

ACCESSIBILITY OF ACTIVE GROUPS IN ACIDIC STYRENE-DIVINYLBENZENE ION EXCHANGE RESINS OF VARIOUS CROSS-LINKING IN SORPTION OF ETHYL ACETATE FROM THE GAS PHASE

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Sorption of ethyl acetate was examined at 120°C on macroreticular styrene-divinylbenzene strongly acidic ion exchange resins of various cross-linking. The ethyl acetate molecules were observed to penetrate from the gas phase into a certain depth of the polymeric material of the ion exchanger. As indicated by experimental data, the polymer network of these ion exchange resins consists of cross-linked "nuclei", accessible for molecules from the gas phase with difficulty only. From the surface area of nuclei, mobile cross-linker-free chains are extending. The length of these chains depends on the content of divinylbenzene in the ion exchange resin.

The degree of cross-linking in a polymer network which is expressed as percentage of divinylbenzene in the starting polymerisation mixture, may be regarded as one of the parameters very important for properties of ion exchange resins prepared on the basis of styrene-divinylbenzene copolymers. In connection with investigations on the effect of cross-linking on the activity of organic cation exchangers as catalysts of reactions in the gas phase¹⁻³, the sorption properties of these exchange resins have been now examined. As the sorbate, ethyl acetate has been used, *i.e.*, one of the reaction components in assays on the catalytic activity of the present ion exchange resins¹⁻³. Some time ago, ethyl acetate has also been used in sorption measurements on ion exchangers, but under other circumstances.

EXPERIMENTAL

Materials. Ethyl acetate, analytical grade, Lachema (Brno, Czechoslovakia), was purified and deaerated according to an earlier reported procedure⁴. Macroreticular ion exchange resins of the divinylbenzene content 10, 15, 25, 40, and 60% (designation: MS-10, MS-15, MS-25, MS-40, MS-60) were prepared by sulfonation of the parent polymers produced by the Research Institute of Synthetic Resins and Varnishes, Pardubice, Czechoslovakia (for the properties see Table I). The sulfonation was performed in the presence of dichloromethane according to the procedure of Malinský and Seidl⁵.

Measurement. Sorption measurements were performed on a quartz fibre sorption balance of the usual design. Apparatus and measurement were identical with those of Komers and Tomanová⁴.

RESULTS AND DISCUSSION

The sorption isotherms of ethyl acetate on ion exchange resins of various cross-linking are shown on Fig. 1. Experimental data were correlated⁶ with the use of equations derived on the basis of Langmuir's ideas on adsorption on equal active centres both in the classical form considering adsorption on a single centre without dissociation (1) and in the modified version involving adsorption on two centres with dissociation (2) and without dissociation (3). This set was completed by equation (4) for the description of adsorption on nonhomogeneous surfaces. In these equations, S designates the adsorbed amount, p the partial pressure of the sorbate, K the adsorption coefficient, c_L the concentration of active centres, and α , β the coefficients of equation (4).

$$S = c_L K p / [1 + K p] \quad (1)$$

$$S = c_L (K p)^{1/2} / [1 + 2(K p)^{1/2}] \quad (2)$$

$$S = 2c_L K p / [1 + (1 + 4K p)^{1/2}]^2 \quad (3)$$

$$S = \alpha p^\beta \quad (4)$$

As inferred from processing the experimental data by the method of nonlinear regression (Table I), equation (2) referring to adsorption on two centres with dissociation proved to be the most suitable of the whole set. Komers and Tomanová⁴ arrived at the same conclusion in an investigation of the ethyl acetate sorption on similar

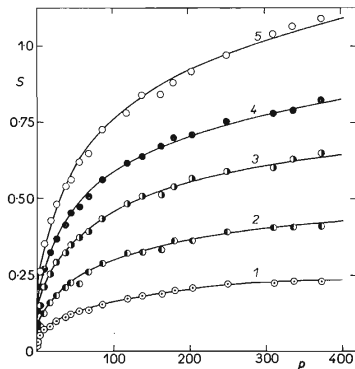


FIG. 1

Adsorption Isotherms of Ethyl Acetate on MS-10 (1), MS-15 (2), MS-25 (3), MS-40 (4), and MS-60 (5) Ion Exchange Resins at 120°C

Dots represent the experimental values; curves were calculated with the use of equation (2). S the adsorbed amount in mmol/g; p sorbate pressure in Torr.

sorbents. Constant values of equation (2) corresponding to the lowest values of the sum of deviation squares are shown in Table I for the particular sorbents.

TABLE I
Physical, Chemical, and Catalytical Properties of Macroreticular MS Ion Exchange Resins

Property	MS-10	MS-15	MS-25	MS-40	MS-60
Titration capacity ^a mmol/g	4.00	3.81	3.80	3.20	3.02
Specific surface ^b , m ² /g	3.2	33	44	120	230
Porosity ^c , %	13	45	58	59	63
Average pore radius ^d Å	225	445	445	320	225
Sum of deviation squares for					
model (1)	3.44 · 10 ⁻³	8.77 · 10 ⁻³	3.06 · 10 ⁻²	5.38 · 10 ⁻²	1.01 · 10 ⁻¹
model (2)	2.75 · 10 ⁻⁴	5.38 · 10 ⁻⁴	1.71 · 10 ⁻³	3.59 · 10 ⁻³	7.74 · 10 ⁻³
model (3)	2.09 · 10 ⁻³	4.71 · 10 ⁻³	1.77 · 10 ⁻²	3.23 · 10 ⁻²	6.07 · 10 ⁻²
model (4)	2.60 · 10 ⁻¹	8.70 · 10 ⁻¹	2.05	3.40	5.57
Constants for model (2)					
$K \cdot 10^4$, Torr ⁻¹	7.15	9.06	11.4	13.3	10.5
c_L , mmol/g	0.92	1.57	2.26	2.78	3.85
c'_e , μmol/m ²	287	47.6	51.4	23.1	16.7
$c_{L,rel}$ ^f	0.41	0.69	1.00	1.23	1.70
Catalytical activity ^g					
methanol	0.28	0.63	1.00	1.19	1.21
propanol	0.44	0.72	1.00	1.29	1.20
2,2,2-trimethylethanol	0.12	0.53	1.00	1.03	1.06
average	0.28	0.63	1.00	1.19	1.21

^a Determined by titration in aqueous media. ^b Determined by adsorption of nitrogen according to the BET method. ^c Calculated from the mercury and helium density values. ^d From measurements of pore distribution by adsorption of n-heptane and by mercury porosimetry. ^e c'_e designates sorption capacity referred to a surface unit. ^f $c_{L,rel}$ designates relative sorption capacity of 1 g of the MS ion exchange resins referred to the MS-25 resin. ^g Catalytical activity in transesterification of ethyl acetate with three different alcohols¹ and expressed as relative values of the initial reaction rate referred to data of MS-25 ion exchange resin (120°C, gas phase, partial pressure of both the ester and the alcohol 0.25 atm).

Differences in cross-linking considerably affect values of the c_L constant expressing concentration of accessible active centres whereas the adsorption coefficients K are almost independent of the cross-linking. As calculated, reliability regions in determinations of adsorption coefficients for the 95% probability level overlap; consequently, the same adsorption coefficients can be used in description of adsorptions on the all examined ion exchange resins of various cross-linking. This conclusion corresponds to the idea on the homogeneous surface of this type of sorbents. The sorption of ion exchangers thus appears to be affected by differences in sorption capacities only. Furthermore, the differences in sorption capacities of ion exchangers differing in cross-linking cannot be exclusively ascribed to differences in specific surface areas. The sorption capacity referred to 1 m^2 of the surface is 17.5 times higher with the MS-10 ion exchanger than with the MS-60 resin (Table I). It may be thus inferred that the sorbate molecules penetrate from the gas phase into a certain depth under the surface. This depth apparently depends on cross-linking; the lower is the cross-linking of the ion exchange resin, the deeper is the penetration of ethyl acetate molecules.

It would not be reasonable to ascribe an extraordinary importance to absolute values of sorption capacities. These data highly depend on the concrete mathematic form of the correlation equation, the mechanistic basis of which can be only a rough approximation of the virtual relations. The much more suitable relative values are therefore used in the further discussion since they are not dependent of the form of the correlation equation.

It is of interest to compare the relative sorption capacities with relative activities determined by Setínek¹ for the same series of ion exchange resins (Table I). The values of Setínek were obtained in transesterifications of ethyl acetate with three alcohols at 120°C , *i.e.*, at a temperature identical with that of the sorption measurements. It may be seen from Table I that the relative catalytic activity values of variously cross-linked ion exchange resins are in principle independent of the transesterification alcohol regardless the considerably different absolute values of reaction rates. The relative adsorption capacities and the relative catalytic activities of ion exchange resins with various cross-linking degrees are in a very good accordance. As indicated by these observations, the relative catalytic activities may also be interpreted as measures of the number of active centres involved in the reaction. Furthermore, similar numbers of active centres were accessible both in the adsorption and catalytic measurements. Such an accord is remarkable with results obtained under very different conditions. The sorption data were measured in a static apparatus, the sorbate being in contact with the ion exchanger for several tens of hours whereas the kinetic data were obtained in a flow reactor. As demonstrated earlier, the dependence of the number of accessible centres on the degree of cross-linking cannot be exclusively ascribed to changes of the specific surface but penetration of molecules

from the gas phase into a certain depth under the surface must also be taken into account. As inferred from accordance of data on the relative number of acidic groups accessible from the gas phase obtained under such different conditions, the two layers of the polymer, accessible and inaccessible from the gas phase, appear to be sharply separated. The explanation could be based on the idea that the cross-linking degree is not the same in the whole mass of the ion exchange resin. Considerable heterogeneity in cross-linking of the polymer network of macroreticular ion exchange resins was demonstrated by Millar and coworkers⁷ in investigations on kinetics and equilibria of the ion exchange on various macroreticular ion exchangers in aqueous media. The heterogeneity is ascribed to two phenomena, one of them being a slightly higher reactivity of divinylbenzene in the polymerisation reaction when compared with styrene⁸; thus, a polymer of a lower cross-linking degree is formed towards the end of the polymerisation than in the initial stage. The other phenomenon consists in solvation of polymer chains by the diluent which is added as a pore-forming agent into the mixture of monomers in the preparation of macroreticular ion exchange resins. This solvation markedly decreases entanglement of chains during the polymerisation; the resulting polymer then consists of cross-linked nuclei from which free styrene chains extend. Such a molecular structure could explain the existence of a sharp boundary between the polymer layer accessible for the ethyl acetate molecules from the gas phase and the other polymer layer. Molecules from the gas phase apparently penetrate the surface layer consisting of free polystyrene chains much more readily than the layer consisting of a cross-linked polymer network. The chain length of the cross-linker-free polymer should depend on the ratio of styrene to divinylbenzene. It may be assumed that only the surface layer will be accessible for molecules from the gas phase in the case of the MS-60 ion exchange resin with the <1 : 1 styrene-divinylbenzene ratio. In the case of the MS-40 resin containing three molecules of styrene per two molecules of divinylbenzene, the thickness of the zone consisting of linear polystyrene chains should be about 150% of the monolayer represented by the sorption capacity of the MS-60 resin surface. The observed sorption capacity value per the surface area unit is 1.4 times higher with the MS-40 ion exchange resin than with the MS-60 resin; this finding is in a very good accordance with the above idea. Similarly, the surface chains of the MS-25 ion exchanger (3 : 1 styrene-divinylbenzene ratio) should consist in average of three molecules of styrene and the sorption capacity of the surface area unit of this in principle uncrossed-linked polymer layer should correspond to a threefold sorption capacity of the MS-60 resin surface area unit; the observed figure 3.1 is again in accord with the theory. On the other hand, no accordance has been observed in the case of MS-15 and MS-10 ion exchange resins. When compared with the MS-60 resin, the observed sorption capacity per 1 m² of the surface area was 2.9 times (calculated, 5.6) higher with the MS-15 resin and 17.5 times (calculated, 10.0) higher with the MS-10 resin. With these ion exchange resins of a relatively low cross-linking degree, the disagreement with

theoretical data does not surprise. In view of the lower content of divinylbenzene, some unfavourable effects must be taken into account such as the lower polymerisation rate of styrene in contrast to divinylbenzene or texture deformation of the polymer network due to changes in swelling degrees in the course of the particular stages in the preparation of ion exchange resins.

The properties of macroporous styrene-divinylbenzene ion exchange resins proved to be markedly different when compared with those of conventional sorbents. The specific surface determined by the BET method is no more characteristic of the accessibility of active groups for molecules from the gas phase. The low-energy interaction with the sorbate occurring for example in measurements of the specific surface by physical sorption according to the BET method, takes place only on the boundary line between the polymer mass and the gas phase. The energetically more significant chemisorption between the acidic sulfonic groups and ethyl acetate molecules or other polar molecules from the gas phase is apparently capable of modifying the position of free polymer chains in the surface layer and thus make possible penetration into a certain depth of the polymer mass depending on the layer thickness of the uncross-linked polymer. This effect, demonstrated in this paper on ion exchange resins, appears to play an important role in additional other applications of macroporous styrene-divinylbenzene copolymers such as in carriers of immobilised enzymes, supports of heterogenised homogeneous catalysts, column packings for gas chromatography and the like.

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