LIQUID PHASE ADSORPTION OF ORGANIC AMINES ON SULPHONATED STYRENE–DIVINYLBENZENE COPOLYMERS

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Sorption of organic amines from various solvents on standard and macroporous sulphonated styrene–divinylbenzene copolymers has been studied. The amount sorbed depends above all on the molecular mass (size) of sorbate, but its chemical affinity (basicity) toward polymer functional groups plays a role, too. The solvent and copolymer crosslinking effects are in mutual relation and are less pronounced. In addition to the interaction of the sorbate with sulphonic acid groups of the polymer, the sorbate dissolves also in the polymer.

A number of studies can be found in literature that deal with the sorption of organic substances on ion exchangers in the liquid phase. Some refer to the application of ion exchangers to separation of organic compounds, especially in the field of amino acids and antibiotics, *e.g.*[1,2], other aim at explaining general regularities in the interaction of organic compounds with ion exchangers. This interaction can be classified as follows: the interaction of salts of organic substances or of organic compounds capable of dissociation, which proceeds analogously to the usual exchange of inorganic ions and that of organic compounds without dissociation in which *e.g.* van der Waals forces are playing a role. The aim of some studies was to distinguish these two modes of interaction[3,4]. A detailed study of the adsorption of organic compounds on ion exchangers was performed by Reichenberg and Wall[5]. The authors found that in the liquid phase there is tendency to a uniform distribution of organic molecules in the polymer ion exchanger gel and that the adsorbed amount of a given organic substance decreases with increasing crosslinking of the copolymer (up to 15% divinylbenzene content). Libinson and Vagina[6,7] studied the adsorption of different organic amines on an acid ion exchanger with 1—4% divinylbenzene content. Watkins and Walton[8] reported on the adsorption of organic bases on some commercial ion exchangers in a series of solvents and discussed relationships between the adsorbed amount and the type of the sorbate and the kind of the ion exchanger.

In our laboratory the gas phase adsorption of organic compounds on sulphonated, standard (gel) and macroporous styrene–divinylbenzene copolymers was already studied[9,10]. In this work we used the same samples of ion exchangers with a different degree of the copolymer crosslinking to study the liquid phase adsorption. Besides the crosslinking of the copolymer, the effect of solvents was examined, too.

EXPERIMENTAL

Sorbents. Standard (gel) sulphonated styrene-divinylbenzene copolymers containing 2 to 50% of divinylbenzene (designated as SS-2 to SS-50) and macroporous sulphonated styrene-divinylbenzene copolymers containing 10–60% of divinylbenzene (designated as MS-10 to MS-60) were used in this study. The starting polymers were prepared by the Research Institute of Resins and Lacquers, Pardubice, and were sulphonated by concentrated sulphuric acid in the presence of 1,2-dichloroethane as a swelling agent[11]. Prior to using, the samples were ground and sieved to 0·16–0·32 mm particles and then dried in a vacuum drying oven at 150°C/0·1 kPa for 3 h. The samples were stored in a dessicator over phosphorus pentoxide. Their basic properties are listed in Table I.

Sorbates. 1-Propylamine, 2-butylamine, di-1-butylamine, tri-1-butylamine and aniline (all supplied by Lachema, Brno) were dried over $MgSO_4$ and purified by distillation; diphenylamine was used without further purification.

Solvents. Cyclohexane, decaline, benzene, nitrobenzene, dioxane, acetone and cyclohexanone were dried over $MgSO_4$ and purified by distillation.

Other chemicals. Perchloric acid (70%, Jenapharm, GDR), 99% acetic acid (Lachema Brno) and crystal violet were used as obtained.

Procedure. In adsorption measurements, 0·25 g of the ion exchanger was allowed to swell in 5 ml of the solvent for 24 h. Then the amine was added in the appropriate amount, usually in twofold excess (molar) with respect to the sulphonic acid groups of the ion exchanger. To attain equilibrium, the mixture was allowed to stand at room temperature with occasional shaking for 24 h in the case of macroporous samples and for 14 days for standard samples. Then the concentra-

TABLE I

Basic Properties of Ion Exchangers Used

Ion exchanger	Titration exchange capacity mequiv/g	Specific surface m²/g	Mercury density g/ml	Helium density g/ml	Porosity %	Swelling degree after 24 h in % of the original volume	
						dioxan	cyclohexane
SS-2	4·90	<0·1	—	—	—	260	103
SS-8	3·75	<0·1	1·43	1·45	0·01	132	104
SS-15	4·38	<0·1	1·39	1·45	0·04	113	109
SS-25	3·72	<0·1	1·35	1·38	0·02	101	102
SS-50	1·97	<0·1	1·39	1·45	0·04	106	103
MS-10	4·00	16	1·27	1·46	13	172	100
MS-15	3·81	35	0·75	1·36	45	146	107
MS-25	3·80	44	0·61	1·45	58	132	103
MS-40	3·20	120	0·57	1·40	59	112	106
MS-60	3·02	227	0·53	1·45	63	107	108

tion of the organic base in the liquid phase of the mixture was determined by 0·1N perchloric acid solution in glacial acetic acid on crystal violet.

Swelling of the ion exchanger was determined in the following way. The known volume of the ion exchanger was allowed to swell at room temperature in a flask for 24 h, then the sample was transferred into the connected graduated burette where after sedimentation the volume of the swelled sample was determined.

RESULTS AND DISCUSSION

The results referring to the sorption of amines on gel and macroporous ion exchangers are graphically represented in Fig. 1. They show that the amount of the base sorbed

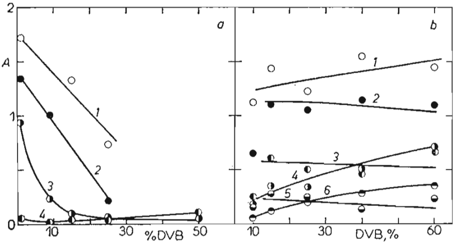

FIG. 1

Dependence of Sorbed Amount A on Cross-linking of Ion Exchangers

a Standard ion exchangers, *b* macroporous ion exchangers, *A* mol base/mol SO_3H, *1* 1-propylamine (in cyclohexane), *2* 1-propylamine (in dioxane), *3* tri-1-butylamine (in dioxane), *4* tri-1-butylamine (in cyclohexane), *5* diphenylamine (in dioxane), *6* diphenylamine (in cyclohexane).

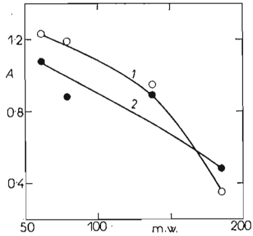

FIG. 2

Dependence of Sorbed Amount of Base A on Molecular Mass of Substrate (ion exchanger MS-25)

Sorbents used: 1-propylamine, 2-butylamine, di-1-butylamine, tri-1-butylamine, *A* mol base/mol SO_3H, *1* cyclohexane as solvent, *2* dioxane as solvent.

depends above all on the size of the sorbate molecule. The bulkier the sorbate, the smaller the sorbed amount. This is demonstrated also in Fig. 2 which shows the sorption of four amines belonging to the same homological series. One can assume that the basicity of all these amines is practically identical. Fig. 1*b* indicates a certain, although small, difference between the adsorbed amount of tri-1-butylamine and diphenylamine. The former sorbs to a greater extent than the latter. These two compounds are practically of the same size. With regard to spacial arrangement of substituents in tri-1-butylamine, the effective volume of this compound is greater than in the case of practically planar diphenylamine. The reason for the lower sorption of diphenylamine is not hence the size of the molecule but the affinity of this compound (basicity) toward sulphonic acid groups of the ion exchanger, which is substantially lower for diphenylamine compared to tri-1-butylamine[12,13]. These conclusions are in harmony with the results obtained in the gas phase sorption of similar organic compounds on the same ion exchangers[9,10].

The effect of the ion exchanger crosslinking and of the kind of solvent on the amount sorbed is not so straightforward. With gel ion exchangers the amount of the sorbed base decreases with crosslinking, and that quite substantially for the samples containing 2–25% of divinylbenzene. Only with cyclohexane as a solvent and with a relatively bulky tri-1-butylamine this dependence was not discernible. This follows obviously from the fact that standard ion exchangers swell poorly in cyclohexane and even in the case of low crosslinking they do not provide the possibility for bulky tri-1-butylamine to penetrate into their polymer mass. In the case of sorption of propylamine this is greater in cyclohexane than in dioxane, although the ion exchangers, especially those crosslinked to a low degree, swell more in dioxane. This is likely due to the interaction of dioxane with sulphonic acid groups of the ion exchanger that leads to the formation of adducts, while cyclohexane is inert solvent. This was proved in the study of kinetics of reesterification of ethyl acetate by propanol on these ion exchangers[14] in which both compounds were used as solvents. Dioxane thus competes with amines and decreases thus their adsorption. With the other substrates, additional factors such as size of their molecules play more important role which makes solvent effects less significant.

A similar situation arises also in the case of macroporous ion exchangers. Here the fact that solvent and sorbate can penetrate into the inside of ion exchanger particles through pores must also be taken into account. For that reason the dependence of the amount of sorbed amines on crosslinking is not so steep as in the case of gel ion exchangers and with cyclohexane as the solvent the amount of the amines sorbed even increases with crosslinking. To explain these phenomena, the effect of both crosslinking and solvent should be analysed. In dioxane the lower crosslinked ion exchangers swell to such a degree that a relatively great amount of the amine can penetrate into the gel mass. This amount is so great that it is not compensated in the case of higher crosslinked ion exchangers (which do not swell to such an extent) by further increase in their porosity. Therefore, the amount of sorbed amine decreases in this case. On the other hand, cyclohexane does not cause so extensive swelling of the low crosslinked ion exchangers and hence the penetration of amines to its mass and thus also their sorption is small. On increasing crosslinking, the porosity markedly increases, which makes the penetration of amines into ion exchanger particles easier and increases thus also the extent of the sorption. This effect is the reason why macroporous, higher crosslinked ion exchangers proved useful for some catalytic reactions in the liquid phase[15].

As we found that solvent exerts a certain effect on the extent of sorption, a series of organic solvents of different type was examined. The solvents were characterized

TABLE II

Sorption of Di-1-butylamine from Organic Solvents (ion exchanger MS-25)

Solvent	Swelling degree after 24 h in % of the original volume	Dipole moment	Dielectric constant	Sorbed amine mol/mol SO_3H
Cyclohexane	103	0·00	2·06	0·90
Decaline	114	0·00	2·13	0·98
Benzene	116	0·08	2·24	0·97
Nitrobenzene	123	3·95	36·45	0·99
Ethyl acetate	133	2·93	6·11	0·84
Dioxane	133	0·00	3·86	0·87
Acetone	135	2·80	21·50	0·92
Cyclohexanone	147	1·90	15·00	1·07

TABLE III

Dependence of Amount of Sorbed Base on Its Molar Ratio to Sulphonic Acid Groups of Ion Exchanger (ion exchanger MS-25)

Base/SO_3H mol. ratio	Total amount sorbed, mmol[a]		Dissolved portion, %	
	1-propylamine	aniline	1-propylamine	aniline
1	0·63	0·58	0	18
2	0·70	0·70	11	43
3	0·76	0·73	21	49
5	0·95	0·78	51	59
10	1·12	0·85	78	73

[a] Irreversibly sorbed amount: 1-propylamine 0·63 mmol, aniline 0·49 mmol.

by parameters summarized in Table II. Although the solvents under study differed markedly in their dipole moments and dielectric constants, *i.e.* in the parameters commonly used to characterize the medium in chemical reactions in nonaqueous media, the differences in the amount of the sorbed base for one ion exchanger were not great. Because of the great extent of the work, the effect of all the solvents for all the series of crosslinked ion exchangers has not been examined. One can assume, however, that cyclohexane and dioxane represent nonpolar and polar solvents sufficiently well and that the results for other solvents would be similar to those shown in Figs 1 and 2.

All the results discussed were obtained using the molar ratio of the base to sulphonic acid groups of the ion exchanger equalling to 2 : 1. At this molar ratio it was found that the most of propylamine bonds chemically to sulphonic acid groups and the rest dissolves in the polymer and can be extracted readily with a small amount of the solvent. On increasing the base to sulphonic acid groups molar ratio, the chemisorbed amount remains the same while the dissolved portion of the amine increases. These results are represented numerically in Table III. This finding agrees with our results obtained for the gas phase sorption of ammonia on ion exchangers[16].

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