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Determination of heats of adsorption on graphite and on a microporous carbon black by gas–solid chromatography

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ABSTRACT

Isosteric heats of adsorption were determined by gas–solid chromatography using the adsorption isotherms of several organic compounds on graphite and on a microporous carbon black at different temperatures. For these compounds a linear relationship was found between heat of adsorption and molar refraction, which allowed a guide to be obtained in order to estimate heats of adsorption for many compounds. An increment method was used for the estimation of heats of adsorption on graphite also.

INTRODUCTION

Gas–solid chromatography is a very convenient and elegant method for the investigation of adsorption processes. It allows the rapid and precise measurement of thermodynamic adsorption characteristics, especially of adsorption isotherms, in order to determine heats of adsorption.

The use of non-porous non-polar adsorbents such as graphite provides an opportunity to study the nature of intermolecular adsorption interactions. The adsorbate molecules adsorb on such surfaces mainly due to dispersion interactions [1]. Kiselev and Jashin [1] and others (*e.g.*, Lopez-Garzon *et al.* [2]) found linear relationships between heats of adsorption and increments based on molecule-specific values such as polarizability, the number of carbon atoms in saturated hydrocarbons and the parachor on non-porous adsorbents.

The aim of this work was the experimental determination of heats of adsorption to obtain information on the possibilities of estimating of heats of adsorption on non-porous surfaces, using a relationship between heats of adsorption and an approximately additive value for the atoms and the bonds present in the molecule of the compound, and also using an increment method. A first attempt was made to transfer these results to a microporous adsorbent.

EXPERIMENTAL

The measurements were carried out on a Chromatron MGC 4000 gas chroma-

tograph with a flame ionization detector. Glass and stainless-steel columns 10–90 cm long and 2.5 mm I.D. were used. The carrier gas was nitrogen at flow-rates in the region 20–30 ml min⁻¹. The volume of samples injected was 0.5–2 μ l.

Natural graphite NFL (particle size 0.09–0.20 mm, BET surface area 2.4 m² g⁻¹, non-porous) and a microporous carbon black (particle size 0.04–0.20 mm, BET surface area 370 m² g⁻¹ and micropore size 0.14 cm³ g⁻¹) were used as adsorbents.

The adsorption isotherms of model compounds were determined for three temperatures in the range 303–623 K by the so-called method of "elution on a characteristic point", which was described in detail by Kiselev and Jashin [1] and Cremer and Huber [3]. This method is based on the determination of adsorption isotherms from a single chromatogram.

An example of adsorption isotherms of methylphosphonic acid dimethylester on graphite at 453, 473 and 523 K is shown in Fig. 1.

The linear dependence of $\ln p$ vs. $1/T$ for methylphosphonic acid dimethyl ester on graphite is shown in Fig. 2. The heats of adsorption were obtained for a surface coverage $a + 0.5 \mu\text{mol g}^{-1}$ for graphite NFL and $a = 50 \mu\text{mol g}^{-1}$ for carbon black.

Indirect proof of the reliability of the method is the agreement of the chromatographic value for the adsorption of ethane on graphite of 23 kJ mol⁻¹ with the value of 28 kJ mol⁻¹ obtained by a Monte Carlo method [4]. The mean error limit of the measured values is about 6 kJ mol⁻¹.

RESULTS AND DISCUSSION

The differential heats of adsorption, q , of 28 compounds with different chemical natures and structures were determined using natural graphite NFL and carbon black and the results are summarized in Table I.

Table I shows that the heats of adsorption on microporous carbon black are

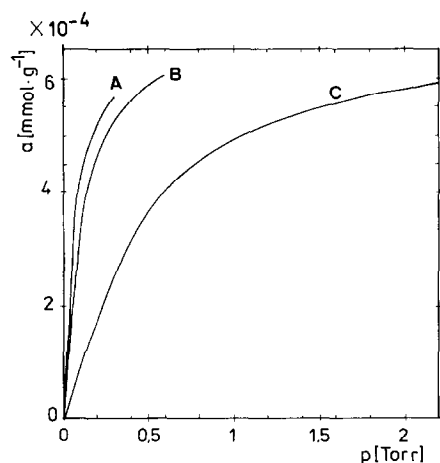


Fig. 1. Adsorption isotherms of phosphonic acid, methyl-dimethyl ester on graphite. Temperature: A = 453; B = 473; C = 523 K.

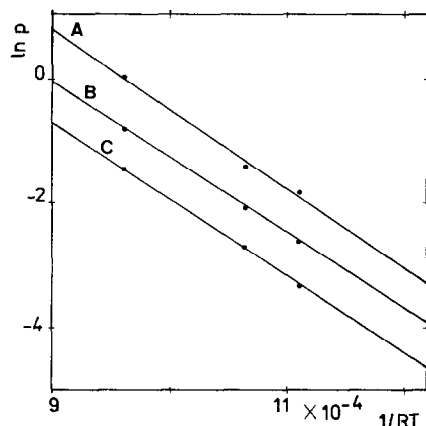


Fig. 2. Adsorption isotherms of phosphonic acid, methyl-dimethyl ester on graphite. A: $q = 51.5 \text{ kJ mol}^{-1}$, $2.015 \cdot 10^{-4} \text{ mmol g}^{-1}$; B: $q = 50.9 \text{ kJ mol}^{-1}$, $3.51 \cdot 10^{-4} \text{ mmol g}^{-1}$; C: $q = 52.9 \text{ kJ mol}^{-1}$, $5.005 \cdot 10^{-4} \text{ mmol g}^{-1}$.

TABLE I

RELATIONSHIP BETWEEN HEATS OF ADSORPTION, q , AND MOLAR REFRACTION, R

| Adsorbate | q (kJ mol ⁻¹) | | R (cm ³) |
|---|-----------------------------|-----------------|------------------------|
| | On graphite | On carbon black | |
| Phosphoric acid, trimethyl ester | 46.9 | | 27.8 |
| Phosphonothioic acid, methyl-O,O-dimethyl ester | 55.6 | | 34.5 |
| Phosphonic acid ethyl-diethyl ester | 56.9 | | 40.7 |
| Phosphoric acid, triethyl ester | 62.0 | | 41.8 |
| Phosphoric acid, tributyl ester | 98.0 | | 69.6 |
| Phosphoric acid, triphenyl ester | 101.3 | | 86.5 |
| Phosphonic acid, methyl-dimethyl ester | 51.5 | | 26.2 |
| Methanol | 21.8 | 42.3 | 8.2 |
| Acetone | 36.4 | 58.2 | 15.6 |
| Dimethyl sulphide | 45.0 | | 19.1 |
| 2-Ethylethanethiol | 48.6 | | 19.2 |
| Benzene | 48.1 | 74.1 | 26.2 |
| Nitrobenzene | 55.7 | 118.5 | 32.9 |
| <i>n</i> -Heptane | 57.8 | 72.9 | 34.6 |
| <i>o</i> -Xylene | 56.1 | | 35.8 |
| <i>n</i> -Nonane | 54.8 | 107.6 | 43.8 |
| <i>n</i> -Nonanol | 63.2 | | 45.0 |
| Dibutyl sulphide | 68.7 | | 47.2 |
| Ethane | 22.6 | | 11.4 |
| <i>n</i> -Heptanol | 56.1 | | 36.1 |
| Phosphoric acid triamide hexamethyl | 67.8 | | 47.7 |
| Phosphorothioic acid, O,O,O-triethyl ester | 68.2 | | 49.3 |
| 2-Butylbutanethiol | 62.4 | | 37.9 |
| Acetic acid | | 43.5 | 13.0 |
| Ethanol | | 42.3 | 13.0 |
| Diethyl ether | | 53.6 | 22.3 |
| Pyridine | | 67.1 | 24.1 |
| Toluene | | 81.2 | 31.1 |

1.5–2 times higher than those obtained on non-porous graphite NFL. This difference is explained by the microporous structure of the carbon black.

As has been pointed out, we tried to find a linear relationship between the heats of adsorption and an incrementable molecule-specific value, in form of the molar refraction, R . R is, to a first approximation, independent of temperature and physical state. For many organic compounds R is approximately additive for the bonds present in the molecule. The results are shown in Fig. 3. There is a significant correlation between q and R . A similar behaviour was observed with both adsorbents. These simple relationships may be written in the following form:

$$q = 21.097 + 0.984R; r = 0.961 \text{ (graphite NFL)}$$

$$q = 20.088 + 2.041R; r = 0.874 \text{ (microporous carbon black)}$$

where r is the correlation coefficient. These equations may be used to estimate heats of adsorption if the molar refraction is known. For the parachor, a plot similar to Fig. 3 was obtained.

The second method for estimating heats of adsorption is based on the fact that the molar refraction, molecular weight, parachor and molar volume are additive values and can be split according to the composition and structure of chemical compounds. In accordance with Engewald *et al.* [5], the steric structure of molecules determines the adsorption energy.

According to Altenburg [6], it is therefore appropriate to correlate experimental data and values connected with the structure of the molecule using semi-empirical methods. We tried to split the heats of adsorption into increments. We concentrated on only a few increments: *e.g.* number of carbon, hydrogen, oxygen, sulphur, nitrogen, phosphorus and halogen atoms, number of covalent double bonds and number of six-membered rings. More than 20 experimental data for graphite and about 30

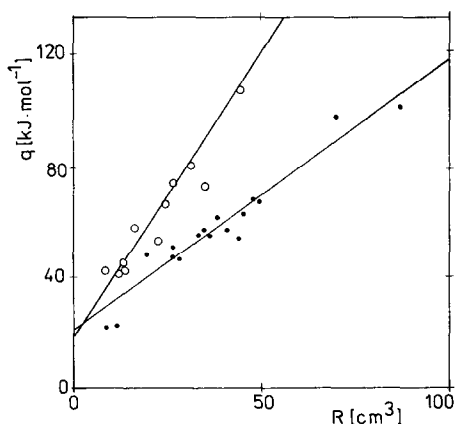


Fig. 3. Linear relationship between heats of adsorption, q , and molar refraction, R , for NFL (●) graphite and (○) microporous carbon black. Graphite NFL: $q = 21.097 + 0.984R$ ($r = 0.961$). Microporous carbon black: $q = 20.088 + 2.041R$ ($r = 0.874$).

TABLE II
REGRESSION COEFFICIENTS OF HEATS OF ADSORPTION INCREMENTS
Significance level 95%.

| Parameter | Value |
|--------------------------------------|----------------|
| x_0 | 17.3 ± 3.8 |
| x_1 (No. of C atoms) | 2.8 ± 1.8 |
| x_2 (No. of H atoms) | 0.9 ± 0.8 |
| x_3 (No. of O atoms) | 3.2 ± 2.2 |
| x_4 (No. of S atoms) | 12.5 ± 4.9 |
| x_5 (No. of N atoms) | 4.0 ± 3.6 |
| x_6 (No. of P atoms) | 2.1 ± 7.8 |
| x_7 (No. of covalent double bonds) | -0.1 ± 2.6 |
| x_8 (No. of six-membered rings) | 4.1 ± 6.5 |
| x_9 (No of halogen atoms) | 1.1 ± 1.3 |

measured by Avgul and Kiselev [8] on graphite carbon black (GTCB) were used to get a representative data fund.

A multilinear regression analysis was carried out using a BASIC program [7]. The simple relationship may be written in the following form:

$$q = b_0 + \sum_1^{10} b_i x_i$$

Heats of adsorption increments resulting from the standardized regression coefficient are summarized in Table II. These results were compared with those obtained from experiments. Table III shows a good agreement of the experimentally obtained data with data obtained by the proposed method for some compounds.

TABLE III
COMPARISON OF EXPERIMENTAL AND CALUCLATED HEATS OF ADSORPTION ON GRAPHITE NFL

| Compound | Heat of adsorption (kJ mol^{-1}) | |
|---------------------------------|---|------------------|
| | Experiment | Increment method |
| Ethane | 22.6 | 28.4 ± 2.9 |
| <i>n</i> -Heptane | 57.8 | 51.4 ± 2.8 |
| <i>n</i> -Nonane | 54.8 | 60.8 ± 3.6 |
| Acetone | 36.4 | 34.4 ± 2.8 |
| <i>n</i> -Nonanol | 63.2 | 63.9 ± 3.8 |
| Benzene | 48.1 | 43.6 ± 3.0 |
| <i>o</i> -Xylene | 56.1 | 52.8 ± 2.8 |
| Nitrobenzene | 55.7 | 52.9 ± 6.4 |
| Phosphoric acid trimethyl ester | 46.9 | 48.7 ± 4.8 |
| Phosphoric acid triethyl ester | 62.0 | 62.5 ± 4.4 |
| Phosphoric acid tributyl ester | 98.0 | 90.3 ± 5.8 |
| Dimethyl sulphide | 45.0 | 40.9 ± 4.7 |
| Dibutyl sulphide | 68.7 | 68.6 ± 5.1 |

It is concluded that the proposed method can be used to estimate heats of adsorption using a data base of experimentally obtained values.

CONCLUSIONS

A linear correlation exists between heats of adsorption and the molar refraction on non-porous surfaces such as graphite and on a microporous carbon black. These data allow the estimation of heats of adsorption for many compounds.

It was found for non-porous adsorbents like graphite and GTCB that heats of adsorption are additive values. An increment method suitable for estimation of heats of adsorption using a data base of experimentally detected values has been demonstrated.

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