JOURNAL OF CATALYSIS 30, 343-349 (1973)

# Adsorption of Weak Bases from the Gas Phase on Organic Ion Exchangers

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Received June 30, 1972

The adsorption of dimethyl ether and tetrahydrofurane has been investigated at 150°C on macroreticular ion exchangers of the styrene-divinylbenzene type containing $-SO_3H$, $-PO(OH)_2$ or $-P(OH)_2$ groups. Dual site adsorption without dissociation is suggested on the basis of the analysis of adsorption isotherms and the investigation of the effect of the number of acid groups on the initial adsorption values. The adsorption coefficients found can be used to express the acid strength of the ion exchangers interacting with gaseous molecules at elevated temperature; the relative logarithmic values for the ion exchangers, respectively, with $-SO_3H$, $-PO(OH)_2$ and $-P(OH)_2$ groups were 0; $-1.64$; and $-2.51$ (from dimethyl ether adsorption). These results are consistent with those calculated from ethyl acetate adsorption [Komers and Tomanová, *Collect. Czech. Chem. Commun.* **37**, 774 (1972)]. On the basis of the adsorption data, the relative basicities of the adsorbed molecules could also be compared.

## INTRODUCTION

Styrene–divinylbenzene copolymers containing acid substituents have been used in our Laboratory as models of solid catalysts with equivalent active centers in several kinetic studies (*1–4*). With these catalysts it is useful to know two main quantities by means of which the catalyst acidity can be expressed: the number of the acid centers and their, at least relative, acid strength. The determination of these quantities performed in the liquid medium [as, e.g. (*5*, *6*)] need not necessarily be valid for the dry ion exchangers when they catalyze reactions of gaseous reactants. In the present work an attempt has been made to determine the acid strength of the functional groups of the organic ion exchangers by means of the adsorption of bases from the gas phase; in order to achieve a well-defined difference in the adsorbing power of the various ion exchangers such as those containing $-SO_3H$, $-PO(OH)_2$ and $-P(OH)_2$ groups, the use of weak bases is preferable. Using dimethyl ether and tetrahydrofurane as well as the previous data (*7*) concerning the adsorption of ethyl acetate, we have tried to test the capability of the method.

## NOMENCLATURE

| | |
|---|---|
| A | adsorbate |
| $A_1$, $A_2$ | fragments formed by dissociative adsorption of the substance A |
| $c_A$, $c_{A_1}$, $c_{A_2}$ | surface concentrations (mmol/g) of the adsorbed substance A and the fragments $A_1$ and $A_2$, respectively |
| $c_l$, $c_{l_2}$ | concentration (mmol/g) of free active centers, of the corresponding type |
| $c_L$ | total concentration of active centers, i.e., of acidic functional groups of ion exchanger (mmol/g) |
| $c_L^0$ | total concentration of all functional groups of |

| | |
|---|---|
| | ion exchanger (acidic and neutralized) (mmol/g) |
| $K_A$ | adsorption coefficient of the substance A ($Torr^{-1}$) |
| $K'_A$ ($= K_A s$) | experimental adsorption coefficient of the substance A adsorbed according to the model c ($Torr^{-1}$) |
| $K'_{A,0}$ ($= K_A s^0$) | experimental adsorption coefficient of the substance A adsorbed according to the model c on the original ($c_L = c_L^0$) ion exchanger containing the acidic groups only ($Torr^{-1}$) |
| $l$ | vacant active center |
| $l_2$ | vacant dual adsorption site consisting of two adjacent active centers |
| $p_A$ | partial pressure of the substance A (Torr) |
| rel | relative value |
| $Q$ | sum of squared deviations of the measured adsorbed amount from that calculated according to the corresponding model |
| $s$ | number of acidic groups in the neighborhood of a given center in a distance appropriate for a dual site adsorption of the substance A |
| $s^0$ | total number of functional groups (acidic and neutralized) in the appropriate distance from a given center |

## EXPERIMENTAL METHODS

### *Materials*

Dimethyl ether (reagent grade, 99.8%, Fluka AG, Buchs SG, Switzerland) was degassed repeatedly in a liquid nitrogen trap before use. Tetrahydrofurane (reagent grade, VEB Laborchemie, Apolda, GDR), was repeatedly distilled, degassed and dried using sodium bis(2-methoxyethoxy)aluminum hydride; the apparatus used was described earlier (*8*). Sulfonated macroreticular styrene–divinylbenzene copolymer (S) (25% divinylbenzene) was a commercial product of the Research Institute for Synthetic Resins and Lacquers, Pardubice, Czechoslovakia. By partial neutralization of the sulfonic groups with potassium hydroxide the ion exchangers containing 73.5% (0.75 S) and 32.5% (0.35 S) of the original acid groups were prepared (*4*). According to previous work (*4, 9*) we can assume that the distribution of the potassium ions in the polymer mass is uniform and that the surface concentration of $-SO_3H$ groups is proportional to their bulk concentration. The surface area (of about 55 $m^2/g$) and the pore size distribution of the sulfonated ion exchangers were not affected by the neutralization degree (*10*). The preparation of the other sorbents with $-PO(OH)_2$ groups (PO) and with $-P(OH)_2$ groups (P) and the properties of all the sorbents used have been described elsewhere (*4, 10*). Pore size distribution measurements revealed that the prevailing pore radius of the macroreticular ion exchangers used was of about 100–170 Å.

### *Apparatus and Procedure*

The measurements of dimethyl ether adsorption were performed at 150°C in a standard volumetric apparatus as described before (*10*). With the ion exchangers PO, P and 0.75 S the adsorption was measured up to the equilibrium pressures of about 30 Torr, while with the ion exchangers S and 0.35 S the highest pressure used was 500 Torr. In the latter case, the sample was then evacuated by a diffusion pump for 24 hr at 25°C and a new isotherm was taken at 150°C; the difference between the two isotherms was considered to correspond to the strong adsorption [see e.g. (*11*)]. The adsorption of tetrahydrofurane was measured gravimetrically using a quartz spring balance of the McBain type at 150°C; the measurements were made up to the pressures of 16 and 36 Torr, respectively. The apparatus was described in a previous paper (*7*).

## RESULTS AND DISCUSSION

In the interpretation of the experimental data, three different models were used (all of them assuming equivalence of the active groups in each ion exchanger): (a) the Langmuir concept of the single site adsorption without dissociation leading to the isotherm equation (1):

$$c_A = c_L K_A p_A/(1 + K_A p_A), \qquad (1)$$

(b) the concept of dual site adsorption involving total dissociation of the molecule defined by Eq. (2):

$$A(g) + 2l \rightleftarrows A_1(ads) + A_2(ads). \qquad (2)$$

In the case of dissociation into two unequal fragments [probable with organic molecules, see also (12)] the equation of the isotherm becomes (3):

$$c_{A_1} = c_{A_2} = c_A = c_L(K_A p_A)^{1/2}/[1 + 2(K_A p_A)^{1/2}]. \qquad (3)$$

(c) the concept of the dual site adsorption without dissociation of the molecule [see also (*13*)] which is less commonly used:

$$A(g) + l_2 \rightleftarrows A(ads). \qquad (4)$$

In this case, we can derive from the equilibrium equation $K_A = c_A/p_A c_{l_2}$ [if we accept that $c_{l_2} = c_l(s/2)(c_l/c_L)$; see (*14*)] and from the active sites balance the isotherm Eq. (5):

$$c_A = 2\,K_A s p_A c_L/[1 + (1 + 4\,K_A s p_A)^{1/2}]^2 = 2\,K'_A p_A c_L/[1 + (1 + 4\,K'_A p_A)^{1/2}]^2, \qquad (5)$$

where $K'_A = K_A s$.

Using Eqs. (1), (3) and (5) we first treated the data concerning dimethyl ether strongly adsorbed on the sulfonated ion exchangers S and 0.35 S at pressures up to 500 Torr. The results obtained by nonlinear regression (*15*) indicated that the overall range of the surface coverage cannot be unambiguously interpreted by any of the above-mentioned simple concepts. Therefore, the initial adsorption data up to 20 Torr corresponding to the surface coverage of about 0.2 were treated separately. As is evident from Fig. 1 and Table 1 good agreement was achieved between the calculated and experimental results with the models a and c whereas model b assuming the dissociative adsorption could be rejected. A similar statistical evaluation of adsorption data on tetrahydrofurane measured on the ion exchangers S, PO and P up to the surface coverage of 0.2–0.3 revealed the preference of the models a and c and the nonsuitability of the model b again (Table 1).

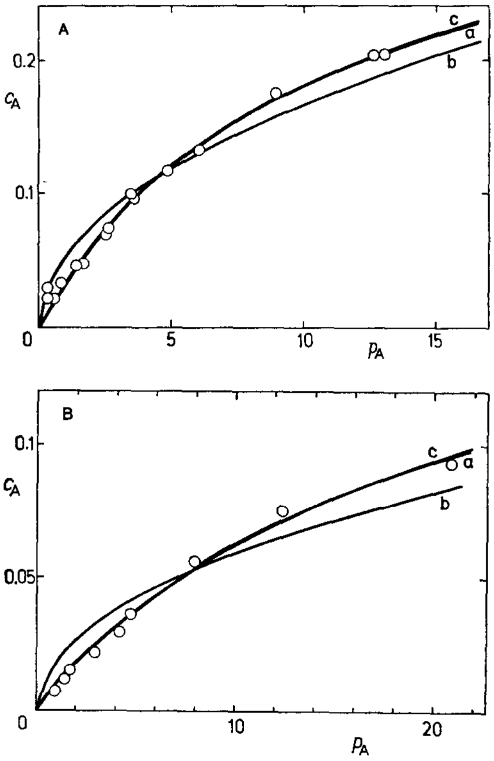

FIG. 1. Adsorption isotherms of dimethyl ether on ion exchanger S (A) and 0.35 S (B) at 150°C. The points represent experimental values ($c_A$ in mmol/g; $p_A$ in Torr), the curves are calculated for models (a), (b) and (c) according to Eqs. (1), (3) and (5), using the optimum values of constants obtained by nonlinear regression method of experimental data.

The discrimination between the two well-fitting models a and c (both assuming either single or dual site adsorption without dissociation) could not be made on the basis of adsorption isotherm analysis only. However, measuring the adsorption on the ion exchangers with varying number of sulfonic groups made the discrimination possible. Only the data concerning the initial surface

TABLE 1

NONLINEAR EVALUATION OF THE SUITABILITY OF THE ADSORPTION MODELS USED[a]

| | Values of the sum of squared deviations $Q$ in the adsorption of | | | | |
|---|---|---|---|---|---|
| | Dimethyl ether on ion exchangers | | Tetrahydrofurane on ion exchangers | | |
| Model | S | 0.35 S | S | PO | P |
| a | $2.68 \times 10^{-1}$ | $2.81 \times 10^{-2}$ | $3.81 \times 10^{-3}$ | $5.38 \times 10^{-4}$ | $1.88 \times 10^{-3}$ |
| c | $2.60 \times 10^{-1}$ | $3.41 \times 10^{-2}$ | $4.51 \times 10^{-3}$ | $6.34 \times 10^{-4}$ | $2.24 \times 10^{-3}$ |
| b | $14.53 \times 10^{-1}$ | $38.5 \times 10^{-2}$ | $8.90 \times 10^{-3}$ | $13.65 \times 10^{-4}$ | $3.60 \times 10^{-3}$ |
| $Q_{crit}$ | $4.22 \times 10^{-1}$ | $6.6 \times 10^{-2}$ | $8.05 \times 10^{-3}$ | $11.37 \times 10^{-4}$ | $3.97 \times 10^{-3}$ |

[a] The models for which the sum of squared deviations $Q$ is higher than the critical value of this quantity $Q_{crit}$ (calcd for 95% probability level) can be rejected *(15)*.

coverage were taken into account, i.e., the tangents of the initial part of the adsorption isotherms* $dc_A/dp_A$. From Eqs. (1) and (5) for $p_A \rightarrow 0$ and differentiating with respect to $p_A$ it can be written:

for the single site adsorption

$$dc_A/dp_A = K_A c_L = K_A c_L{}^0 (c_L/c_L{}^0), \quad (6)$$

and for the dual site adsorption without dissociation

$$dc_A/dp_A = K_A s c_L/2 = K'_A c_L/2. \quad (7)$$

If the neutralization decreasing the number of active groups is supposed to take place uniformly in the whole ion exchanger mass *(4, 16)*, then the $s$ value expressing the number of active sites present in an appropriate distance from a given center will linearly decrease with the relative number of the acidic groups

$$s = s^0 (c_L/c_L{}^0). \quad (8)$$

Inserting (8) in (7) and rearranging it we arrive at

$$\begin{aligned} dc_A/dp_A &= (K_A s^0 c_L{}^0/2)(c_L/c_L{}^0)^2 \\ &= (K'_{A,0} c_L{}^0/2)(c_L/c_L{}^0)^2. \quad (9) \end{aligned}$$

If we plot log $(dc_A/dp_A)$ versus log $(c_L/c_L{}^0)$ the value of the slope of the logarithmic dependence should distinguish between the models a and c [see Eqs. (6) and (9)]. Its value read from Fig. 2 for tetrahydrofurane is 2.08 (1.76 ÷ 2.36, if we take into account the relative mean error in determining $dc_A/dp_A$) and proves the preference of the dual site to the single site model. With the adsorption data of dimethyl ether the value 1.7 (1.34 ÷ 1.95) of the slope was obtained, which suggested that the adsorption on more than one site is more likely to take place again.

The above treated concepts, a, b, and c, express only the fundamental adsorption models differing in the number of the sorbent sites interacting with one molecule

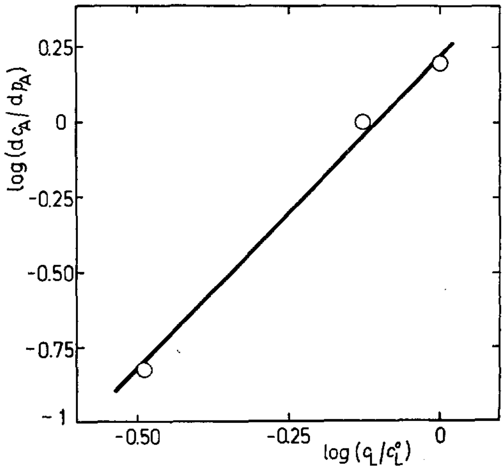

FIG. 2. Plot of the initial values of the tangents of tetrahydrofurane adsorption isotherms at 150°C vs relative concentration of acidic groups of sulfonated ion exchangers.

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* The relative mean error of determination of the initial tangent of adsorption isotherms (when measured repeatedly) was ±0.24 for the most active ion exchanger S; for the less active ones the relative error was lower (e.g., ±0.1 for the ion exchanger 0.35 S).

of the sorbate and the assumption as to whether this molecule is dissociated or not during adsorption. The chemical nature of the adsorbed complex is not described by these models and to each of them several very different molecular mechanisms may correspond; their discussion, however, is beyond the scope of the present work. It should only be pointed out that the dual site adsorption of the ether or tetrahydrofurane molecule which proved to be the most probable model is feasible even though these molecules contain only one basic center, i.e., an electron-donating oxygen atom, since another part of the molecule may act as electron acceptor. There is some evidence for such a donor–acceptor model of adsorption on ion exchangers involving hydrogen bond formation, e.g., from alcohol dehydration and ir studies [cf. (*4*, *17*)].

From the validity of Eq. (9) it follows that the adsorption coefficient $K'_{A,0}$ is independent of the neutralization degree of the ion exchanger (i.e., of the presence of potassium ions); this proves the assumption of the uniformity of active sites. A similar independence of adsorption coefficient was found while investigating the *tert*-butanol dehydration kinetics on the same ion exchanger series (*4*).

The adsorption isotherms both of dimethyl ether and tetrahydrofurane corresponding to the initial surface coverage on ion exchangers S, PO and P differing in acid strength enabled us to calculate the adsorption coefficient values $K'_A$ $(= K_A s)$ using Eq. (7). They are listed in Table 2 together with the values for ethyl acetate calculated from the data measured previously (*7*). The value $c_L = 1.145$ mmol/g determined for the ion exchanger S from the dimethyl ether adsorption was used in this calculation. The values for PO and P were obtained from the value for S ion exchanger by correcting it with respect to different surface area using the ratios of the $c_L$ values obtained for S, PO and P ion exchangers from ethyl acetate adsorption (*7*).

The values of the equilibrium adsorption constants of a basic compound should represent a measure of the acid strength of the functional groups in the ion exchangers series. This relatively expressed scale of acid strength should remain the same when various bases are used. As can be seen from Table 2 this expectation is fulfilled fairly well with the pair dimethyl ether–ethyl acetate. Slighter differences in the relative values of adsorption coefficients, particularly in the values for the P and PO ion exchangers were found with tetrahydrofurane. Nevertheless, the order of the acid strength remains qualitatively the same. The deviation in the relative $K'_A$ values for tetrahydrofurane might be due to a different molecular mechanism of adsorption though the basic adsorption model is the same as for dimethyl ether (cf. preceding paragraphs).

For practical purposes, the logarithmic scale of the relative acid strength presented in Table 3 is more suitable. It is immediately clear from Table 3 that the difference between the scales obtained using the two molecules is negligible. An attempt was made to confront this order of the acid strength with the dissociation constant

TABLE 2

VALUES OF ADSORPTION COEFFICIENTS $K'_A$ OF DIMETHYL ETHER, TETRAHYDROFURANE AND ETHYL ACETATE AT 150°C ON ION EXCHANGERS OF DIFFERENT ACID STRENGTH CALCULATED ACCORDING TO EQ. (7)

| Ion exchanger | Dimethyl ether | | Tetrahydrofurane | | Ethyl acetate (7) | |
|---|---|---|---|---|---|---|
| | $K'_A$(Torr$^{-1}$) | $K'_{A,rel}$ | $K'_A$(Torr$^{-1}$) | $K'_{A,rel}$ | $K'_A$(Torr$^{-1}$) | $K'_{A,rel}$ |
| S | $(8.7 \pm 2.1) \times 10^{-2}$ | 1.0 | $2.7 \pm 0.67$ | 1.0 | $(2.1 \pm 0.5) \times 10^{-1}$ | 1.0 |
| PO | $(2.0 \pm 0.40) \times 10^{-3}$ | 0.023 | $(2.0 \pm 0.48) \times 10^{-1}$ | 0.074 | $(4.0 \pm 0.82) \times 10^{-3}$ | 0.019 |
| P | $(2.7 \pm 0.46) \times 10^{-4}$ | 0.0031 | $(1.6 \pm 0.36) \times 10^{-1}$ | 0.059 | $(8.0 \pm 1.3) \times 10^{-4}$ | 0.0038 |

TABLE 3

Logarithmic Scale of Relative Acid Strength of the Ion Exchangers S, PO and P

| Ion exchanger | $-\log K'_{A,rel}$ | |
|---|---|---|
| S | 0 | |
| PO | 1.64[a] | 1.72[b] |
| P | 2.51[a] | 2.42[b] |

[a] Determined from dimethyl ether adsorption.

[b] From ethyl acetate adsorption (*7*).

values published both for the inorganic and the organic acids relating to the functional groups of the ion exchangers under study. The most frequently reported values of p$K$ for phosphoric and phosphorous acids obtained by comparable methods are 2.1 and 2.0, respectively (*18, 19*); for phenylphosphoric and phenylphosphorous acids the most recently reported values (*20*) are 1.90 and 1.54, respectively. The order of acid strength $P^{III} > P^{V}$ resulting from these values, though they are fairly close to each other, is different from that in Table 3. This, however, does not seem surprising if we take into account the rather different conditions of the adsorption measurements and the different chemical structure of the acids in the styrene–divinylbenzene ion exchanger. A direct potentiometric determination of the acidity of the ion exchangers S, PO and P (*4, 16*) led to the same acid strength sequence as shown in Table 3. It is worth mentioning that the kinetic data of *tert*-butanol dehydration in the gaseous phase (*4*) on the same ion exchanger series led to the activity sequence identical with the order of acid strength S > PO > P and that straight-line dependence was achieved by plotting the logarithm of the rate constant vs the acid strength scale from Table 3.

The adsorption measurements of different bases on acidic ion exchangers allowed us to compare their relative basicity under the conditions used. In spite of some anomalous behavior of tetrahydrofurane, the order of the adsorption coefficient values (Table 2) remained always as follows: tetrahydrofurane > ethyl acetate > dimethyl ether. The results, e.g., for the ion exchanger S, led to the following values of relative basicity for the mentioned series of compounds: 31:2.4:1 (corresponding to 2.5:1.4:1 in the relative p$K$ scale). This order is consistent with the p$K$ values found in the literature (*21*) for tetrahydrofurane and dimethyl ether (in relative values 2.75 and 1). The p$K$ value of ethyl acetate cannot be involved for comparison because it was determined by a different method (*22*).

## Conclusions

Two aspects of the present study should be emphasized:

1. The possibility to vary the number of active sites in a controlled manner offered by the ion exchangers can be made use of in elucidating some adsorption mechanism problems; it may also serve for similar purposes in kinetic studies of catalytic reactions (*4, 17*).

2. The adsorption of weak bases from the gas phase can be used to characterize the acidity of substituted organic polymers at elevated temperatures. The results of this study were used for correlating kinetic data of some gas phase reactions catalyzed by ion exchangers with their acid strength (*4, 23, 24*).

## Acknowledgments

The authors thank Dr. K. Setínek, Dr. K. Jeřábek, and Mr. Z. Prokop for kindly supplying the ion exchangers and for helpful discussions concerning their adsorption and kinetic properties. The assistance of Mrs. J. Aunická in carrying out the experimental part of this work is greatly appreciated.

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