

## SORPTION OF ETHYL ACETATE ON SOME MACRORETICULAR RESINS

R. KOMERS and D. TOMANOVÁ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, Prague - Suchbát*

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The sorption of ethyl acetate has been investigated both on the styrene-divinylbenzene copolymer and on the same copolymer containing following functional groups:  $-\text{SO}_3\text{H}$ ,  $-\text{P}(\text{OH})_2$ ,  $-\text{PO}(\text{OH})_2$  and  $-\text{CH}_2\text{Cl}$ . The apparatus used for the measurements was of the McBain balance type with quartz helical springs. The specific surface areas of the individual sorbents were determined. The adsorption isotherms of ethyl acetate were measured at 20, 70, 120 and 150°C. The values of the monolayer, adsorption heats and adsorption coefficients of ethyl acetate were calculated. Further, the areas corresponding to the acidic adsorption centre were determined. It was found that its value did not change with the type of the functional group mentioned above. The results achieved suggest the existence of two types of sorption on the acidic ion exchangers.

In connection with the investigation of the transesterification reaction of organic esters using macroreticular ion exchangers as catalysts which was carried out in our group<sup>1</sup>, it was found to be necessary to know the nature and the extent of the sorption of ethyl acetate on the ion exchangers of the same type used in the reaction kinetics studies. For this reason the adsorption isotherms of ethyl acetate were measured both on the styrene-divinylbenzene copolymer and the same copolymer containing various functional groups. The temperature range of the measurements was chosen to be as nearly the same as when it is used in the kinetic experiments and also with the regard to the chemical stability of the adsorbents.

Similar study was also carried out by Herrman<sup>2</sup> who investigated the sorption of water, ethanol, acetic acid and ethyl acetate on the sulfonic acid resin Dowex 500.

## EXPERIMENTAL

*Chemicals.* Ethyl acetate (reagent grade product, Lachema, Brno) was dried with anhydrous magnesium sulphate and purified by multiple rectification before use. Its purity was checked by gas-chromatographic analysis. After rectification air and other possible gases absorbed in the product were eliminated by repeated condensation and expansion in vacuum. This operation was carried out in the presence of metallic sodium. The apparatus used was described earlier<sup>3</sup>.

Macroreticular styrene-divinylbenzene copolymer (S) and macroreticular sulfonic acid resin (S-S) prepared from S were commercial products of the Research Institute for Synthetic Resins and Lacquers, Pardubice. The skeleton of both compounds was cross-linked with 25% of divinylbenzene. The ion exchanger containing  $-\text{P}(\text{OH})_2$  groups (S-P) was prepared by the reaction

of the primary copolymer S with  $\text{PCl}_3$  and by hydrogenolysis of the resulting product, the ion exchanger with  $-\text{PO}(\text{OH})_2$  functional groups (S-PO) was synthesised from the compound S-P by oxidation with nitric acid in the cold. The procedure for the preparation of both ion exchangers was taken from the literature<sup>4</sup>. The styrene-divinylbenzene resin containing  $-\text{CH}_2\text{Cl}$  groups (S-C) was synthesised again from the copolymer S according to the procedure described earlier<sup>5</sup>. Ion exchangers S-P, S-PO and S-C were prepared by Jeřábek from our Institute in connection with the utilisation of these compounds for the reaction kinetics studies. With all the resins in question the elemental analysis was carried out and the specific surface areas were determined<sup>6</sup> (nitrogen adsorption at  $-195^\circ\text{C}$ ). The results are summarised in Table I.

TABLE I  
Specific Surface Areas and Composition of Resins

| Resin | Area<br>$\text{m}^2/\text{g}$ | % C   | % H  | % S   | % P   | % Cl  |
|-------|-------------------------------|-------|------|-------|-------|-------|
| S     | 129                           | 91.33 | 7.88 | —     | —     | —     |
| S-S   | 51                            | 58.63 | 5.35 | 13.92 | —     | —     |
| S-P   | 104                           | 60.53 | 5.95 | —     | 13.56 | —     |
| S-PO  | 27                            | 58.94 | 5.91 | —     | 13.06 | —     |
| S-C   | 130                           | 77.05 | 6.67 | —     | —     | 14.40 |

*Apparatus and Procedure.* The adsorption measurements were performed gravimetrically using the quartz fibre sorption balance of McBain<sup>7</sup> of the usual design. The quartz spring had one hundred coils of 20 mm in diameter and the thickness of the quartz fibre was 300  $\mu$ . The sensitivity of the spring was  $3.70 \pm 0.06$  mg per 1 mm. The design of the apparatus made possible measuring six samples of adsorbent in one run<sup>8</sup>. The changes in the adsorbent weight were followed by cathetometer.

First of all 0.2–0.3 g of sorbents were evacuated at  $100^\circ\text{C}$  till the constant weight was reached. Under continuing evacuation the temperature was increased to  $125^\circ\text{C}$  and maintained steady till the weight reached the constant value again. The first and the second evacuations took 37 and 21 hours respectively. Finally the temperature was increased up to  $150^\circ\text{C}$  and the evacuation was completed under given conditions. Additional 22.5 hours were necessary to reach the constant values of the sorbent weights. The pressure was measured with McLeod gauge during evacuation. The vacuum amounted to  $1 \cdot 10^{-3}$  Torr.

When this operation had finished the adsorption isotherms of ethyl acetate were measured at 20, 70, 120 and  $150^\circ\text{C}$  in the conventional way. Between measuring individual isotherms the adsorbents were regenerated by pumping at  $150^\circ\text{C}$  till the weight reached the same value as before the adsorption started. This period took 24 hours. The vacuum attained was close to  $1 \cdot 10^{-3}$  Torr. The desorbed gas was collected by evacuating the system through a liquid nitrogen trap and analysed by a gas chromatograph. In all the cases only pure ethylacetate was found.

## RESULTS AND DISCUSSION

First of all we investigated the stability of the used resins during the evacuation at elevated temperature depending on time. We ascertained that all the resins in question were stable enough also at 150°C and showed only a small loss of weight. After evacuation at 150°C for 81 hours it was 5.6, 9.3, 5.2, 6.9 and 4.2% respectively for S, S—S, S—P, S—PO and S—C and no other change was observed. We can suppose that no decomposition of adsorbents takes place under the given conditions and the loss of the weight is predominantly caused by the desorption of water and some gases.

*Adsorption Isotherms and Isobars*

The different behaviour of ethyl acetate on the sulfonic acid resin (S—S) is evident from the results achieved. While the sorption of ethyl acetate on the other four adsorbents decreases with the temperature in the expected way, the ion exchanger S—S shows the maximum of the adsorbed amount at 70°C in the pressure range from 0 to 12 Torr, as it is apparent from Fig. 1. Besides, the temperature dependence of the sorption is the smallest on this sorbent (Fig. 2). With this sorbent the isobars at higher pressures (Fig. 3) have the descending course with the increasing temperature similarly to those of the other four ion exchangers. Our results concerning the sorption of ethyl acetate on the sulfonic acid resin (S—S) are not in accord with the observations of Herrman<sup>2</sup> who has not found a measurable sorption of ethyl acetate on this resin. This fact can be explained by a constant moisture content in the resin during his adsorption measurements.

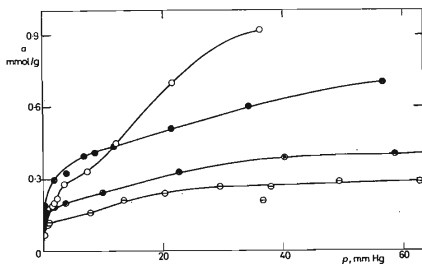


FIG. 1

Adsorption Isotherms of Ethyl Acetate on the Resin S—S

○ 20°C; ● 70°C; ◻ 120°C; ◻ 150°C.

TABLE II

The Ethyl-Acetate Monolayer and the Area of the Active Centre on the Investigated Resins, the Amount of the Occupied Functional Groups and the Results of the Titration in Aqueous Medium

| Resin  | S     | S-S   | S-P   | S-PO  | S-C   |
|--|-------|-------|-------|-------|-------|
| BET:   |       |       |       |       |       |
| $a_m$ , mmol/g                                   | 0.839 | 0.656 | 0.608 | 0.602 | 0.856 |
| Langmuir:  |       |       |       |       |       |
| $a_m$ , mmol/g                                   | —     | 0.666 | 1.446 | 0.582 | 1.417 |
| $a_s^a$ , mmol/m <sup>2</sup>                    | —     | 0.013 | 0.014 | 0.021 | 0.011 |
| $\text{\AA}^2$ <sup>b</sup>                      | —     | 12.8  | 12.0  | 15.4  | 15.2  |
| % of the occupied functional groups <sup>c</sup> | —     | 15.3  | 33.0  | 6.9   | 34.9  |
| meq./g <sup>d</sup>                              | —     | 2.2   | 2.8   | 7.2   | —     |

<sup>a</sup>Adsorbed amount related to the surface area unit; <sup>b</sup>the area of the active centre; <sup>c</sup>these values were calculated when relating the values of the Langmuir monolayer on the total number of the functional groups calculated from the elemental analysis (Table I); <sup>d</sup>the results of the titration of the ion exchangers in aqueous medium with 0.1M-NaOH volumetric solution.

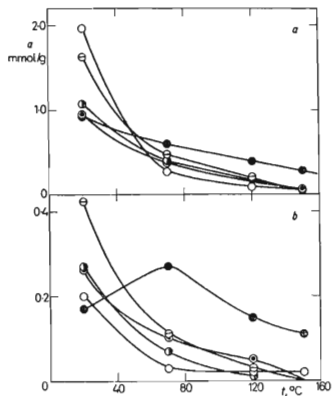


FIG. 2

Adsorption Isobars of Ethyl Acetate *a*) at 36 Torr, *b*) at 1 Torr

○ S; ● S-S; ◐ S-P; ⊙ S-PO; ⊖ S-C.

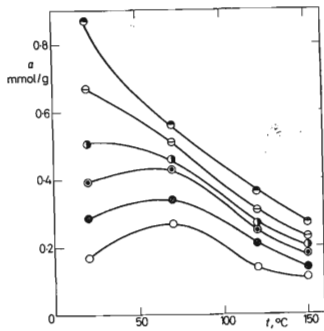


FIG. 3

Adsorption Isobars of Ethyl Acetate on the Resin S-S

○ 1; ● 4; ◐ 10; ◑ 14; ⊖ 20; ⊙ 30 Torr.

In order to correlate the experimental data the following equations were applied: Temkin<sup>9</sup> Eq., Freundlich<sup>10</sup> Eq., BET<sup>11</sup> and Langmuir<sup>12</sup> Eq., the latter being used both in the simple form and the modified one for the dissociative adsorption<sup>13</sup>. The Temkin equation was found unsatisfactory for isotherms measured on any resin and at any temperature used. Better correlation was achieved according to Freundlich equation; the isotherms on resin S, S—S and S—C and those measured on S—PO and S—P fitted its linear form at 20 and 70°C respectively. The isotherms measured at higher temperatures deviated from the linear course with increasing temperature. However, they did not tend to one point in any case. The linearisation according to the BET-equation could be applied for isotherms measured at 20 and 70°C on all investigated resins. The linear course was fitted at 20°C in the usual range of the relative pressures ( $x = 0.05-0.35$ ); at 70°C  $x = 0.04-0.09$  because the design of the apparatus did not permit work at higher pressures. The values of the ethylacetate monolayer corresponding to the individual resins were calculated by means of the BET-equation, the results are given in Table II.

An attempt was also made to use the Langmuir equation for the linearisation of the experimental data. The isotherms measured on all investigated resins did not fit a linear course at any temperature, if plotted according to simple Langmuir relation ( $p/a$  vs  $p$ ). We have succeeded in plotting the experimental points according to the equation for the dissociative adsorption

$$1/a = 1/a_m + (1/\sqrt{b}) a_m (1/\sqrt{p}), \quad (1)$$

where  $a$  is the adsorbed amount,  $a_m$  is the amount corresponding to the monolayer,  $b$  is the adsorption coefficient and  $p$  is the equilibrium pressure. This correlation provided linear dependence in all cases as it is shown in Fig. 4. The deviations from the linear course were ascertained with the resin S—S at 120°C and in a way with the resin S—C at 70 and 120°C. In these cases the deviated points belonged to the lower pressures. This fact can be explained on the basis of the used manner of plotting where considerable emphasis is put on the points corresponding to the low pressures<sup>14</sup>. It may be of interest to notice that with the resin S—P, S—PO and S—C (Fig. 4b, c, d) the linearised isotherms (1) at all temperatures cut the ordinate in one point which gives the reciprocal value of the monolayer. This fact points to the temperature independence of the monolayer on the sorbents mentioned above. A similar effect can be also observed with the resin S—S (Fig. 4a), however the straight line for 20°C does not tend to the common point. The monolayer values calculated by the Langmuir equation are given in Table II. With the styrene-divinylbenzene copolymer (resin S) the linearisation according to Eq. (1) was apparently also satisfactory, however the calculated monolayer values possessed the negative mark. For this reason the relation (1) has no physical meaning in this case.

Therefore, in our further considerations only the value of the monolayer calculated by BET-equation was used for the resin S. This value is in good agreement with that of the resin S—C. Contrary to both mentioned resins the values of BET-monolayers are a little lower for the resins containing acidic groups. The monolayer values for all investigated ion exchangers were calculated by the Langmuir equation derived for the dissociative adsorption.

Comparing the results obtained by the equations (1) and BET we can observe very good agreement between the monolayer values of ion exchangers S—S and S—PO, whereas the values for the S—P and S—C calculated by the Langmuir equation are approximately double than those calculated by the BET method. The values of the ethyl-acetate monolayer obtained by the Langmuir equation for the dissociative adsorption were recalculated on the unit of the surface area of sorbents. The surfaces given in the Table I were used for the calculation. Good agreement among the adsorbed amounts corresponding to the surface area unit is shown in the Table II.

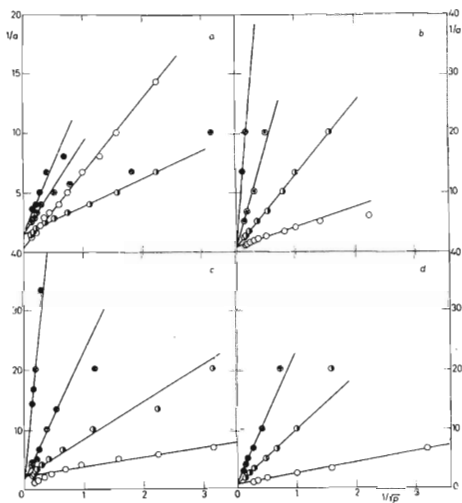


FIG. 4

Adsorption Isotherms of Ethyl Acetate Expressed by the Langmuir Equation  
 a S—S; b S—PO; c S—P; d S—C. ○ 20°C; ◐ 70°C; ⊙ 120°C; ● 150°C.

The resins S—S, S—P and S—C adsorb practically the same number of mmol of ethyl-acetate on the surface area unit, this value however, is double for the resin S—PO. A possible explanation is that the functional groups of the three former resins have the monobasic acid nature while the  $\text{PO}(\text{OH})_2$ -group behaves as a dibasic acid<sup>15</sup>. If the value for S—PO is divided by two the result is consistent with those corresponding to the other ion exchangers again. Therefore, we were authorised to calculate the active centre area corresponding to the individual resins (Table II) the mean value of which is  $\sigma = 13.8 \text{ \AA}^2$  with the relative error of 13.7%.

The fraction of the functional groups occupied by the ethyl-acetate molecules is different for the individual resins as it is also shown in Table II. This fact can be explained in such a way that the percentage of the occupied centres is dependent on the surface area which was changed due to the different chemical operations performed to introduce the functional groups into unsubstituted skeleton of the resin S. Moreover, the data given in Table I and II show that this percentage is directly related to the surface area of the corresponding ion exchangers. The results obtained by titrating the resins in liquid medium (Table II) are not consistent with the values of monolayer from the adsorption measurements. The explanation appears to lie in partial swelling the ion exchangers in liquid medium which enables the penetration of the titration reagent to the larger amount of the acidic groups than in the gas phase. The results denote that the percentage of the acidic groups which are accessible from the gas phase is probably affected by the resin porosity.

### Heats of Adsorption

The isotherms measured at several temperatures were used for the calculation of the isosteric adsorption heats according to the Clausius–Clapeyron equation. The adsorption heats were plotted *versus* the surface coverage (Fig. 5). Starting from  $\theta = 0.24$  the experimental points for the resins S, S—P, S—PO and S—C lie practically on one straight line and the change of the surface coverage has a negligible effect on the heat of adsorption. This fact indicated that the use of the Langmuir equation was substantiated. The rapid increase of the  $q$ -values on the resins S—PO and S—C can be observed with the decrease of  $\theta$  in the region lower than  $\theta = 0.24$ .

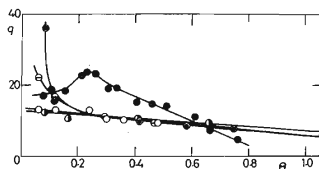


FIG. 5  
Dependence of  $q$  (Isoster.) upon  $\theta$   
○ S; ● S—S; ● S—P; ⊙ S—PO; ⊕ S—C.

This is most probably due to the heterogeneity of their surface at very low coverage. The completely different behaviour of the sulfonic acid resin (S—S) is evident from the Fig. 5. In the region of the lower coverage the  $q$ -value increases up to  $\Theta = 0.24$  and the maximum appears on the curve. Then the line decreases almost linearly showing a considerably steeper slope compared with those observed with the other resins. Owing to the fact that the adsorption heats corresponding to  $\Theta = 0.24$  or lower surface coverage were calculated from the points of the adsorption isobars close to their maximum (Fig. 3), the sorption seems to be highly improbable to reach the equilibrium state<sup>16</sup> in this region. Therefore the meaning of the adsorption heat cannot be ascribed to the values measured at the lower surface coverage (up to  $\Theta = 0.24$ ). Fig. 5 can be also used for the relative comparison of the measure of the adsorbate interactions with the adsorbent surface. Plotting  $q$  vs  $\Theta$  for the resin S, S—P, S—PO and S—C practically the same tangents of the straight part are found (approximately  $\Delta q/\Delta\Theta = 7$  kcal/mol), while the slope is roughly fivefold for the ion exchanger S—S ( $\Delta q/\Delta\Theta = 34$  kcal/mol). The  $q$ -value concerning the four mentioned resins extrapolated to  $\Theta = 1$  is 7 kcal/mol. Very good agreement can be observed comparing this value with the data of the evaporation heats found in the literature<sup>17</sup> (8.6, 7.8, 6.9 and 6.3 kcal/mol respectively at 20, 70, 120 and 150°C).

TABLE III

The Adsorption Coefficients of Ethyl Acetate on the Investigated Resins

| Resin | The value of $b$ ( $\text{mm}^{-1}$ ) at the temperature |        |        |        |
|-------|--|--------|--------|--------|
|       | 20°C   | 70°C   | 120°C  | 150°C  |
| S—S   | 0.0041   | 0.4120 | 0.0392 | 0.0166 |
| S—P   | 0.0380   | 0.0033 | 0.0004 | 0.0001 |
| S—PO  | 0.9821   | 0.0724 | 0.0067 | 0.0003 |
| S—C   | 0.1406   | 0.0059 | 0.0010 | —      |

The adsorption coefficients of ethyl-acetate on the resins S—S, S—P, S—PO and S—C were calculated from the Eq. (1). The results are listed in Table III. As it was expected their values decrease with the increasing temperature and became almost zero at 150°C. A different behaviour can be observed with the ion exchanger S—S again. While the smallest value of the adsorption coefficient was found at 20°C it was significantly higher at 70°C showing a descending tendency with further temperature increase.





The temperature dependence of the adsorption coefficients  $b$  was employed for calculating the adsorption heats of ethyl acetate on all investigated resins

$$b = b_0 \exp [-\Delta H/RT]. \quad (2)$$

Excellent agreement was achieved not only among the individual values of the adsorption heat calculated for all resins containing functional groups but also between those values and  $q$ -value corresponding to  $\Theta = 0.24$  (Fig. 5). In all the cases  $\Delta H$  found was 11.5 kcal/mol. Moreover, this value is identical with that of adsorption heat ( $q = 13.5$  kcal/mol) obtained from the plot in Fig. 5 by extrapolating  $q$  to zero surface coverage (with the exception of the resin S—S). With the resins S—PO and S—C the points deviating from the linear course were neglected from  $\Theta = 0.24$ . It is of interest that  $\Delta H$  of ethyl acetate on the resin S—S possesses also the value of 11.5 kcal/mol in spite of the different adsorption course and of the slope of  $q/\Theta$  (Fig. 5). The chemisorption is supposed to play a predominant role on this ion exchanger at a lower coverage. Calculating  $\Delta H$  from the adsorption coefficients the  $b$ -value at 20°C did not fit the linear dependence and therefore it was omitted.

From the results obtained some conclusions can be drawn. The shape of the adsorption isobars indicates two different kinds of the adsorption of ethyl acetate on the ion exchanger S—S. This fact seems to be also proved both with the anomalous course of the  $q$ - $\Theta$ -dependence and with the dependence of the adsorption coefficient upon the temperature. With the ion exchanger S—S the chemisorption is more likely to play a role at the surface coverage lower than  $\Theta = 0.24$ , while the physical adsorption is predominant at higher coverage. However, with the other resins rather the physical adsorption was observed. This fact is evident from the adsorption heats obtained. With regard to the physical adsorption the effect of chemisorption comes to the expression to a relatively smaller extent (at coverages to  $\Theta = 0.24$ ; see higher  $q$ -values in this region). The chemisorption cannot be considered in connection with the resin S because the Eq. (1) used is lacking the physical meaning in this particular case.

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