CHROM. 10,642

GAS CHROMATOGRAPHIC INVESTIGATION OF THE ADSORPTION OF POLYMETHYLCYCLOHEXANES ON GRAPHITIZED THERMAL CARBON BLACK

W. ENGEWALD

Chemistry Section, Leipzig University, Liebigstrasse 18, 701 Leipzig (G.D.R.)

and

E. V. KALASHNIKOVA, A. V. KISELEV, R. S. PETROVA, K. D. SHCHERBAKOVA and A. L. SHILOV

Laboratory of Adsorption and Chromatography, Chemistry Department, State University of Moscow, 117234 Moscow (U.S.S.R.)

(Received October 3rd, 1977)

SUMMARY

The thermodynamic functions of adsorption (Henry constants, retention indices, changes in internal energy and entropy at zero sample size) of geometric and structural isomers of polymethylcyclohexanes on graphitized thermal carbon black have been determined and their relationship to the structures of the molecules has been established. A molecular statistical calculation of these functions for the adsorption of cyclohexane, methylcyclohexane and some di-, tri- and tetramethylcyclohexanes has been carried out using the atom–atom approximation for the potential function of intermolecular interaction with graphitized thermal carbon black. Examples of the separation of some mixtures of these hydrocarbons are given.

INTRODUCTION

A gas chromatographic (GC) investigation of polymethylcyclohexanes is of theoretical interest with regard to the various conformational forms of their molecules. It also is of great practical importance as polyalkylcyclohexanes are a major component of the naphthene fraction of oil. Naphthenes with five- and six-membered rings are isolated from the gasoline and kerosene fractions of oil by thermal diffusion and adsorption separation (on active charcoal, Sephadexes and zeolites)[1–3]. Further separation is achieved chromatographically. The very small boiling point range of polymethylcyclohexane isomers makes their complete separation by gas–liquid chromatography (GLC) difficult and the separation of many mixtures of naphthene hydrocarbons has been successful only with the use of capillary columns with different liquid phases having a high performance (up to 100,000 theoretical plates)[2–10].

The relationship between the retention characteristics in GLC and the molecular structures of alkyl-substituted cyclohexanes has been investigated by a number

of workers[11-16]. Such a relationship should be much more evident in the case of gas–solid chromatography (GSC) on a homogeneous surface[17,18]. Attempts to separate isomers of dimethylcyclohexane by GSC on zeolite 13X in a column 1.2 m long showed that even in this case of adsorption in the cavities of porous crystals, the geometric structure of the molecule played the decisive role[3]. Better results would be expected for adsorption on the plane surface of graphitized thermal carbon black (GTCB) as the retention properties in this instance are very sensitive to the geometry of the molecule[18-21]. GTCB has been used successfully to separate structural and stereoisomers[17-24]. In addition, the thermodynamic characteristics of the adsorption of hydrocarbons on GTCB can be calculated by means of the molecular statistical theory of adsorption using the atom–atom approximation for the potential function of intermolecular interaction[18-21]. In this investigation, a column packed with GTCB was used for the analysis of the polymethylcyclohexanes. Some of the isomers were separated earlier[25].

EXPERIMENTAL

The GC measurements were carried out on a Pye argon gas chromatograph with a β-ionization detector and a glass column (120 cm × 0.25 cm I.D.). Sterling MT (3100°) D4 GTCB with a specific surface area of 7.6 m²/g was used as adsorbent, the size of the pellets being 0.3–0.4 mm. The pressure drop over the column was 255–300 torr. The temperature in the thermostat was measured with mercury thermometers accurate to ±0.1 °C. The samples were injected from a hypodermic syringe, the sample volume being 0.3 cm³ of vapour diluted with air. The retention times of the adsorbates were measured 3–5 times at each temperature and the error in the measurement did not exceed 1 sec. As the peaks were narrow and symmetrical and the retention time did not depend on the amount of sample injected, the retention volumes at each temperature were calculated from the average time of the emergence of the peak maximum. For each adsorbate 10–15 measurements were made in the temperature range from 90–220 °C.

In conformity with the thermodynamic theory of retention[18], the retention volumes of very small (approaching zero) samples were used as Henry constants: $V_{A,1} = K_{\Gamma,c,1} = K_1$ cm³/m² or μm, where A denotes the surface area of the adsorbent in the column, Γ the Gibbs adsorption, c the concentration of adsorbate in the bulk gas and 1 indicates the first coefficient in the virial expansion of the equation of the adsorption isotherm ($\Gamma_c \rightarrow 0$). As well as the retention volumes, the Kováts retention indices, I, were determined. As the retention indices are ratios of logarithms of relative retention volumes (relative retention times), they are determined from the experiments with greater accuracy than the absolute values of $V_{A,1}$. The dependence of the logarithm of the retention volume on the reciprocal temperature of the column is approximated by a straight line and can be expressed by the following equation[18]:

$$\ln K_1 = \frac{-\overline{\Delta U_1}}{RT} + \left(\frac{\overline{\Delta S_1^*}}{R} + 1 \right)$$

The coefficients in this equation, obtained by the least-squares method, give the molar differential changes in internal energy ($\overline{\Delta U_1}$) and in entropy ($\overline{\Delta S_1^*}$) of adsorbates.

$-\overline{\Delta U_1}$ is equal to the limiting differential heat of adsorption, $\bar{q}_{v,1}$, at $\Gamma \to 0$. In the literature, the so-called isosteric heat of adsorption, $\bar{q}_{st}$, is often used. At small c and Γ, $\bar{q}_{st} = -\overline{\Delta U_1} + RT$, and hence $\bar{q}_{st}$ depends on T in a more complex manner than $\overline{\Delta U_1}$.

The accuracy of the experimental measurements was not sufficient to reveal the temperature dependence of $\overline{\Delta U_1}$ and $\overline{\Delta S_1}^*$, that is, for determining the change in heat capacity, $\overline{\Delta C_1}$, on adsorption.

$V_{A,1}$, I, $\overline{\Delta U_1}$ and $\overline{\Delta S_1}^*$ are related to the potential energy of the intermolecular interaction of molecules with GTCB and therefore depend on their structures[18-26].

The adsorption of the following 31 C_7–C_{11} alkylcyclohexanes differing in the position of the substituents and their spatial orientation was studied: methylcyclohexane, ethylcyclohexane, 1,1-dimethylcyclohexane, dimethylcyclohexanes (1r2c-, 1r2t-, 1r3c-, 1r3t-, 1r4c- and 1r4t-), isopropylcyclohexane, trimethylcyclohexanes (1r3c5t-, 1r3c5c-, 1r2t3t-, 1r2c3c-, 1r2t3c-, 1r2c4c-, 1r2t4c-, 1r2c4t- and 1r2t4t-), tetramethylcyclohexanes (1r2t3t5t-, 1r2c3c5t-, 1r2t3c5t-, 1r2c3c5c-, 1r2c3t5t-1r2t3c5c-, 1r2t4c5t-, 1r2c4t5t-, 1r2c4c5c-, 1r2t4t5t- and 1r2t4t5c-) and 1r2c3c4c5c-pentamethylcyclohexane.

RESULTS AND DISCUSSION

Adsorption of C_7 and C_8 alkylcyclohexanes on GTCB

The values of $V_{A,1}$, I, $\overline{\Delta U_1}$ and $\overline{\Delta S_1}^*$ for cyclohexane and C_7 and C_8 alkylcyclohexanes on GTCB are given in Table I (the Kováts indices in Tables I–III are compared with the indices measured on a micropacked column with GTCB). With the 1,2- and 1,4-dimethylcyclohexanes, the trans-isomers (1r2t and 1r4t) are retained on GTCB more strongly than the cis-isomers; the $V_{A,1}$ (trans)/$V_{A,1}$ (cis) ratios for the 1,2- and 1,4-dimethylcyclohexanes are 1.77 and 2.51, respectively. With the 1,3-dimethylcyclohexanes, the cis-isomer is retained more strongly and the ratio $V_{A,1}$ (trans)/$V_{A,1}$ (cis) is 0.57. This order of emergence of the compounds does not correspond to the increase in boiling points but depends on the geometry of the isomers: the isomers with an equatorial arrangement of the substituents, i.e., the more planar molecules, are retained more strongly.

Ethylcyclohexane is retained on GTCB more weakly than any of the dimethylcyclohexanes with the same maximal number of possible points of contact with the flat surface. This can be explained by the conformational mobility of the ethyl group[18,20]. The most weakly retained of all the C_8 isomers is 1,1-dimethylcyclohexane, the molecule of which is the least advantageously disposed on the surface of GTCB. Fig. 1 shows that only the 1r2c- and 1r4c-isomers of dimethylcyclohexane were not separated on GTCB.

Adsorption of C_9 alkylcyclohexanes on GTCB

The adsorption properties of isopropylcyclohexane and the 1,2,3-, 1,3,5- and 1,2,4-isomers of trimethylcyclohexane are shown in Table II. As with the dimethylcyclohexanes, the separation of the trimethylcyclohexanes on GTCB takes place in conformity with the geometric structure of their molecules. The isomers with eee configuration of the substituents are retained on GTCB more strongly than other

TABLE I

THERMODYNAMIC CHARACTERISTICS OF RETENTION OF CYCLOHEXANE AND C₇ AND C₈ ALKYLCYCLOHEXANES ON GTCB

No.	Adsorbate	B.p. (°C)[27]	Range of column temperature (°C) From	To	$V_{A,i}^{100°}$ (µm)	I^{GTCB} 100 °C*	200 °C*	200 °C**	$-\overline{\Delta U}_i$ (kJ/mole)	$-\overline{\Delta S}_i^*/R$
1	Cyclohexane	80.7	70	160	0.93	508			28.6 ± 0.3	10.4 ± 0.1
2	Methylcyclohexane	100.9	90	190	3.9	606			35.7 ± 0.3	11.2 ± 0.1
3	Ethylcyclohexane	131.8	100	190	14.7	701			42.6 ± 0.3	11.7 ± 0.1
	Dimethylcyclohexanes:									
4	1,1	119.5	90	160	6.0	637	663	661	36.2 ± 0.4	10.9 ± 0.4
5	1,2c (ea)	129.7	100	180	9.1	667	695	693	38.7 ± 0.3	11.3 ± 0.1
6	1,2t (ee)	123.4	100	190	16.1	707	721	718	42.5 ± 0.3	11.9 ± 0.1
7	1,3c (ee)	120.1	100	190	17.7	715	730	728	42.5 ± 0.2	11.8 ± 0.05
8	1,3t (ea)	124.5	100	180	10.1	674	694	689	40.0 ± 0.3	11.6 ± 0.08
9	1,4c (ea)	124.3	100	180	8.5	662	685	683	38.2 ± 0.3	11.2 ± 0.1
10	1,4t (ee)	119.4	100	190	21.3	729	747	745	42.7 ± 0.4	11.8 ± 0.1

* Measured in the University of Moscow.

** Measured in the University of Leipzig on a micropacked column.

TABLE II

THERMODYNAMIC CHARACTERISTICS OF RETENTION OF C_9 ALKYLCYCLOHEXANES ON GTCB

No.	Adsorbate	B.p. (°C)[13,27]	Range of column temperature (°C) From	Range of column temperature (°C) To	$V_{A,1}^{150°C}$ (μm)	$I_{A,1}^{G7CB}$ 130°C*	150°C*	160°C*	190°C*	130°C**	160°C**	190°C**	$-\Delta U_1$ (kJ/mole)	$-\overline{\Delta S_1^*}/R$
11	Isopropylcyclohexane	154.6	140	210	7.0		786				805		46.0 ± 0.4	12.1 ± 0.1
	Trimethylcyclohexanes:													
12	1t3c5t (eea)	142	140	210	7.6		793	794					47.8 ± 0.3	12.6 ± 0.1
13	1t3c5c (eee)	139	140	210	10.9		826	827			827		48.6 ± 0.6	12.4 ± 0.2
14	1t2t3t (eea)	151	130	160	6.1	770	773			770			44.5 ± 0.9	11.8 ± 0.4
15	1t2c3c (eae)	151	145	210	6.3	775	777			778			45.1 ± 0.5	12.0 ± 0.1
16	1t2t3c (eee)	146	145	210	8.7	801	803			795			48.3 ± 0.7	12.6 ± 0.2
17	1t2t4c (eea)	145	135	175	4.8		753		759			762	42.7 ± 0.9	11.6 ± 0.2
18	1t2c4c (aee)	146	140	210	5.6		768		773			777	44.2 ± 0.6	11.9 ± 0.2
19	1t2c4t (eae)	146	135	175	7.1		787		791			792	46.5 ± 1.7	12.3 ± 0.5
20	1t2t4t (eee)	142	140	210	13.1		840		842			838	49.8 ± 0.6	12.6 ± 0.2

* Measured in the University of Moscow.

** Measured in the University of Leipzig on a micropacked column.

TABLE.III

THERMODYNAMIC CHARACTERISTICS OF RETENTION OF C_{10} AND C_{11} ALKYLCYCLOHEXANES ON GTCB

No.	Adsorbate	B.p. (°C)[8,14]	Range of column temperature (°C)		$V_{A,1}$ (μm)		I^{GTCB}				$-\overline{\Delta U_1}$ (kJ/mole)	$-\overline{\Delta S_1^*}/R$
			From	To	160 °C	200 °C	160 °C*	200 °C**	240 °C*	240 °C**		
	Tetramethylcyclohexanes:											
21	1r2t3t5t (aaee)	163.0	155	210	5.5		791				45.2 ± 0.8	11.8 ± 0.2
022	1r2c3c5t (eaea)	169.0	155	210	7.9		825				47.1 ± 0.9	12.0 ± 0.2
23	1r2t3c5t (eeea)	162.0	155	190	10.1		849				50.5 ± 1.3	12.7 ± 0.3
24	1r2c3c5c (eaee)	165.0	155	210	12.5		871				50.7 ± 0.8	12.5 ± 0.2
25	1r2c3t5t (aeee)	164.5	155	210	17.6		904				55 ± 1.4	13.3 ± 0.4
26	1r2t3c5c (eeee)	159.0	155	210	27.9		936				59.4 ± 0.9	14.2 ± 0.3
27	1r2t4c5t (eeaa)	163.5	150	215	6.2		804	814	822	823	45 ± 1	11.7 ± 0.3
28	1r2c4t5t (eaea)	170	150	210	10.2		844	855	865	863	49 ± 2	12.3 ± 0.8
29	1r2c4c5c (aeea)	174	150	200	10.4		849	858	868	869	50 ± 1	12.6 ± 0.9
30	1r2t4t5t (eeea)	165	150	210	12.2		862	870	880	885	50 ± 1	12.4 ± 0.8
31	1r2t4t5c (eeee)	160.5	150	210	34.8	9.3	958	967	977	975	57 ± 2	13.3 ± 0.7
	Pentamethylcyclohexane:											
32	1r2c3c4c5c (eaeae)	193.3	195	220		8.6		953				

* Measured in the University of Moscow.
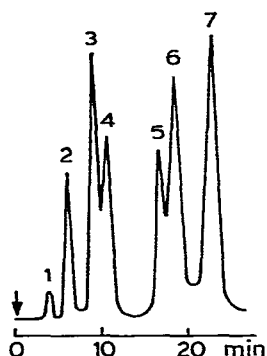** Measured in the University of Leipzig on a micropacked column.

Fig. 1. Chromatogram of a mixture of methylcyclohexane and dimethylcyclohexanes on GTCB at 125 °C. Peaks: 1 = methylcyclohexane; 2–7 = dimethylcyclohexanes; 2 = 1,1(ea); 3 = 1r4c(ea) + 1r2c(ea); 4 = 1r3t(ea); 5 = 1r2t(ee); 6 = 1r3c(ee); 7 = 1r4t(ee).

isomers, despite the fact that the boiling points of the latter are higher. The difference in the retention of isomers with the same number of axial substituents is significantly less than that for isomers with different numbers of axial substituents.

For each of the structural isomers, an analytical separation into *cis*- and *trans*-isomers was carried out. A satisfactory separation was not obtained only with the eea and eae isomers of 1,2,3-trimethylcyclohexane. The chromatogram of the complete mixture of the isomers of trimethylcyclohexane is shown in Fig. 2.
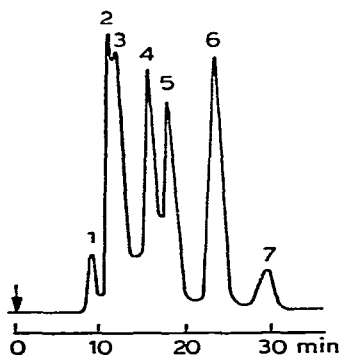

Fig. 2. Chromatogram of a mixture of isomers of trimethylcyclohexane on GTCB at 125 °C. Peaks: 1 = 1r2t4c(eea); 2 = 1r2c4c(aee); 3 = 1r2t3t(eea) + 1r2c3c(eae); 4 = 1r2c4t(eae) + 1r3c5t(eea); 5 = 1r2t3c(eee); 6 = 1r3c5c(eee); 7 = 1r2t4t(eee).

Adsorption of C_{10} and C_{11} polymethylcyclohexanes on GTCB

The adsorption properties of the higher polymethylcyclohexanes are shown in Table III. The retention of the isomers of 1,2,3,5-tetramethylcyclohexane increases as the number of equatorial substituents increases. An analogous dependence is observed for the isomers of 1,2,4,5-tetramethylcyclohexane. With the tetramethylcyclohexanes GTCB also shows a high selectivity for molecules of different geometry. For instance, the retention volume of the eeee isomer of 1,2,4,5-tetramethylcyclohexane

is almost three times greater than that of the eeea isomer. The range of the retention indices of the tetramethylcyclohexanes investigated was 167 units while the boiling points changed only from 159 to 174 °C. The separation of the 1,2,3,5- and 1,2,4,5-isomers of tetramethylcyclohexane into geometric isomers is shown in Figs. 3 and 4. The separation of all of the isomers of 1,2,3,5-tetramethylcyclohexane was achieved in the temperature range under investigation. With 1,2,4,5-tetramethylcyclohexanes the eaea and aeea isomers emerged from the packed column as one peak; a more effective micropacked column with GTCB resolved this peak incompletely (Fig. 4).

Of the isomers of 1,2,3,4,5-pentamethylcyclohexane, only one, $1r2c3c4c5c$ (eaeae), was investigated. The retention of this isomer was close to that of $1r2t4t5c$-tetramethylcyclohexane (eeee).
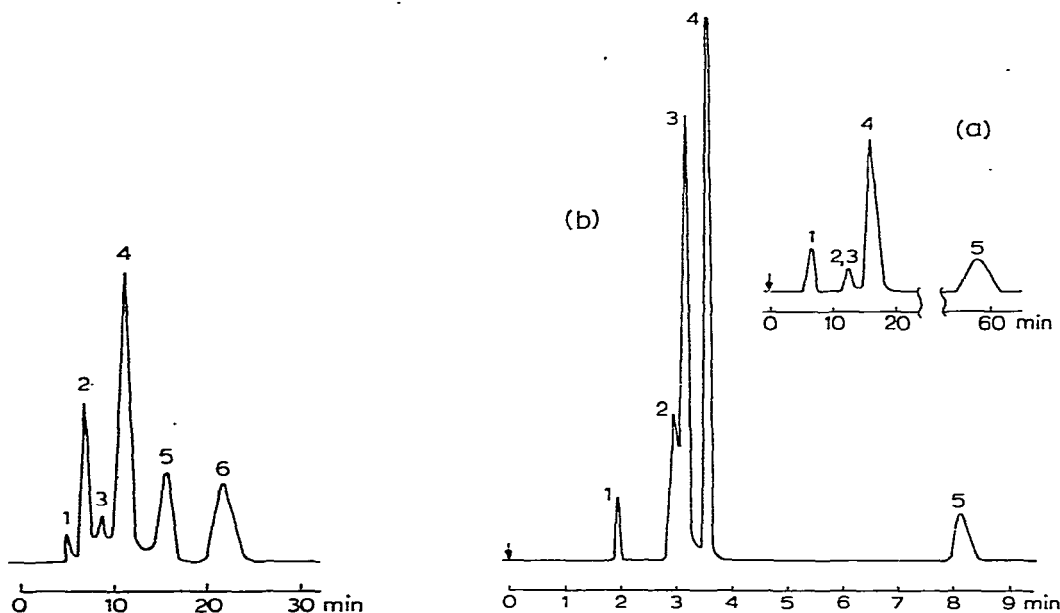

Fig. 3. Chromatogram of a mixture of isomers of 1,2,3,5-tetramethylcyclohexane on GTCB at 155 °C Peaks: 1 = aaee; 2 = eaea; 3 = eeea; 4 = eaee; 5 = aeee; 6 = eeee.

Fig. 4. Chromatograms of a mixture of isomers of 1,2,4,5-tetramethylcyclohexane on GTCB: (a) packed column, 145 °C; (b) micropacked column, 2.1 m × 0.34 mm I.D., 0.08–0.09-mm fraction, carrier gas hydrogen, 240 °C. Peaks: 1 = eeaa; 2 = eaea; 3 = aeea; 4 = eeea; 5 = eeee.

DISCUSSION

It is evident that the main factor that determines the adsorption of the alkyl-cyclohexanes on the planar surface of the non-specific GTCB adsorbent is the geometric structure of the molecules, which determines the potential energy of their intermolecular interaction with graphite[18,20]. The strongest adsorption, as has been noted previously, is observed for more planar molecules, independent of their boiling points and molecular weights. Fig. 5 shows that the methylcyclohexanes are characterized by the absence of a linear dependence of $\ln V_{A,1}$ and $-\overline{\Delta U_1}$ on the number
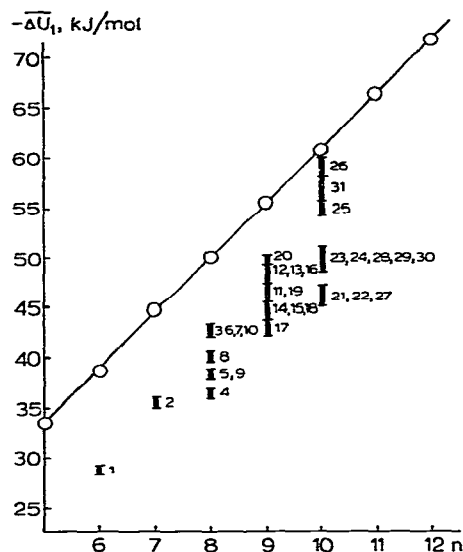
Fig. 5. Dependence of $-\overline{\Delta U_1}$ on the number of carbon atoms in a molecule for adsorption on GTCB of n-alkanes (circles) and derivatives cyclohexane (vertical bars). The substances are numbered as in Tables I–III.

of carbon atoms, n, in the molecule. For example, $-\overline{\Delta U_1}$ for 1r2t4t-trimethylcyclo-hexane with an eee configuration and having a complete equatorial disposition of substituents is 49.8 kJ/mole, but for 1r2t3t5t-tetramethylcyclohexane with an aaee configuration it is only 45.2 kJ/mole. The difference in retention volumes is even greater: at 160 °C they are 9.5 and 5.5 μm, respectively, despite the fact that the molecular weight of the former compound is 14 units less and the boiling point 21° less than those of the latter.

A comparison of the retention data for the trimethylcyclohexanes on the solid GTCB adsorbent and on a liquid phase demonstrates the higher selectivity of GTCB with respect to compounds with similar physical properties and different molecular structure. This is clear from Table IV, which gives the retention indices of trimethyl-

TABLE IV

RETENTION INDICES OF ALL ISOMERS OF TRIMETHYLCYCLOHEXANE ON GTCB AND ON APIEZON L

Trimethylcyclohexane	$I^{GTCB}_{150\,°C}$	$I^{Apiezon\ L}_{110\,°C}$
1r3c5t	793	893
1r3c5c	826	874
1r2t3t	773	944
1r2c3c	777	940
1r2t3c	803	923
1r2t4c	753	914
1r2c4c	768	923
1r2c4t	787	925
1r2t4t	840	895

TABLE V

CALCULATED AND EXPERIMENTAL VALUES OF THERMODYNAMIC CHARACTERISTICS OF ADSORPTION ON GTCB FOR CYCLO-HEXANE AND ITS METHYL DERIVATIVES

Compound	Calculated							Experimental		
	z_{0v} (nm)	$-\Phi_{0v}$ (kJ/mole)	T (°K)	$Ln\,K_1$ (μm)	$-\overline{\Delta U_1}$ (kJ/mole)	$\dfrac{\overline{\Delta S_1^*}}{R}$	$\dfrac{\overline{\Delta C_1}}{R}$	T (°K)	$-\overline{\Delta U_1}$ (kJ/mole)	$\dfrac{\overline{\Delta S_1^*}}{R}$
Cyclohexane (bond lengths: C–C = 0.153 nm, C–H = 0.109 nm)	0.395	36.8	250	4.85	32.5	11.8	2.0	343–433	28.6	10.3
			350	0.48	31.0	11.2	1.7			
			450	−1.84	29.8	10.8	1.3			
			550	−3.27	28.8	10.6	1.1			
Cyclohexane (bond lengths: C–C = 0.154 nm, C–H = 0.110 nm)	0.396	36.4	250	4.74	32.2	11.8	2.0			
			350	0.40	30.7	11.2	1.7			
			450	−1.90	29.5	10.8	1.3			
			550	−3.31	28.5	10.5	1.1			
Methylcyclohexane (e)	0.394	43.6	350	2.04	37.6	11.9	2.3	363–463	35.7	11.2
			400	0.44	36.8	11.6	2.2			
			450	−0.78	35.8	11.4	2.0			
			500	−1.72	35.0	11.2	1.9			
Methylcyclohexane (a)	0.409	43.2	350	1.57	35.4	11.6	2.6			
			400	0.06	34.4	11.3	2.2			
			450	−1.08	33.6	11.1	1.9			
			500	−1.97	32.9	10.9	1.6			
1,1-Dimethylcyclohexane	0.418	44.9	350	2.54	38.3	11.6	2.0	363–433	36.2	10.9
			450	−0.34	36.8	11.2	1.7			
			550	−2.10	35.5	10.9	1.5			
1r2t-Dimethylcyclohexane (ee)	0.394	50.3	350	3.61	44.5	12.7	2.8	373–463	42.5	11.9
			450	0.29	42.1	12.0	2.8			
			550	−1.70	40.0	11.4	2.5			
1r4t-Dimethylcyclohexane (ee)	0.392	49.8	350	3.81	44.4	12.4	2.2	373–463	42.7	11.8
			450	0.49	42.5	11.9	2.2			
			550	−1.54	40.7	11.4	2.1			

Compound			T					Range		
1r3c5c-Trimethylcyclohexane (eee)	0.392	57.6	350	5.13	49.9	13.0	2.5	413–483	48.6	12.4
			400	3.01	48.8	12.7	2.4			
			450	1.39	47.8	12.4	2.4			
			500	0.13	46.8	12.1	2.4			
			550	−0.88	45.7	11.9	2.4			
1r3c5t-Trimethylcyclohexane (eea)	0.398	58.7	350	5.03	51.7	13.7	4.1	413–487	47.8	12.6
			400	2.84	50.0	13.2	4.1			
			450	1.19	48.3	12.7	4.0			
			500	−0.076	46.7	12.3	3.8			
			550	−1.08	45.3	12.0	3.5			
1r2t3c-Trimethylcyclohexane (eee)	0.395	55.8	350	5.02	49.6	13.0	2.5	418–483	48.3	12.6
			400	2.91	48.5	12.7	2.7			
			450	1.31	47.4	12.4	2.8			
			500	0.057	46.2	12.1	2.8			
			550	−0.94	45.0	11.8	2.7			
1r2t4t5c-Tetramethylcyclohexane (eeee)	0.390	63.1	350	7.30	58.2	13.7	2.1	423–483	57	13
			400	4.82	57.3	13.4	2.4			
			450	2.92	56.3	13.1	2.6			
			500	1.43	55.1	12.8	2.8			
			550	0.23	54.0	12.6	2.9			
1r2c4t5t-Tetramethylcyclohexane (eaea)	0.418	57.2	350	5.83	51.9	13.0	2.6	423–483	49	12
			400	3.62	50.8	12.7	2.7			
			450	1.94	49.7	12.3	2.7			
			500	0.63	48.6	12.1	2.6			
			550	−0.43	47.5	11.8	2.6			

cyclohexanes on GTCB (this work) and on Apiezon L[13]. The range of I values on GTCB for the 1,3,5-isomers is 1.7 times greater than that on Apiezon L; for the 1,2,3-isomers this range is 1.4 times greater and for the 1,2,4-isomers 3 times greater.

This high sensitivity of the retention on GTCB to the geometric features of the molecular structure of the polymethylcyclohexanes permitted an analysis of this series of compounds with similar physical properties on a short packed column of low efficiency. While maintaining such a high selectivity of the adsorbent (GTCB or carbochromes[28]) the next task is to obtain a substantial increase in the efficiency of the packed column and the preparation of suitable capillary adsorption columns.

Molecular statistical calculation of the adsorption properties

Table V gives the thermodynamic characteristics of adsorption (K_1, $\overline{\Delta U_1}$, ΔS_1^* and $\overline{\Delta C_1}$) for the adsorption on GTCB of cyclohexane and some of its methyl derivatives obtained by a molecular statistical calculation using the atom–atom approximation.

This method of calculation[18,20] was developed for the adsorption of quasi-rigid molecules; it assumes free movement of the molecules along a homogeneous surface and harmonic oscillation perpendicular to the surface. When rotational isomers were present, it was assumed[18,20] that each of the rotational isomers was adsorbed as a quasi-rigid molecule. The potential energy of intermolecular interaction of the molecule with the adsorbent is calculated for 625 combinations of Euler's angles, ψ and θ, characterising the orientation of the molecule on the surface; the values z_{00} and Φ_{00} in Table V are the distance of the centre of mass of the molecule from the surface and the potential energy in the deepest potential minimum, respectively.

In this work we used two potential functions for the interaction of carbon and hydrogen atoms in the molecules of the adsorbate with the carbon atoms of graphite, which were obtained for alkanes[18,20,29]:

$$\varphi_{C(alkane)\ldots C(graphite)} = -1.386 \cdot 10^{-3}\, r^{-6} - 2.148 \cdot 10^{-5}\, r^{-8} +$$
$$+ 1.89 \cdot 10^5 \exp(-35.7\, r)$$
$$\varphi_{H(alkane)\ldots C(graphite)} = -0.498 \cdot 10^{-3}\, r^{-6} - 0.950 \cdot 10^{-5}\, r^{-8} +$$
$$+ 3.60 \cdot 10^4 \exp(-35.7\, r)$$

where the distance r is expressed in nanometres and φ in kilojoules per mole.

For cyclohexane in the chair form with tetrahedral angles (Fig. 6), the calculation was carried out with lengths of the C–C and C–H bonds of 0.154 and 0.110 nm (curve 1) and 0.153 and 0.109 nm (curve 2). The decrease in the bond lengths leads to an increase in the K_1 values, the difference being 4–11 % at different temperatures.

The calculation for the flattened chair form of cyclohexane (the angle CCC is 112°, the HCH angle is 108°, C–C = 0.154 nm and C–H = 0.110 nm) gives values of K_1 that are 2–3 % less than those for the molecule with tetrahedral angles. This difference is not greater than the error of the chromatographic measurements. This demonstrates the high sensitivity of the thermodynamic characteristics of adsorption and retention on GTCB to the fine details of molecular structure.

To simplify the calculations, tetrahedral angles were assumed for the methylcyclohexane (mono-, di-, tri- and tetra-); the bond lengths taken were C–C = 0.154 and C–H = 0.110 nm. The molecules were considered to be quasi-rigid with the methyl groups in the staggered conformation relative to the cyclohexane ring. With
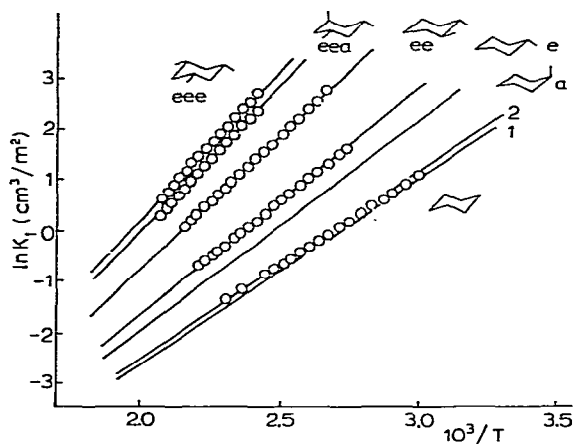
Fig. 6. Calculated values (lines) and experimental values (circles) of Henry constants for adsorption on GTCB of cyclohexane, methylcyclohexane, 1r2t-dimethylcyclohexane (ee), 1r3c5t-trimethylcyclohexane (eea) and 1r3c5c-trimethylcyclohexane (eee).
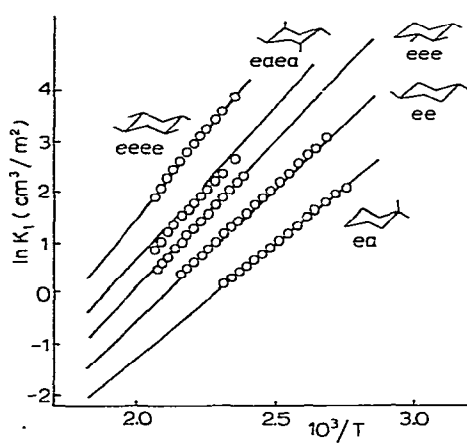
Fig. 7. Calculated values (lines) and experimental values (circles) of Henry constants for adsorption on GTCB of 1,1-dimethylcyclohexane, 1r4t-dimethylcyclohexane (ee), 1r2t3c-trimethylcyclohexane (eee), 1r2c4t5t-tetramethylcyclohexane (eaea) and 1r2t4t5c-tetramethylcyclohexane (eeee).

methylcyclohexane and 1,1-dimethylcyclohexane, the calculation was also carried out for the eclipsed conformation of the equatorial substituent relative to the ring. The values of K_1 obtained are 2–6% higher for methylcyclohexane and 6–14% higher for 1,1-dimethylcyclohexane.

The calculated line for methylcyclohexane with the axial substituent lies well below experimental points, which shows the preferability of the equatorial conformation on the surface.

The agreement of the experimental data with the results of the molecular statistical calculation can be considered to be reasonable. Although these results are preliminary and the next task is to improve the precision of the chromatographic measurements and to avoid the simplifications used in the calculation, we can draw the conclusion that the atom–atom potential functions for the intermolecular interaction of carbon and hydrogen atoms with the carbon atoms of GTCB, obtained for alkanes, can be applied successfully to the alkylcyclohexanes. Calculations using these functions will enable us to predict the retention order of derivatives of cyclohexane on GTCB and a comparison of the results of the calculation with the experimental data makes it possible to discuss the conformation of the molecules on the surface.

REFERENCES

1 Al. A. Petrov, *Khimiya Naftenov (Chemistry of Naphthenes)*, Nauka, Moscow, 1971.
2 J. V. Brunnock and L. A. Luke, *Anal. Chem.*, 40 (1968) 2158.
3 J. V. Brunnock and L. A. Luke, *J. Chromatogr.*, 39 (1969) 502.
4 V. G. Berezkin, V. S. Gavrichev and L. N. Kolomiyetz, *Gazovaya Khromatografiya v Neftekhimii (Gas Chromatography in Oil Chemistry)*, Nauka, Moscow, 1975.
5 R. E. Leveque, *Anal. Chem.*, 39 (1967) 1811.
6 W. N. Sanders and J. B. Maynard, *Anal. Chem.*, 40 (1968) 527.

7 P. Merchant, *Anal. Chem.*, 40 (1968) 2153.
8 S. S. Berman, V. A. Zacharenko and A. A. Petrov, *Neftekhimiya*, 7 (1967) 850; 9 (1969) 500.
9 Al. A. Petrov and L. P. Kolesnikova, *Zh. Anal. Khim.*, 97 (1972) 1050.
10 E. J. Gallegos, J. M. Whittemore and R. F. Klaver, *Anal. Chem.*, 46 (1974) 151.
11 G. Schomburg, *J. Chromatogr.*, 23 (1966) 18.
12 G. Dielmann, D. Schwengers and G. Schomburg, *Chromatographia*, 7 (1974) 215.
13 G. Mann, M. Mühlstädt and J. Braband, *Tetrahedron*, 24 (1968) 3607.
14 G. Mann, H. Werner, M. Mühlstädt and W. Engewald, *Tetrahedron*, 27 (1971) 3223.
15 G. Mann, H. Werner, D. Miethe and M. Mühlstädt, *Tetrahedron*, 28 (1972) 1839.
16 R. J. Sidorov and A. A. Khvostikova, *Zh. Anal. Khim.*, 30 (1975) 340.
17 A. V. Kiselev and Ya. I. Yashin, *La Chromatographie Gas–solide*, Masson, Paris, 1969; *Gas-adsorption Chromatography*, Plenum Press, New York, 1969; *Adsorbtsionnaya Gazovaya i Zhidkostnaya Khromatografiya (Gas and Liquid Adsorption Chromatography)*, Khimiya, Moscow, 1978.
18 N. N. Avgul, A. V. Kiselev and D. P. Poshkus, *Adsorbtsiya Gazov i Parov na Odnorodnykh Poverkhnostiakh (Adsorption of Gases and Vapours on Homogeneous Surfaces)*, Khimiya, Moscow, 1975.
19 A. V. Kiselev, D. P. Poshkus and K. D. Shcherbakova, *J. Chromatogr. Sci.*, 12 (1974) 788.
20 A. V. Kiselev and D. P. Poshkus, *J. Chem. Soc. Faraday Trans. II*, 72 (1976) 950.
21 C. Vidal-Madjar, M. F. Gonnord and G. Guiochon, *J. Colloid Interface Sci.*, 52 (1975) 102.
22 A. S. Boikova and K. D. Shcherbakova, *Neftekhimiya*, 7 (1967) 451.
23 E. V. Kalashnikova, A. V. Kiselev, K. D. Shcherbakova and I. S. Zamanskaya, *Chromatographia*, 5 (1972) 278.
24 W. Engewald, J. Graefe, A. V. Kiselev, K. D. Shcherbakova and Th. Welsch, *Chromatographia*, 7 (1974) 229.
25 W. Engewald, G. Mann, H. Werner and K. D. Shcherbakova, *Z. Chem.*, 12 (1972) 307.
26 E. V. Kalashnikova, A. V. Kiselev, D. P. Poshkus and K. D. Shcherbakova, *J. Chromatogr.*, 119 (1976) 233.
27 V. M. Tatevskii (Editor), *Physico-chemical Properties of Individual Hydrocarbons*, Gostoptechizdat, Moscow, 1960.
28 T. V. Barmakova, A. V. Kiselev and N. V. Kovaleva, *Kolloidn. Zh.*, 36 (1974) 133 and 934.
29 D. P. Poshkus and A. J. Afreimovitch, *J. Chromatogr.*, 58 (1971) 55.