A GAS CHROMATOGRAPHIC STUDY OF THE ADSORPTION
OF ALKANES AND ALKENES ON GRAPHITIZED THERMAL
CARBON BLACK

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Dedicated to Professor F. Čůta on the occasion of his 80th birthday.

The adsorption of C_5—C_{10} n-alkanes and 1-alkenes on Sterling MT graphitized thermal carbon black was studied over a temperature interval from 175 to 215°C. Specific retention volumes V_g and V_s were calculated from the experimental retention times and the differential heats of adsorption were obtained by linear regression from their temperature dependence. The standard changes in the chemical potential and entropy were further calculated for the substances studied. The precision of the measurement of the chromatographic data was checked in relation to the precision and accuracy of the calculated thermodynamic quantities. On the basis of the experimental results, the effect of the adsorbate contribution to the thermodynamic adsorption quantities was evaluated and compared with theoretical assumptions.

During the initial stages of the development of gas chromatography, solid adsorbates were used as column packings for separation of permanent gases and low-boiling liquids. Classical adsorbents could not be used for analyses of a broader range of substances, because the adsorption isotherms of most substances are non-linear leading to non-symmetrical chromatographic peaks. This undesirable phenomenon is caused chiefly by the geometrical and chemical inhomogeneity of adsorbents. The possibility of catalytic reactions on the adsorbent surface is another disadvantage.

These drawbacks have been overcome by the use of liquid stationary phases. However, GLC has some disadvantages compared with GSC, stemming mainly from the volatility of liquid phases. Therefore, the use of solid adsorbents and methods for preparation of materials with homogeneous surfaces have again been studied. Substances with defined and uniform pore-size have also been introduced into gas chromatographic procedures, both natural and artificial zeolites, porous glasses, porous polymers and classical adsorbents prepared by controlled synthesis or modified geometrically.

Surface homogeneity can be attained by thermal treatment, chemical modification by active substances, deposition of monomolecular layers of strongly adsorbing substances on the adsorbent surface, deposition of crystalline organic compounds on graphitized carbon black, blocking of active sites on inhomogeneous surfaces by liquids or adsorbing carrier gas.

The easiest way to obtain chemically and physically homogeneous surfaces is high-temperature treatment of carbon black in the absence of oxygen and other oxidants. Thermal treatment of carbon black *in vacuo*, in an inert medium or in a reducing atmosphere up to 3000°C not only

eliminates various chemical compounds of carbon with oxygen and hydrogen, but also leads to a growth of graphite crystallites and improves their ordering.

After thermal treatment at 3000°C, the crystal lattice parameters and the density of the particles of graphitized thermal carbon black (GTCB) approach the values characteristic of graphite. Nevertheless, GTCB particles differ from graphite in that they are polyhedra with planes formed of the basic planes of the graphite lattice. This results in considerable homogeneity of the GTCB surface, as the edges, at which the polyhedron planes touch and where the regular arrangement of carbon atoms in the basic planes is disturbed, form only a very small part of the homogeneous surface. Thus graphitized carbon black and especially GTCB are extremely homogeneous both chemically and crystallographically. This finding is very important, because in this way it is possible to obtain adsorbents with identical and almost homogeneous surfaces. Such a surface is readily reproducible chemically and geometrically, which makes it possible to predict and reproduce the adsorption properties of a surface unit. Therefore, these properties of GTCB can be considered as defined physico-chemical constants characterizing the adsorption on basic graphite planes.

With zero coverage of the GTCB surface, the adsorption energy depends very little on the dipole or quadrupole moment and on the distribution of the local electron density at the bonds of the adsorbed molecules[1,2]. The energy of the dispersion interaction depends primarily on the distance of the force centres in the adsorbed molecule from the adsorbent surface and on the polarizability and magnetic susceptibility of the adsorbate. Hence the steric configuration of the adsorbed molecule and its orientation with respect to the surface are decisive factors.

This special feature of adsorption on GTCB is progressively utilized more both for the development of the theory of molecular adsorption[1,3−8] and for practical applications in adsorption chromatography[1,6−8,9−22]. As mentioned above, the adsorption properties of a GTCB-type adsorbent are thermodynamic adsorption properties characterizing the adsorbate–adsorbent interaction[1,3,4,9−13,17−21].

These quantities obtained in thermodynamic equilibria for a number of molecules with various compositions and structures can then be used for determining the atom-atom potential functions for intermolecular interactions and thus for theoretical computation of the thermodynamic adsorption quantities on the basis of the known structure of the adsorbate molecules and the absorbent composition[5,11]. In addition, these quantities are indispensable in solving the opposite problem, namely in drawing conclusions on the structure of the adsorbate molecules from known atom-atom potential functions[6,8]. These values are also useful for determination of the characteristics of experimentally unknown substances and are used especially in identification of unknown substances by the GSC method[1,8].

Among thermodynamic adsorption quantities, the specific retention volumes related to the adsorbent surface unit, V_s (or per gram of adsorbent, V_g), the heats of adsorption and the standard entropy changes can be most precisely measured by GC at zero coverage of the GTCB surface (the heat capacities have been determined for only a few systems). Under these conditions, these quantities are unaffected by adsorbate–adsorbent interactions.

In order that the thermodynamic adsorption quantities obtained by gas chromatography have quantitative character, the gas–solid system must be in thermodynamic equilibrium, so that the adsorbate chemical potential in the gaseous phase and in the adsorbed state, μ_g and μ_s, respectively, are identical.

Ideal equilibrium chromatography, *i.e.* chromatography on a homogeneous adsorbent surface (at zero surface coverage) in the absence of intermolecular adsorbate–adsorbent interations leads to symmetrical peaks whose parameters are the basis of computation of thermodynamic adsorption quantities.

Recently, adsorption of graphitized carbon black has been studied in detail by Kiselev and coworkers[9,10,17-20]. The adsorption of saturated, unsaturated, aromatic and cyclic hydrocarbons and halogen derivatives of alkanes has been followed, as well as the adsorption of hydrocarbons containing an oxygen heteroatom[13,21-23]. The adsorption was studied using GC, which enables the calculation of thermodynamic constants from dependences of the retention data. From these data, conclusions can be drawn concerning the dependence of the thermodynamic properties on the nature of the molecular adsorption forces.

Because adsorption at higher temperatures has not yet been studied in detail, the present work summarizes the results of detailed measurements of the thermodynamic adsorption quantities at temperatures from 175 to 215°C.

EXPERIMENTAL

The adsorption was studied on GTCB Sterling MT (Cabot Co., Boston, USA) with a specific surface area of 7·6 m²/g. A series of n-alkanes and 1-alkenes was used.

The experiments were performed on a Carlo Erba Fractovap model C gas chromatograph with a flame ionization detector. Nitrogen carrier gas was used at a flow-rate of 23—25 ml/min. The 0·5—1·5 μl samples were injected in the form of saturated vapours using a 10 μl Hamilton syringe. A glass packed column 0·6 m long and with an internal diameter of 3 mm was used, containing 4·2810 g of GTCB Sterling MT with a grain size of 0·25—0·30 mm.

The results were evaluated statistically on a Hewlett–Packard 9830 A computer.

RESULTS

From the experimental retention times, the specific retention volumes related to one gram of the adsorbent or to a unit of the adsorbent surface were computed for the selected set of substances and are given in Table I and II.

By linear regression, the linear dependences of log V_g on the number of carbon atoms in the molecule were calculated for both homologous series,

$$\log V_g = a + bn \tag{1}$$

and the following constants were obtained: n-alkanes ($a = -2·37$, $b = 0·41$); 1-alkenes ($a = -2·36$, $b = 0·40$).

The differential heats of adsorption were calculated for n-alkanes and 1-alkenes, with standard deviations (from 10 measurements), from the slopes of the linear log V_g vs $1/T$ dependences; the values obtained were compared with the literature data[9,10]. The results are summarized in Table III. Addition of a CH_2 group to the carbon chain leads to an increase in the differential heat of adsorption, ΔH, by a certain increment, characteristic of the given homologous series.

$$\Delta H = \Delta H_0 + \Delta H_{CH_2} . n . \tag{2}$$

TABLE I

Specific Retention Volumes (V_g) for n-Alkanes and 1-Alkenes on GTCB at Zero Coverage of the Surface over a Temperature Range of 448·15—488·15 K

Hydro-carbons	V_g, ml/g								
	column temperature, K								
	448·15	453·15	458·15	463·15	468·15	473·15	478·15	483·15	488·15
n-Pentane	0·78	0·70	0·67	0·57	0·50	0·49	0·45	0·39	0·37
n-Hexane	2·64	2·25	1·93	1·75	1·51	1·38	1·27	1·16	1·04
n-Heptane	7·07	6·18	5·07	4·53	4·07	3·33	3·15	2·92	2·60
n-Octane	20·59	17·05	13·29	12·07	10·47	8·65	7·95	7·18	6·30
n-Nonane	57·79	47·33	37·99	30·72	25·44	23·44	20·57	18·10	15·67
n-Decane	152·88	128·71	101·27	82·97	67·44	58·06	51·73	40·62	36·99
1-Butene	0·28	0·27	0·25	0·25	0·20	0·19	0·18	0·17	0·16
1-Hexene	1·94	1·67	1·59	1·48	1·27	1·15	1·12	0·96	0·88
1-Heptene	5·73	4·73	4·10	3·70	3·32	2·78	2·62	2·43	2·24
1-Octene	15·94	13·47	10·96	9·49	8·57	7·07	6·72	6·05	5·33
1-Nonene	43·88	36·89	29·59	25·32	20·75	19·67	16·79	15·09	13·00
1-Decene	115·82	100·45	75·50	63·08	54·56	48·38	43·46	34·02	31·29

TABLE II

Specific Retention Volumes, V_s, for n-Alkanes and 1-Alkenes on GTCB at Zero Coverage of the Surface over a Temperature Range of 448·15—488·15 K

Hydro-carbons	V_s, ml/m^2								
	column temperature, K								
	448·15	453·15	458·15	463·15	468·15	473·15	478·15	483·15	488·15
n-Pentane	0·10	0·09	0·09	0·08	0·07	0·06	0·06	0·05	0·05
n-Hexane	0·35	0·30	0·25	0·23	0·20	0·18	0·17	0·15	0·08
n-Heptane	0·93	0·81	0·67	0·60	0·54	0·44	0·41	0·38	0·34
n-Octane	2·76	2·24	1·75	1·59	1·38	1·14	1·05	0·95	0·82
n-Nonane	7·60	6·23	5·00	4·04	3·35	3·08	2·71	2·38	2·06
n-Decane	20·12	16·94	13·33	10·92	8·87	7·64	6·81	5·35	4·87
1-Butene	0·04	0·04	0·03	0·03	0·02	0·02	0·02	0·02	0·02
1-Hexene	0·26	0·22	0·21	0·20	0·17	0·15	0·15	0·13	0·12
1-Heptene	0·75	0·62	0·54	0·49	0·44	0·37	0·34	0·32	0·29
1-Octane	2·10	1·77	1·44	1·25	1·13	0·93	0·88	0·80	0·70
1-Nonene	5·77	4·85	3·89	3·33	2·73	2·59	2·21	1·99	1·71
1-Decene	15·24	13·22	9·93	8·30	7·18	6·37	5·72	4·48	4·12

TABLE III

Differential Heats of Adsorption, ΔH, for n-Alkanes and 1-Alkenes on GTCB over a Temperature Range of 448·15—488·15 K

Hydrocarbons	ΔH_1, kJ/mol	s, kJ/mol	ΔH_1, kJ/mol[a]
n-Pentane	34·79	0·14	36·30
n-Hexane	39·20	0·23	43·13
n-Heptane	45·51	0·10	48·98
n-Octane	53·15	0·12	55·68
n-Nonane	58·12	0·14	61·13
n-Decane	65·58	0·09	67·40
1-Butene	27·61	0·12	29·10
1-Hexene	34·49	0·31	41·87
1-Heptene	42·06	0·10	46·89
1-Octene	48·76	0·04	54·00
1-Nonene	54·11	0·11	59·45
1-Decene	59·65	0·11	64·06

[a] Kiselev's data[3,9,10].

TABLE IV

Standard Changes in the Chemical Potential ($\Delta\mu^0$) of n-Alkanes and 1-Alkenes During Adsorption on GTCB (zero surface coverage) over a Temperature Range of 448·15—488·15 K

Hydro-carbons	$\Delta\mu^0$ kJ/mol								
	column temperature, K								
	448·15	453·15	458·15	463·15	468·15	473·15	478·15	483·15	488·15
n-Petane	8·50	9·03	9·52	9·97	10·59	10·82	11·21	11·91	12·30
n-Hexene	3·95	4·58	5·23	5·67	6·27	6·71	7·12	7·58	8·08
n-Heptane	0·26	0·78	1·55	2·00	2·44	3·27	3·51	3·86	4·36
n-Octane	− 3·76	− 3·04	−2·13	− 1·77	−1·25	−0·51	−0·20	0·24	0·77
n-Nonane	− 7·56	− 6·88	−6·12	−5·38	−4·71	−4·44	−3·95	−3·49	−2·93
n-Decane	−11·18	−10·65	−9·85	−9·20	−8·48	−7·99	−7·62	−6·73	−6·41
1-Butene	12·30	12·61	12·98	13·18	14·25	14·59	14·79	15·39	15·56
1-Hexane	5·07	5·71	5·98	6·32	6·99	7·45	7·63	8·30	8·75
1-Heptene	1·06	1·79	2·36	2·77	3·23	3·93	4·25	4·60	4·96
1-Octene	− 2·75	− 2·15	−1·39	−0·85	−0·46	0·28	0·50	0·92	1·44
1-Nonene	− 6·53	− 5·95	−5·17	−4·62	−3·89	−3·74	−3·14	−2·75	−2·18
1-Decene	−10·14	− 9·72	−8·74	−8·16	−7·67	−7·28	−6·93	−6·03	−5·74

The values of constants ΔH_0 and ΔH_{CH_2} are as follows: n-alkanes $(\Delta H_0 = 2.60, \Delta H_{CH_2} = 6.24)$; 1-alkenes $(\Delta H_0 = 3.68, \Delta H_{CH_2} = 5.56)$.

From the temperature dependences of the specific retention volumes at zero coverage, related to a surface unit, the standard changes of all thermodynamic functions of the adsorbate can be found on transfer from the gaseous to the adsorbed state. For example, the standard change in the adsorbate chemical potential can be found from the relationship

$$\Delta\mu^0 = -RT_c \cdot \ln V_s . \tag{3}$$

The standard entropy change of the adsorbate can further be found from ΔH and $\Delta\mu^0$ using the equation

$$\Delta S^0 = (\Delta H + \Delta\mu^0) T_c^{-1} \tag{4}$$

which characterizes the mobility of the molecules on the adsorbent surface.

The $\Delta\mu^0$ and ΔS^0 values are summarized in Tables IV and V. The dependences of ΔS^0 on the molecular structure are depicted in Figs 1 and 2, showing the entropy change in dependence on the number of adsorbate structural units or on the adsorbate differential heat of adsorption.
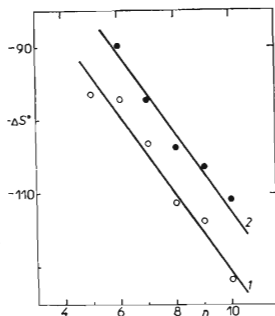

FIG. 1

Dependence of the Standard Entropy Change, ΔS^0 (J mol^{-1} K^{-1}) on the Number of Carbon Atoms, n, in the Molecule of n-Alkanes (1) and 1-Alkenes (2), on GTCB at a Temperature of 473·15 K

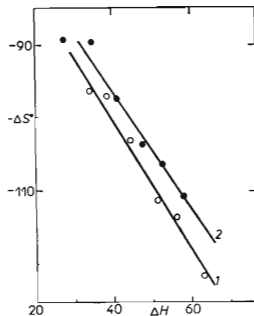FIG. 2

Dependence of the Standard Entropy Change, ΔS^0 (J mol^{-1} K^{-1}) on the Heat of Adsorption, ΔH^0 (kJ mol^{-1}) for n-Alkanes (1) and 1-Alkenes (2), on GTCB at a Temperature of 473·15 K

DISCUSSION

The results given in the experimental part permit more general conclusions to be drawn characterizing the effect of the adsorbate molecular structure on the thermodynamic adsorption quantities in adsorption on GTCB.

The adsorbates used belonged to two homologous series, C_5—C_{10} alkanes and C_6—C_{10} 1-alkenes. This selection permitted study of changes in the thermodynamic adsorption quantities on transfer from alkanes to 1-alkenes and of the effect of an increase in the length of the carbon chain by addition of CH_2 groups inside a homologous series.

The specific retention volumes, V_g and V_s, and the differential heats of adsorption, ΔH, decrease on transfer from a homologous series of n-alkanes to that of 1-alkenes. This decrease occurs not only because the effect of a decrease in the number of hydrogen atoms in the molecule predominates over the effect of an increased interaction of carbon atoms bound by a double bond, but predominantly because the double bond limits the chain mobility. On the other hand, the easier orientation of n-alkane molecules with respect to the GTCB surface owing to free rotation around single bonds permits closer contact with the surface and thus higher energy of non-specific adsorbate–adsorbent interactions.

TABLE V

Standard Entropy Changes (ΔS^0) for n-Alkanes and 1-Alkenes During Adsorption on GTCB (Zero Surface Coverage) over a Temperature Range of 448·15 — 488·15 K

Hydro-carbons	ΔS^0, J/mol K								
	column temperature, K								
	448·15	453·15	458·15	463·15	468·15	473·15	478·15	483·15	488·15
n-Pentane	− 96·6	− 96·7	− 96·7	− 96·6	− 96·9	− 96·4	− 96·2	− 96·6	− 96·5
n-Hexane	− 96·3	− 96·6	− 97·0	− 96·9	− 97·1	− 97·0	− 96·9	− 96·8	− 96·9
n-Heptane	−102·1	−102·1	−102·7	−102·6	−102·4	−103·1	−102·5	−102·2	−102·2
n-Octane	−110·2	−110·6	−111·4	−110·9	−111·6	−111·2	−110·7	−110·5	−110·5
n-Nonane	−112·8	−113·1	−113·5	−113·9	−114·1	−113·5	−113·3	−113·1	−113·1
n-Decane	−121·4	−121·2	−121·6	−121·7	−122·0	−121·7	−121·2	−121·8	−121·2
1-Butene	− 89·1	− 88·8	− 88·6	− 88·1	− 89·4	− 89·2	− 88·7	− 89·0	− 88·4
1-Hexene	− 89·4	− 89·8	− 89·4	− 89·2	− 89·7	− 89·7	− 89·1	− 89·6	− 89·6
1-Heptene	− 96·2	− 96·8	− 96·9	− 96·8	− 96·7	− 97·2	− 96·9	− 96·7	− 96·3
1-Octene	−102·7	−102·9	−103·4	−103·4	−103·2	−103·6	−103·0	−102·8	−102·8
1-Nonene	−106·2	−106·3	−106·8	−106·9	−107·3	−106·5	−106·6	−106·3	−106·4
1-Decene	−110·5	−110·2	−111·1	−111·2	−111·0	−110·7	−110·3	−111·0	−110·4

The differential heats of adsorption obtained are somewhat lower than the literature data. However, the latter[9] were obtained by measurement over a wide temperature interval ($75-225°C$) in $25°C$ steps. As these values were obtained from a single linear $\log V_g$ vs $1/T$ dependence over the whole temperature range, the slope value was affected substantially by the retention volumes at lower temperatures.

The $\log V_g$ and ΔH values are linear functions of the number of carbon atoms in the molecule for both homologous series. An increase in the length of the hydrocarbon chain by addition of CH_2 groups leads to an increase in the $\log V_g$ and ΔH values. It holds for the $\log V_g$ dependence on n for alkanes at 473.15 K and for the ΔH dependence on n at $448.15-488.15$ K that

$$\log V_g^{473,15} = -2.37 + 0.41n \tag{5}$$

$$\Delta H = 2.60 + 6.24n \,, \tag{6}$$

whereas for 1-alkenes

$$\log V_g^{473,15} = 2.36 + 0.40n \,, \tag{7}$$

$$\Delta H = 3.68 + 5.56n \,. \tag{8}$$

It is evident from equations (5) and (7) that the $\log V_g^{473,15}$ increment values are almost identical for n-alkanes and 1-alkenes. However, the increments in the heats of adsorption (Eq. (6) and (8)) differ more markedly (6.24 and 5.56 kJ/mol). An increase in the chain length of n-alkanes by one CH_2 group causes a greater energy increase than with 1-alkenes.

This finding is in agreement with theoretical assumptions. The double-bond decreases the number of positional isomers, thus affecting the potential energy of interaction of the individual force centres with carbon atoms in GTCB. It also follows from this dependence that there is a certain column temperature at which the elution order of alkenes and alkanes changes.

Equations (5)–(8) also have practical importance, as they can be used for identification of unknown substances analyzed gas chromatographically. On comparison of our experimental increments ΔH_{CH_2} (6.24 and 5.56 kJ/mol) with those given by Kiselev and coworkers[9] (6.20 and 5.70 kJ/mol) it can be seen that there is good agreement for n-alkanes and the difference for 1-alkenes does not exceed 4%. The lower increment values for alkanes given in the present work can be explained by the high purity of the adsorbates used.

The effect of the molecular structure is also reflected in the values of the standard chemical potential and entropy changes (Tables IV and V). The mobility of the adsorbed molecules on the GTCB surface can be evaluated on the basis of these thermodynamic adsorption quantities.

The higher entropy values obtained in the adsorption of 1-alkenes are given by the greater mobility of the molecules on the GTCB surface. Owing to the limited steric mobility of a chain with a double-bond, adsorbate–adsorbent interactions are suppressed and the adsorbate molecule is bound to the surface by weaker dispersion forces.

It can be seen from Fig. 1 that the entropy decreases linearly with an increasing number of carbon atoms in the adsorbate molecule for both n-alkanes and 1-alkenes. On lengthening of the hydrocarbon chain, the number of force centres interacting with the surface increases. This leads to a decrease in the mobility of the molecules on the surface and a consequent decrease in the entropy of the system.

Similar conclusions can also be drawn from the ΔS^0 dependence on ΔH(Fig.2). This dependence was studied by the Soviet authors[24−26], who concluded that it is especially characteristic of non-specific intermolecular interactions during adsorption.

This survey indicates that a change in the constitution of the adsorbate molecules during adsorption on a nonspecific adsorbent is reflected in the values of the thermodynamic quantities.

This dependence is important in several respects. It is possible to obtain physicochemical data on new substances from GC data and to predict the chromatographic behaviour of many important compounds from known constants. It also contributes to deeper understanding of intermolecular interactions and thus to the development of the theory of molecular adsorption. Finally, it is a stimulus for the preparation of new highly homogeneous adsorbents which will further broaden the potentialities of gas and liquid chromatography.

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