

CHROM. 6695

A CONTRIBUTION TO THE MEASUREMENT OF ADSORPTION ISOTHERMS BY THE PULSE CHROMATOGRAPH TECHNIQUE

J. VOLF, J. KOUBEK and J. PAŠEK

Department of Organic Technology, Prague Institute of Chemical Technology, Prague (Czechoslovakia)

(Received February 26th, 1973)

SUMMARY

The pulse chromatograph technique was applied to the measurement of adsorption isotherms in systems that involve large adsorbed amounts and some "irreversible" adsorption. The assumptions necessary for successful measurement were verified. A method that permits direct calibration on strongly sorbing sorbent was developed. The adsorption isotherms of aliphatic amines on cobalt and alumina were measured over a wide temperature range and the isosteric heats of adsorption were calculated.

INTRODUCTION

The pulse chromatograph technique is often used in the measurement of adsorption isotherms because of its speed and the simplicity of the apparatus required¹⁻³. In the derivation of the relationships involved²⁻⁵, a series of assumptions were made without sufficient attention being devoted to their verification in the applications of this technique. The pulse chromatograph technique was used in the present work to investigate the systems cobalt-aliphatic amines and γ -alumina-aliphatic amines. Both systems are notable for the high degree of adsorption together with some "irreversible" adsorption, which give rise to difficulties in the application of this technique in the calculation of adsorption isotherms, calibration of the detector and in maintaining isothermal conditions in the sorbent bed. In limiting the effect of diffusion phenomena, it is advisable to use conditions of measurement such that the concentration gradient is small (low feed amount and sufficiently long columns). It is not possible to fulfil both conditions together in the systems that we studied. Increasing the amount of sorbent led to increases in "irreversible" adsorption and in the minimum feed amount required, so that it was necessary to work with relatively high feed amounts. It was necessary to test the influence of all disruptive effects under these conditions and to attempt to eliminate them.

EXPERIMENTAL

Apparatus

The apparatus used for the measurement of adsorption isotherms did not differ in principle from the usual chromatographic equipment. The katharometer with direct gas flow in the cell was placed in a thermostat and its temperature was maintained at 98° for all measurements. The glass column in which the sorbent was placed was heated to the desired temperature in an electrically heated glass jacket. This arrangement permitted regeneration of the sorbent surface at high temperatures (260° for cobalt and 450° for alumina). In measuring adsorption isotherms on alumina, a column of I.D. 8 mm and length 600 mm, filled with *ca.* 0.6 g of sorbent, was used. In the case of cobalt, the middle section of the column was widened to 12 mm I.D. and filled with *ca.* 7 g of cobalt. The remaining volume in both instances was filled with glass beads. The detector signal was registered on a linear recorder, Type EZ-3 (Laboratorní přístroje, Prague).

Materials

Amines used in measurements were the commercial products distilled to a purity of at least 99.9%. Alumina was prepared by the standard method used in our laboratory⁶. Pure metallic cobalt was prepared as follows. A boiling solution of $\text{Co}(\text{NO}_3)_2$ was treated with a saturated solution of $(\text{NH}_4)_2\text{CO}_3$, and the resulting precipitate was washed thoroughly with distilled water, collected on a filter and dried at 120°. The carbonate was calcined for 4 h at 450°. The Co_3O_4 obtained was pelletized, crushed and graded by sieving. The weighed amount of Co_3O_4 placed in the sorption column for the individual experiments was reduced with hydrogen for 2 h at 260°. Under such conditions, all of the Co_3O_4 was converted into pure metal. Helium used in the measurements on alumina was purged of oxygen with a liquid purifier⁷ before input and dried with a molecular sieve (Nalsit 4A). Hydrogen used in the measurements on cobalt was catalytically purified of oxygen on an industrial cobalt catalyst. The alumina had a total surface area of 180 m²/g and the cobalt 12 m²/g (determined chromatographically).

THEORETICAL

Problems in the calculation of adsorption isotherms and calibration of the detector

The method of calculating adsorption isotherms is based on the relationship between the shape of the chromatographic peak and the adsorption isotherm. In the application of chromatographic techniques to systems involving strong adsorption, considerable tailing occurs. In the sorption of aliphatic amines on cobalt and alumina, interaction between sorbate and sorbent is very strong and gives rise to marked tailing and some "irreversible" adsorption. A considerable amount of the amine remains firmly bonded on the surface and can be removed only by washing with carrier gas for an infinite period of time or by increasing the temperature. Tailing and "irreversible" adsorption also give rise to problems in calibration of the detector. A typical chromatogram for diethylamine on alumina is given in Fig. 1. It is evident from the mass balance that the area of the chromatographic peak accounts for only a part of the feed. The tail, the exact evaluation of which is impossible, contains an

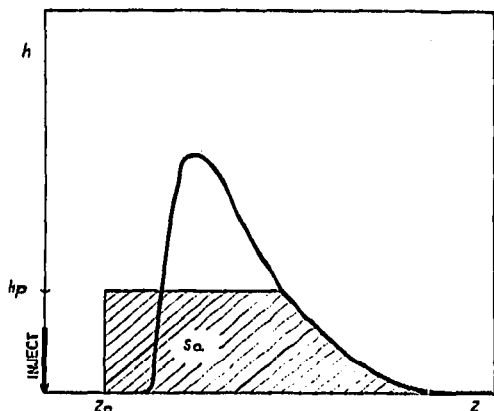


Fig. 1. Typical chromatogram of diethylamine on alumina. h = Pen deflection, Z = chart distance or time, S_a = area corresponding to adsorbed amount at partial pressure p , h_p = pen deflection corresponding to p , Z_0 = position of peak maximum of non-adsorbed inert gas.

amount of "irreversibly" bonded sorbate (for diethylamine on alumina, 0.2–0.4 mmole/g). This effect also complicates the calibration procedure because similar problems are encountered in obtaining the area of the calibration peak. Dollimore *et al.*¹ solved this problem by using a suitable column packing on which the sorbate tails to a lesser extent. This procedure permits calibration of the detector under the given conditions (flow of carrier gas, type of sorbate and, when a heat conductivity detector is used, its temperature). Problems related to the finding of a suitable packing for amines and to the maintenance of all of the conditions mentioned, or their exact knowledge in using the calibration graph, led us to the establishment of a calibration method that can be executed directly on a strongly adsorbing sorbent.

The principle of this simple calibration is evident from Fig. 2. The shape of the elution peak (more exactly, of the rear of the peak) is given by the adsorption

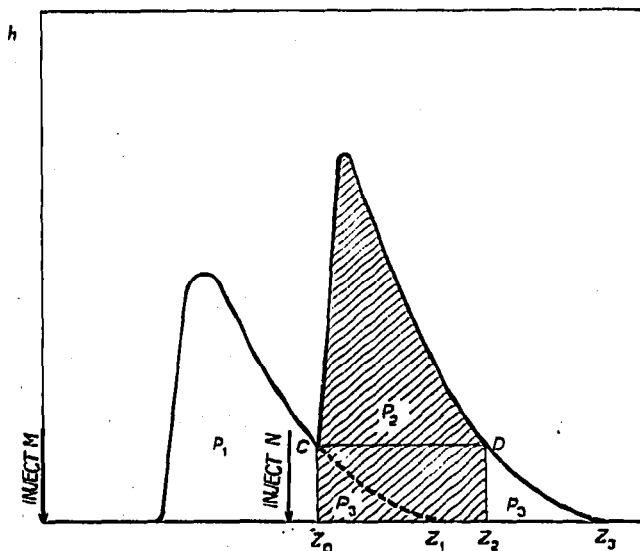


Fig. 2. Evaluation of calibration peak area.

isotherm and is therefore independent of the amount of feed. On this assumption, curves $C-Z_1$ and $D-Z_3$ have the same shape. An arbitrary amount of sorbate ($M \mu\text{l}$), greater than the "irreversibly" adsorbed amount to which area $P_1 + P_3$ corresponds, is injected on to the column. Before washing is completed, a known amount ($N \mu\text{l}$) is injected. The area under both elution peaks corresponds to the total feed $M + N$:

$$M + N = k(P_1 + P_2 + P_3) \quad (1)$$

Similarly, M also corresponds to the area under the first elution peak:

$$M = k(P_1 + P_3) \quad (2)$$

Subtracting eqn. 2 from eqn. 1 yields

$$N = k P_2 \quad (3)$$

The shaded area P_2 therefore corresponds to feed N . The advantage of this method lies in the fact that point D can be found with much greater accuracy than point Z_3 (or Z_1). The proportions of Fig. 2 do not exactly illustrate the true chromatogram. In reality, point Z_3 (or Z_1) lies at a much greater distance along the z axis. Fig. 2 also demonstrates the dependence of peak height on the state of the sorbent surface at the moment of injection. The chromatogram shown was obtained for $M = N$ where the first amount of sorbate, M , was injected on to the clean sorbent surface.

We used the following process (equivalent to that used by Dollimore *et al.*¹) in order to determine the area of the elution peak after injection on to a clean surface.

We evaluated the peak area only to a certain distance z_n (beyond which partial pressure, h_n , cannot be measured with sufficient accuracy) and calculated the remainder of the tail (area S_t) knowing the feed amount (F_e) and area S_k corresponding to the calibration feed amount (F_k). For area S_t :

$$S_t = \frac{F_e}{F_k} \cdot S_k - S_p \quad (4)$$

The area S_p is evaluated from the elution peak with great accuracy (as far as a known value of $z = z_n$). A series of areas S_{zn} (see Fig. 1) and hence a series of adsorbed amounts corresponding to various heights (partial pressures) is calculated such that a series of areas S_{pn} (areas bounded by the straight lines $z = z_0$, $h = h_n$, $z = z_n$ and the tail of the peak, point z_0 being given by the position of the peak maximum of non-adsorbed inert gas) is first obtained and then added to S_z .

Discussion of the factors that affect measurements, and their elimination

In deriving relationships for use in calculations, certain assumptions were made whose maintenance is a condition for successful measurement. It is assumed that: the sorbent bed is isothermal; equilibrium is immediately established between the gaseous and solid phases; the effects of axial mixing and external diffusion are negligible. Suitable experimental procedures permit the fulfilment of these conditions. Isothermal operation is an obvious condition for measurement. Temperature is usually measured with a thermocouple placed outside the column, since placing a well directly into the sorbent bed may lead to difficulty in maintaining plug-flow conditions of the carrier gas. Before the actual measurement of adsorption isotherms on cobalt, it was found by inserting the thermocouple into the sorbent bed that there

is no rise in temperature on feeding triethylamine during the adsorption-desorption process. Alumina, which sorbs about ten times more amine, behaved in a different manner. Orientation experiments showed a rise of 12° (diethylamine, $t = 230^\circ$). Heat exchange could not be improved by decreasing the column diameter, as this would require elongation of the sorbent bed, resulting in increased temperature gradient and pressure drop. Improved heat exchange was achieved by diluting the sorbent with crushed glass of the same mesh size. A 1:5 dilution of the sorbent with glass was chosen, with which the maximum temperature rise was 2.3° . The time dependence of temperature in the sorbent bed was measured by means of a linear recorder (Fig. 3). The temperature rise was dependent neither on carrier gas flow-rate (in the range 30–100 ml/min) nor on the measurement temperature (in the range 150 – 230°). The temperature measured outside the column was then corrected by $+1.1^\circ$ (value given by the position of the centre of the area under the graph of time dependence of the temperature in the sorbent bed).

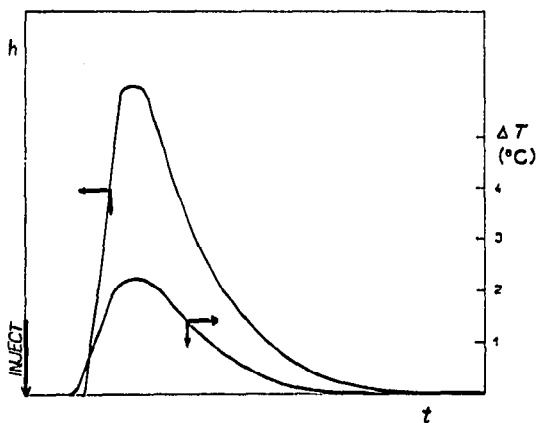


Fig. 3. Time dependence of temperature in sorbent bed (diluted alumina) with corresponding chromatogram. Sorbate, diethylamine; $t = 230^\circ$.

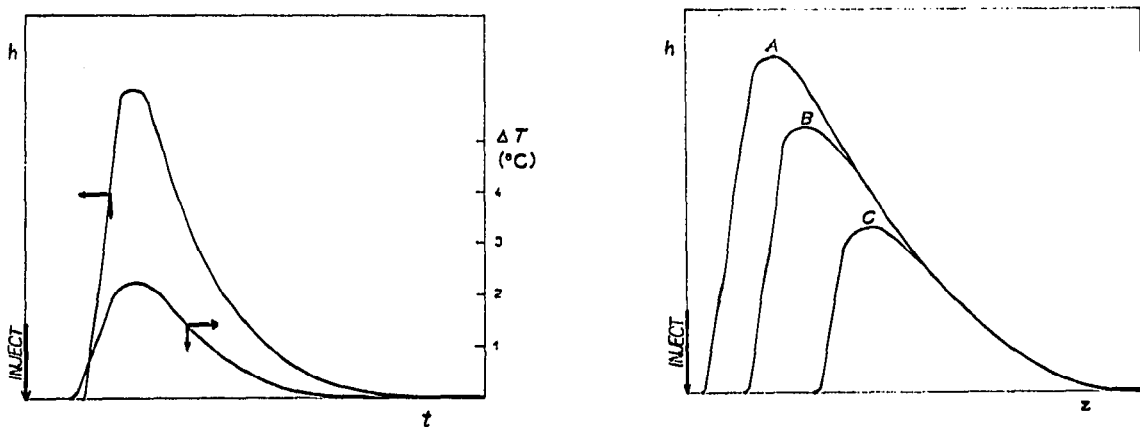


Fig. 4. Effect of amount of feed on measured adsorption isotherm. Feed of diethylamine: A, $19 \mu\text{l}$; B, $16 \mu\text{l}$; C, $12 \mu\text{l}$.

The effect of the mode of packing of the alumina-glass mixture on the measured adsorption isotherm was also investigated. In the first case the column was filled with a homogeneous mixture, and in the second with alternate thin layers of glass and alumina. Adsorption isotherms measured for each case did not differ within the limits of experimental error.

The effect of the amount of feed on the adsorption isotherm, for which the shape of the rear of the peak is decisive, was also studied. It can be seen from the chromatograms in Fig. 4 that the adsorption isotherm is independent of the pulse size. A certain deviation from the characteristic shape occurs at the maximum of the elution peak, where disruptive diffusion effects evidently have the greatest effect. For this reason, adsorption isotherms were calculated only from the lower two-thirds of the peak area. Adsorption isotherms measured on various amounts of sorbent did not differ within the limits of experimental error.

The choice of a suitable carrier gas flow-rate has a direct bearing on the effect of the external diffusion, axial mixing and the maintenance of equilibrium between the gas phase and the surface of the sorbent. For maintaining this equilibrium, the lowest possible flow-rate is most suitable. At low flow-rates, however, axial diffusion begins to exert a disruptive effect. Bechtold⁸ made a graphical correction for axial diffusion by assuming that it has the same value at the front of the peak as at the rear of the peak at each concentration level. In our work, the deviation of the front of the peak from the perpendicular to the z axis gradually decreased with increasing flow-rate to the value given by the resultant of the maximum rate of pen movement (vector \vec{R}) and the chart speed (vector \vec{P}). At flow-rates greater than 30 ml/min, the resultant of vectors $\vec{R} + \vec{P}$ coincided with the front of the peak (see Fig. 5). The deviation of the front of the peak was therefore not caused by the effect of axial diffusion but was given by the recorder characteristics. That external and internal diffusion do not operate at flow-rates of 34–112 ml/min is shown by the independence of the measured adsorption isotherms on the flow-rate (see Fig. 6). This independence shows also the great rapidity with which equilibrium is established. At flow-rates less than 30 ml/min, the disruptive effects of diffusion phenomena began to come into play.

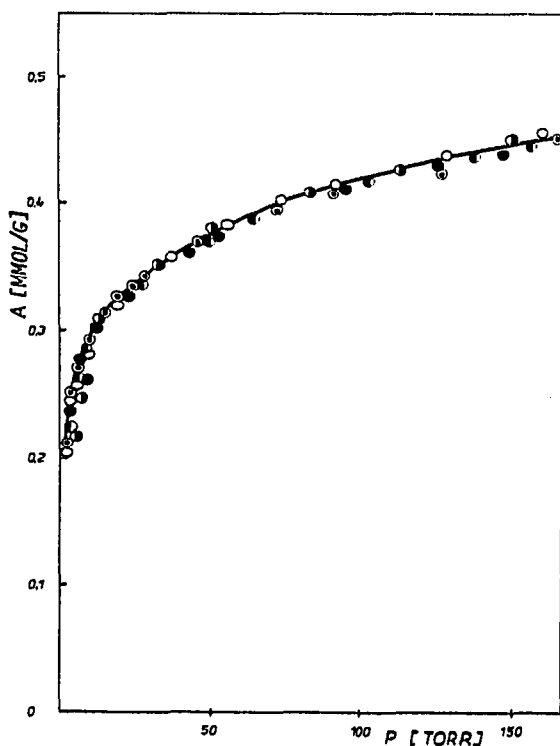
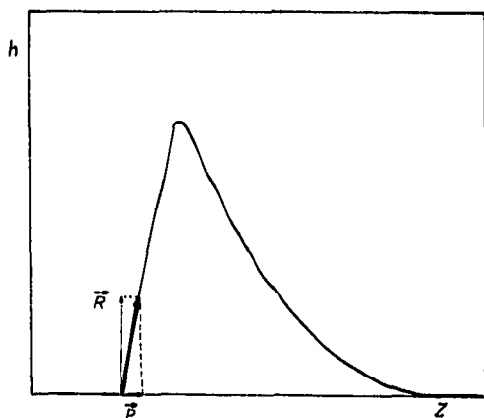


Fig. 5. Deviation of the front of the peak.

Fig. 6. Effect of flow-rate on adsorption isotherms. Flow-rate (ml/min): ●, 22.3 (adsorption isotherm corrected by the given method⁸); ○, 34.4; ○, 58.0; ●, 80.7; ⊙, 112.7 (for the last four the adsorption isotherm was calculated without correction).

By using the given correction for axial diffusion, it was possible to obtain results the same as those at higher flow-rates where this correction is not made (Fig. 6).

Adsorption isotherms were measured using different alumina particle sizes (0.2–0.4 and 0.4–0.6 mm) in order to establish the effect of internal diffusion. The agreement of the calculated adsorption isotherms confirms that internal diffusion does not affect measurement.

In addition to these factors, the experimental arrangement of the entire apparatus may affect the measurement. In work with the pulse technique, great importance is attached to the speed with which the measurement system reacts to concentration changes in the carrier gas. For this reason, the heat conductivity detector with a diffusion or semi-diffusion arrangement of the cell is not suitable for this technique. In this work, a katharometer with direct gas flow in the cell was used⁹.

Part of the procedure involved in measuring adsorption isotherms is the preparation of the surface of the sorbent. Since it is not advantageous, for experimental reasons, to work always with unused sorbent, surface regeneration is necessary. The method of surface regeneration by washing for an extended period of time without increasing the flow-rate, used by Dollimore *et al.*¹, considerably decreases the main

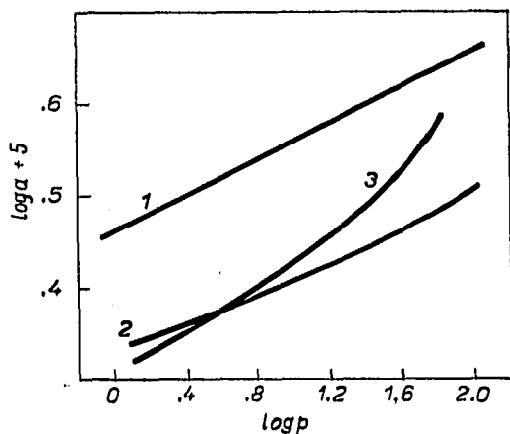


Fig. 7. Adsorption isotherms of (1) ethylamine, (2) diethylamine and (3) triethylamine on cobalt at 58° (p is expressed in torr, α is adsorbed amount expressed in moles/g of sorbent).

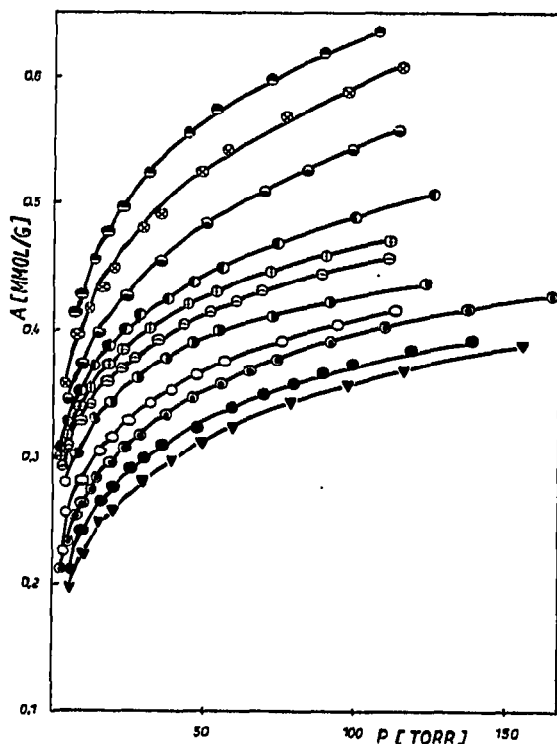


Fig. 8. Adsorption isotherms of diethylamine on alumina. Temperature (°C): \ominus , 130.0; \otimes , 148.5; $\omin�$, 163.7; \bullet , 177.3; \oplus , 185.5; $\omin�$, 198.5; \bullet , 207.0; \circ , 246.5; \odot , 262.1; \bullet , 283.5; \blacktriangledown , 302.5. (A is adsorbed amount expressed in mmoles/g of sorbent).

advantage of this technique, *i.e.*, speed. For the sorption of amines on cobalt and alumina, this method cannot be used because of "irreversible" adsorption. Regeneration is best carried out at higher temperatures as far as the catalyst character permits. In our work, cobalt was regenerated in a flow of hydrogen (30 min, $t = 260^\circ$) and alumina in a flow of air (30 min, $t = 450^\circ$). No amine fragments remained on surfaces so treated and the measurement of adsorption isotherms was reproducible. Further regeneration had no effect on the measured adsorption isotherms.

RESULTS

Fig. 7 gives the adsorption isotherms of ethyl-, diethyl- and triethylamines on cobalt at 58° . Fig. 8 shows the adsorption isotherms of diethylamine on alumina in the temperature range $130\text{--}300^\circ$. It is evident that the adsorption isotherms do not pass through the origin because of "irreversible" adsorption. Similarly, the adsorption isotherms of triethylamine on cobalt were measured in the range $58\text{--}110^\circ$. In both instances the temperature ranges had an upper limit owing to the occurrence of amine decomposition reactions on the sorbents. In the range of reversible adsorption, the dependence of the isosteric heat of adsorption on surface coverage was calculated by means of the Clausius-Clapeyron equation (Figs. 9 and 10).

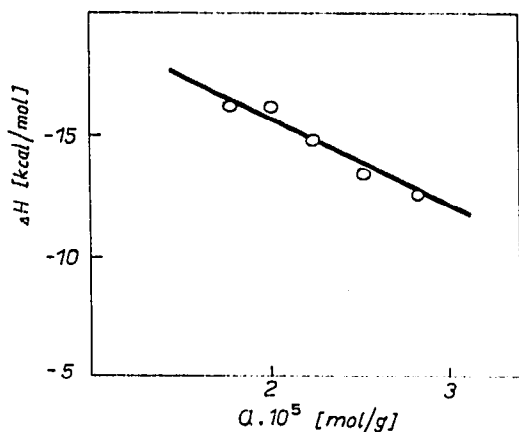


Fig. 9. Dependence of isosteric heat of adsorption of triethylamine on cobalt on surface coverage (α).

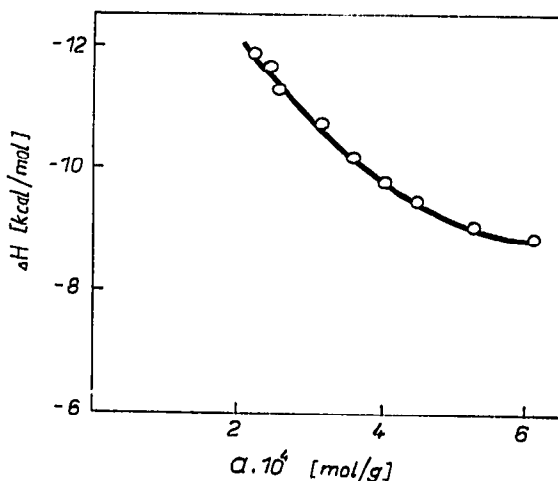


Fig. 10. Dependence of isosteric heat of adsorption of diethylamine on alumina on surface coverage (α).

CONCLUSION

The possibility of applying the pulse chromatograph technique to measuring the adsorption isotherms of strongly bonded sorbates with some "irreversible" adsorption has been verified. Satisfactory results can be obtained by using a suitable experimental arrangement and an appropriate choice of conditions.

REFERENCES

- 1 D. Dollimore, G. R. Heal and D. R. Martin, *J. Chromatogr.*, 50 (1970) 209.
- 2 A. Saint-Yrieix, *Bull. Soc. Chim. Fr.*, (1965) 3407.
- 3 H. Knözinger and H. Spannheimer, *J. Chromatogr.*, 16 (1964) 1.
- 4 H. W. Habgood, in E. A. Flood (Editor), *The Solid-Gas Interface*, Vol. II, Arnold, London, 1967, pp. 611-846.
- 5 A. A. Kiselev and Ja. J. Jashin, *Gazoadsorbciionnaja Chromatografija*, Izd. Nauka, Moscow, 1967, p. 104.
- 6 J. Pašek, *Collect. Czech. Chem. Commun.*, 28 (1963) 1007.
- 7 J. Tenygl, *Chem. Listy*, (1964) 573.
- 8 E. Bechtold, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 49.
- 9 H. Purnell, *Gas Chromatography*, Wiley, New York, 1962.