Physical Chemistry

L. D. Belyakova, A. V. Kiselev, N. V. Kovaleva

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

L. D. Belyakova, A. V. Kiselev, N. V. Kovaleva

Gas-Chromatographic Determination of the Energy of Hydrogen Bonding in Adsorption Layers

(Presented by Academician A. N. Frumkin on 26 III 1964)

In adsorption layers on nonpolar saturated surfaces, mutual hydrogen bonds form between molecules of alcohols, amines, and similar substances already at low surface coverages. As a result, the heats of adsorption measured in a calorimeter in such cases include both the energy of the nonspecific interaction of alcohol molecules with the surface—for example, with graphitized carbon black ([1,2])—and the energy of mutual hydrogen bonding between alcohol molecules. Thus, in a calorimeter one measures heats of adsorption that considerably exceed the heats of condensation, whereas a theoretical estimate of the energy of nonspecific ([3]) interaction of individual alcohol molecules with the basal face of graphite gives values substantially lower than the heats of condensation ([4]). Only in the case of adsorption of water on graphitized carbon black, when the surface coverage remains very small even at room temperature and at high relative pressures of water vapor, did the heats of adsorption measured in a calorimeter prove to be lower than the heats of condensation ([1,4]). In this connection, it was of great interest to determine experimentally the differential heats of adsorption of alcohols at such low surface coverages that the alcohol molecules still remain practically unassociated. For this purpose it is convenient to use the gas-chromatographic method, which makes it possible to work at very low surface coverages and high temperatures, i.e., precisely under conditions unfavorable for association of alcohol molecules on the surface through the formation of hydrogen bonds. Indeed, with the aid of this method ([5]), heats of adsorption of water and ammonia were found that are much lower than those determined in a calorimeter at high coverages and lower than the heats of condensation.

In the present work, the heats of adsorption of individual molecules of n-alkanes and n-alcohols on graphitized thermal carbon black were determined by the gas-chromatographic method, and the results were compared with calorimetric measurements and theoretically calculated values. The investigations were carried out using a Khrom-1 chromatograph with a flame-ionization detector and a steel column 6 mm in diameter and about 85 cm long. MT-3100° carbon black with a very homogeneous surface ([5–7]), kindly provided to us by U. R. Smith, K_ bot, USA, was used. The surface area of this carbon black, determined by BET from low-temperature adsorption of nitrogen, was $\simeq 7.6$ m^2/g. The car-

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

bon black was rolled into beads in a ball mill without addition of a binder ([5]). To pack the column, 15.0 g of sieved carbon-black beads of size 0.25–0.5 mm were taken. The flow rate of the carrier gas (nitrogen) in different experiments ranged from 30 to 60 ml/min. The retained volumes at different flow rates, but at identical temperatures, were well reproducible. Measurements were carried out in the temperature range from 70 to 200°C.

Figure 1 presents several typical chromatograms of *n*-hydrocarbons and *n*-alcohols on MT-3100° carbon black. The form of the chromatograms indicates suf-

the sufficient homogeneity of the surface of the soot being studied and the nonspecific nature of the adsorption. Using the formula given in ([8], [9]), the values of the specific retention volumes V_{R_g} were calculated from the chromatograms. The absolute values of the retention volumes were then determined

$$V_{R_s} = \frac{V_{R_g}}{s}, \quad (9)$$

where s is the specific surface area of the adsorbent. These quantities are physicochemical constants characterizing, at a given temperature, the nature of the interaction in the system adsorbate–basal face of graphite ([9]).

Fig. 1. Chromatograms of *n*-hexane (1), methanol (2), ethanol (3), *n*-propanol (4), *n*-butanol (5), and *n*-pentanol (6) on graphitized thermal soot MT-3100° at 140°.

Fig. 2. Dependences of $\lg V_{R_g}/T$ on thermal soot MT-3100° on the reciprocal absolute column temperature $1/T$ for methanol (1), ethanol (2), *n*-propanol (3), *n*-butanol (4), and *n*-pentanol (5).

Some of the values obtained for V_{R_s} for *n*-alkanes on soot MT-3100° are given in Table 1. The same table also gives the mean values of V_{R_s} for soots with different specific surface areas, graphitized near 3000°, obtained in ([10]) by introducing soot into the pores of an inert support and at somewhat higher coverages (using a catarometer). The data obtained in the present work agree well with the data of ([10]), which also indicates the homogeneity of the surface of all these soots and the weak adsorbent–adsorbate interaction for hydrocarbons at these coverages.

Table 1

Absolute values of retention volumes V_{R_s} (ml/m^2) on soot MT-3100° and on a series of soots graphitized near 3000°, studied in ([10])

Fig. 3

Figure 2: Fig. 3

Adsorbates	Soot MT-3100°	Soot MT-3100°	Soots graphitized near 3000° ([10])	Soots graphitized near 3000° ([10])
	100°	150°	100°	150°
n-C_5H_{12}	0.74	0.22	0.69	0.186
n-C_6H_{14}	3.10	0.58	3.09	0.61
n-C_7H_{16}	12.4	1.83	14.1	2.04

From plots of the dependence of the logarithms of the ratios of the retention volumes to the absolute column temperature on the reciprocal of this absolute temperature (Fig. 2), heats of adsorption were calculated, as in ([9]-[11]). Such a calculation gives the value of the differential isosteric heat of adsorption at zero coverage ([11]). The heats of adsorption calculated in this way were compared with values obtained by static (calorimetric and isosteric) methods, and also with values of potential adsorption energies calculated theoretically.

In Fig. 3 are given the values of the heats of adsorption of n-hydrocarbons and n-alcohols on the investigated soot MT-3100° and on a series of graphitized soots,

obtained by gas-chromatographic [10], calorimetric [1,6,12], and isosteric [13–16] methods, as well as the results of calculating the energy of nonspecific interaction of individual molecules with the basal face of graphite [4,17,18]. In the case of hydrocarbons the adsorbate-adsorbate interaction is nonspecific, owing to which the heat of adsorption increases

Fig. 3. Dependence of the differential heat of adsorption on graphitized carbon blacks near 3000° on the number of carbon atoms in the molecule.
a —For n-hydrocarbons. Heats of adsorption at low coverages determined: 1 —by static methods [6,12–16], 2 —[10] and 3 —(present work) by the gas-chromatographic method. 4 —theoretically calculated potential adsorption energies of individual molecules.
b —For n-alcohols. Heats of adsorption determined: 1 —calorimetrically [1] and 2 —by the gas-chromatographic method, 3 —theoretically calculated potential adsorption energies of individual molecules [4].

with increasing coverage slowly and approximately linearly, which makes it possible to extrapolate these values reliably to zero coverage [6,12]. In the case of alcohols such extrapolation is impossible, since at all surface coverages accessible in calorimetric measurements the heats of adsorption of alcohols already include the energy of mutual hydrogen bonding [1,2]. Accordingly, as can be seen from

Fig. 3a, in the case of hydrocarbons the results of calorimetric and isosteric determinations of the heats of adsorption coincide with the gas-chromatographic data. Moreover, all these values are close to the theoretically calculated energies of nonspecific adsorption. Owing to the absence of specific interactions [3] in liquid hydrocarbons, their heats of condensation are small and less than the heats of adsorption on carbon black [6,12]. In the case of alcohols (Fig. 3b), however, an entirely different picture is obtained. The heats of adsorption determined by the gas-chromatographic method are 4.8 kcal/mol lower than the calorimetric ones and are close to the theoretically calculated values of the energy of nonspecific adsorption of individual molecules of the corresponding alcohols on the basal face of graphite [1–4]. The heats of adsorption of alcohols on MT-3100° carbon black, determined by the gas-chromatographic method, are, in addition, considerably lower than the heats of condensation, in accordance with the fact that the heats of condensation of alcohols are high because of the specific interactions between their molecules in the liquid.

Such a sharp difference is connected, as indicated above, with the fact that gas-chromatographic determination of heats of adsorption is carried out at very low surface coverages, when the alcohol molecules have not yet mutually associated and are adsorbed on the carbon black surface as individual molecules. The difference in the values of the heats of adsorption determined calori-

tric method (including the association energy) and the gas-chromatographic method (adsorption of individual molecules), represents the association energy of alcohols on the surface of the adsorbent. In this case this energy is 4.8 kcal/mole (Fig. 3,b), which is practically entirely attributable to the energy of mutual hydrogen bonding.

Table 2

Adsorbate	$Q_{\text{cal}}(\theta = 0)$	$Q_{\text{g.c.}}(\theta = 0)$	$-\Phi$	$Q_{\text{cal}} - Q_{\text{g.c.}}$
iso-C_4H_9OH	12.8 (4)	9.1	8.3 (4)	3.7
sec.-C_4H_9OH	12.0 (4)	8.5	9.1 (4)	3.5
tert.-C_4H_9OH	10.6 (4)	8.0	8.3 (4)	2.4

Table 2 gives the values of the differential heats of adsorption of a series of isomeric butanols, also determined by calorimetric (Q_{cal}) and gas-chromatographic ($Q_{\text{g.c.}}$) methods: isobutanol (2-methylpropan-1-ol), secondary butanol, and tertiary butanol on graphitized thermal blacks, as well as the theoretically calculated adsorption energies of individual molecules ($-\Phi$).

From Table 2 it is evident that, as for normal alcohols, for isomeric alcohols the heats of adsorption determined by the gas-chromatographic method are lower

than those determined in the calorimeter at high coverages and are close to the theoretically calculated energies of nonspecific adsorption of individual alcohol molecules on the basal face of graphite (1-4). However, if for normal alcohols the difference $Q_{\text{cal}} - Q_{\text{g.c.}}$ is 4.8 kcal/mole, then for isomeric butanols this difference is smaller. This is due to the fact that, for isomeric alcohols, the formation of associates from a large number of molecules is spatially hindered (and for the tertiary alcohol altogether impossible), so that there is less than one hydrogen bond per adsorbed molecule of such an alcohol.

Thus, the gas-chromatographic method for determining heats of adsorption on graphitized blacks makes it possible to determine the adsorption energy of individual molecules, even those capable of mutual association, and, in combination with determinations at higher coverages (for example, by the calorimetric method), also makes it possible to determine the association energy in the adsorption layer. In the case considered, this method made it possible to determine the energy of the hydrogen bond between alcohol molecules. Analogous determinations can also be made for primary and secondary amines.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
23 III 1964

REFERENCES

1. N. N. Avgul' , G. I. Berezin et al., *Izv. AN SSSR, OKhN*, **1961**, 205.

2. N. N. Avgul' , A. V. Kiselev, I. A. Lygina, *Koll. zhurn.*, **23**, 513 (1961).

3. A. V. Kiselev, *ZhFKh*, **38**, No. 10 (1964).

4. N. N. Avgul' , A. V. Kiselev, I. A. Lygina, *Izv. AN SSSR, OKhN*, **1961**, 1404.

5. R. L. Gale, R. A. Beebe, *J. Phys. Chem.*, **68**, 555 (1964).

6. A. A. Isirikyan, A. V. Kiselev, *ZhFKh*, **36**, 1164 (1962); A. A. Isirikyan, A. V. Kiselev, *J. Phys. Chem.*, **65**, 601 (1961).

7. R. A. Bibi, A. V. Kiselev et al., *ZhFKh*, **38**, 713 (1964).

8. A. B. Littlewood, C. S. G. Phillips, D. T. Price, *J. Chem. Soc.*, **1955**, 1480.

9. A. V. Kiselev, R. S. Petrova, K. D. Shcherbakova, *Kinetika i kataliz*, **5**, 526 (1964).

10. A. V. Kiselev, G. A. Paskonova et al., *ZhFKh*, **38**, 161 (1964).

11. S. Ross, J. K. Saelens, J. P. Olivier, *J. Phys. Chem.*, **66**, 696 (1962).

12. N. N. Avgul' , G. I. Berezin et al., *Izv. AN SSSR, OKhN*, **1957**, 1021.

13. A. G. Bezus, V. P. Dreving, A. V. Kiselev, *ZhFKh*, **38**, 59, 947 (1964).

14. A. G. Bezus, V. P. Dreving, A. V. Kiselev, *Koll. zhurn.*, **23**, 369 (1961).

15. R. A. Beebe, M. H. Polley et al., *J. Am. Chem. Soc.*, **69**, 2294 (1947).

16. J. W. Ross, R. J. Good, *J. Phys. Chem.*, **60**, 1167 (1956).

17. N. N. Avgul' , A. V. Kiselev, I. A. Lygina, *Izv. AN SSSR, OKhN*, **1962**, 1346.

18. N. N. Avgul' , A. A. Isirikyan et al., *Izv. AN SSSR, OKhN*, **1957**, 1314.

Note: Figure translations are in progress. See original paper for figures.