrothiophene; [c] $m = 0.23$ mmol/g Torr; [d] slope of tangent line of the isotherm at the origin; $m = 0.08$ mmol/g Torr.

of their spatial arrangement. Sorptions of amines were carried out at 150°C under static conditions on sorption balances, and under dynamic ones in pulse sorption apparatus. Results are summarized in Table III. From the inspection of the table it follows that there is a difference between porous and standard ion exchangers and further that sorbed amount decreases with increasing cross-linking of the molecules of copolymers of both types. Also, sorption decreases with increasing size of the molecule sorbed. Sorption on MS-10 deviates from the above-mentioned dependence on cross-linking and is always markedly lower. The explanation bears upon the already-mentioned fact that the copolymer cross-linked with less than 10% of divinylbenzene does not retain its macroreticular structure after soaking in water and drying. Why experimental data for MS-10 lie below the values for SS-8 cannot be explained from these data. The difference in both methods employed is evident from Table III. Sorption balances, that ensure a sufficiently long time for the course of adsorption, yield equilibrium values, while the pulse method gives the values corresponding to dynamic conditions in the sorption. Relative values are, however, the same for both methods, *i.e.* both confirm the same dependence of sorption on the parameters investigated.

TABLE III

Sorbed Amount of Amines at 150°C

A Values obtained by sorption balances (mmol/g). *B* Values obtained by pulse chromatographic method (mmol/g). *S* Calculated surface area corresponding to the amount sorbed in a tightly arranged monolayer on surface (m²/g).

Ion exchanger	Value	MS-10	MS-15	MS-25	MS-50	MS-70	SS-8	SS-16	SS-25	SS-50
Methylamine	A	5·05	4·50	3·34	2·92	2·50	4·72	4·70	4·51	2·07
	S_A	578	5·5	382	334	286	540	538	516	237
	B	0·78	4·65	2·90	2·29	1·96	1·87	0·92	0·55	0·03
	S_B	89	532	331	262	224	214	105	63	3·5
Trimethylamine	A	2·60	4·35	2·95	2·26	1·84	2·45	1·30	1·35	0·17
	S_A	470	786	533	408	332	442	235	244	31
	B	0·14	3·91	2·45	1·66	1·41	0·36	0·17	0·09	0·00
	S_B	25	706	442	300	255	65	31	16	0
tert-Bytylamine	A	—	4·82	3·24	2·53	—	—	—	—	—
	S_A	—	987	665	5·8	—	—	—	—	—
	B	0·04	3·24	2·32	1·70	1·16	—	—	—	—
	S_B	8·2	662	475	348	237	—	—	—	—

As ion exchangers employed were prepared from corresponding styrene–divinyl-benzene copolymers by sulphonation in a swelled state, one can assume that distribution of sulphonic acid groups is uniform throughout the whole mass of these exchangers. From Table III it is seen that a small molecule of methylamine occupies the predominant part of sulphonic acid groups located within the exchanger. In dry macroreticular ion exchangers which contain no less than a quarter of the total amount of sulphonic acid groups on the surface of the copolymer, as found by approximate calculation, as well as in standard exchangers, which contain only very small surface sulphonic acid groups, methylamine has to penetrate during sorption into the mass of sulphonated copolymer. In the case of MS-50 and MS-70 the amount of methylamine sorbed is greater than their titration capacity, which may be due to capillary condensation in very fine pores. In the case of trimethylamine and tert-butylamine, too, the amount sorbed is greater than the number of surface sulphonic acid groups, so that a part of the amines has to penetrate obviously into copolymer mass. For purposes of illustration, the areas S were calculated which correspond to the amount of a base sorbed in a tightly arranged monolayer on the surface of ion exchanger. Because of these facts the effect of the structure of macromolecule on the sorbed amount of amines (particularly trimethylamine and tert-butylamine) is more distinct on standard ion exchangers. In this case the pores do not contribute to sorption and, hence, the extent of sorption depends only on the ability of molecules of a sorbate to penetrate into the mass of the sorbent.

When selecting sorbates for a study of the effect of basicity of a sorbate on the amount sorbed, several requirements have to be taken into account: sufficiently great difference in their basicity, boiling point below 100°C, the same size of a molecule, and a resistance toward swelling in the sorbates chosen. The above requirements
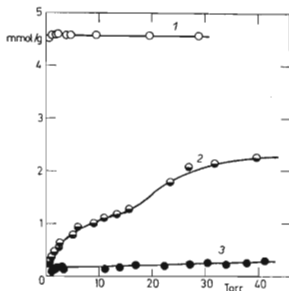

FIG. 3

Adsorption Isotherm of Bases on MS-15 Ion Exchanger at 150°C

1 Piperidine, 2 tetrahydrofuran, 3 thiophene

were best met with these compounds: piperidine, tetrahydrofuran, and thiophene. Some physical properties of these sorbates are listed in Table II. The basicity characterized by dissociation constants[11] in an aqueous medium is not very suitable for characterization of sorption from a gaseous phase. As the value for thiophene is not available, the basicity of a related compound, tetrahydrothiophene, is given. Another way of characterization of the basicity of sorbates which was used by Komers and coworker[12] seems to be more suitable, since the values are determined directly from sorption parameters. The method consists in measuring adsorption isotherms of given bases on a given sorbent, and their basicity is characterized by the slope of the tangent line of the isotherm in the origin (m in Note, Table II). The slope for piperidine is however so great that it cannot be determined. Another possibility is to estimate basicities from shifts observed in the IR spectra of a sorbate--phenol system measured at room temperature in a nonaqueous medium. With piperidine, which is very strong base and gives a complex with phenol which does not exhibit the frequency followed, only the lower limit of the shift could be determined. The data allow to conclude that the sorbates differ sufficiently in their basicity, but a quantitative comparison of their basicity was not possible. The size of molecules was estimated with the aid of Stuart models, and obtained values indicate that the requirement of the same size was practically met.

The method of pulse chromatography could not be used, since thiophene and tetrahydrofuran passed through a sorption column without measurable sorption on the sorbent. Difficulties arosed also from higher boiling points of the sorbates, which with the apparatus employed made a suitable feeding impossible. Measurements were therefore performed on sorption balances at 150°C, and that only with MS-15 and MS-70. With the other ion exchangers the sorptions of thiophene and tetra-

TABLE IV

Results of Sorption Measurements of Organic Bases at 150°C with Sorption Balances

A Experimental values (mmol/g). *S* Calculated surface area corresponding to the amount sorbed in a tightly arranged monolayer on surface (m²/g).

Ion exchanger	Value	MS-15	MS-25	MS-50	MS-70
Piperidine	A	4·59	3·14	2·58	2·04
	S_A	882	606	496	393
Tetrahydrofuran	A	1·84	1·15	1·22	1·05
	S_A	310	194	206	177
Thiophene	A	0·24	0·24	0·48	0·62
	S_A	40·5	40·5	81·0	105

hydrofuran were low, so that measurements of sorption capacities could not be performed. In this way, the isotherms were obtained which for MS-15 are graphically represented in Fig. 3. The other ion exchangers yielded the isotherms of similar form. Piperidine was saturated already at low pressures of sorbate, weaker bases only at a pressure around 40 Torr, which was the maximum pressure that could be achieved in the apparatus with the bases used. Sorption capacities decrease in the order: piperidine, tetrahydrofuran, and thiophene (Table IV), parallel to decreasing values characterizing their basicity. Piperidine, which is a strong base, occupies most sulphonic acid groups. Similarly as in the case of aliphatic amines one has to assume that this base easily penetrates into the ion exchanger mass. This is also indicated by the high values of S in Table IV. Tetrahydrofuran, which shows much smaller affinity toward acidic groups of the ion exchanger, is sorbed to much lesser extent, since it does not penetrate below the surface. Thiophene, the weakest basic sorbate used, occupies presumably only the surface of the ion exchanger. This assumption is supported also by the values of S which in no case attain the values of specific surface area.

Dependence of the sorbed amount of model compounds on the structure of macromolecule of the copolymer (the content of divinylbenzene) should be discussed with regard to the values of exchange capacities. Comparison of the values of sorption capacity of piperidine, per unit of titration capacity of the ion exchanger, reveals that they do not depend on the cross-linking of the copolymer. This agrees with the assumption about the ability of piperidine to penetrate below polymer surface. In

TABLE V

Initial Reaction Rates $r°$ of Dehydration

Ion exchanger	Methanol		tert-Butanol	
	mol/h kg catalyst	mol/h equiv. H^+	mol/h catalyst	mol/h equiv. H^+
MS-10	8·0	1·25	461	7·2
MS-15	12·5	0·94	993	7·5
MS-25	16·9	0·66	1 116	6·7
MS-50	19·4	0·50	1 141	3·0
MS-70	19·1	0·26	912	1·3
SS-8	5·9	1·08	169	31
SS-16	4·4	0·84	20	3·8
SS-25	3·4	0·74	12·4	2·7
SS-50	0·2	0·07	0·6	0·2

the case of macroreticular ion exchangers their developed porous structure aids in occupying a considerable part of acidic groups. If an approximate calculation of the average thickness of the wall of pores is considered (Table I), then for occupation of all acidic groups it is sufficient that the sorbate would be able to penetrate through only several layers of polymer chains. The amount of tetrahydrofuran sorbed per the unit of titration capacity of the ion exchanger increases with increasing cross-linking. This is likely due to the fact that tetrahydrofuran penetrates below the surface of ion exchangers to a lesser extent, but their specific surface area increases much more rapidly with their cross-linking. This situation is very distinct with the weakest base used, thiophene.

As model catalytic reactions for a study of the effect of cross-linking of ion exchanger on its catalytic activity, we used dehydration of methanol and of tert-butanol in a gaseous phase. Both these reactions were subjected to a detailed kinetic analysis in our laboratory[13,14]. In these studies a macroreticular ion exchanger with 25% of divinylbenzene (similar to MS-25) was used. In the present work dehydration of methanol was studied at a temperature of 131°C and a 0·2 at partial pressure of the alcohol. Dehydration of tert-butanol was studied similarly, at a temperature of 95°C and a 0·2 at pressure. Initial reaction rates under the above conditions were used as a criterion of catalytic activity. On the basis of our previous experience it could be expected that the reaction mechanism would be the same for all the ion exchangers under study. The results obtained are summarized in Table V. Similar to adsorption, also kinetic data indicate a great difference between standard and macroreticular substances. On macroreticular ion exchangers the initial reaction rate increases with the amount of divinylbenzene, which can be explained, similarly as in the case of adsorption, by the increase of surface area of catalysts. The initial reaction rates per unit of the surface and exchange capacity (Table V) decrease, however, with increasing cross-linking of copolymers. This indicates that the structure of macromolecule also affect to a certain extent the rate of the reaction. On the contrary, the size of molecule of the reactant does not exert an ascertainable effect. Contrary to macroporous ion exchangers, in the case of standard ion exchangers, the molecule of the reactant has to penetrate into the mass of the resin to contact acidic groups. In such a case cross-linking becomes an important factor, as found. The results obtained with standard ion exchangers demonstrate also the effect of varying size of molecules of reactants, since the rate of dehydration of methanol falls down with cross-linking less that the rate of dehydration of tert-butanol. From the results obtained it can be further concluded that the course of a catalytic reaction is affected by cross-linking of macromolecules of an ion exchanger, similarly as the sorption of organic substances.

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