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Determination of contributions of different types of solute–sorbent interactions in gas-adsorption chromatography by linear regression of adsorption energies

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ABSTRACT

The gas chromatographic adsorption energies of 30 sorbates were processed by using descriptors which define dispersion, orientation and donor–acceptor interactions. Hydrogen treated, thermally graphitized carbon black, barium sulphate and a porous polymer of medium polarity were used as sorbents. A four-variable regression equation for all sorbents with $R \approx 0.97$ and a relative standard deviation of *ca.* 5% was developed. The importance of the different solute–sorbent interactions (SSI) for each sorbent studied is discussed. The contributions of the SSI to the total adsorption energy of Rohrschneider's substances for the sorbents were calculated.

INTRODUCTION

The concept of polarity is widely used for both the classification and the selection of sorbents for gas chromatographic (GC) analyses. This concept expresses the ability of a sorbent to show predominant retention of polar molecules in comparison with non-polar *n*-alkanes. Rohrschneider's method of polarity determination based on the differences in Kováts retention indices (RI) of the set of solutes on two stationary phases is widely used [1]. A method taking into account the energetic inequivalence of RI units on different stationary phase has also been described [2]. Various publications has been devoted to RI simulation [3–7] and to establishing their dependence on adsorbent and adsorbate parameters [8]. As any differences in the polarities and selectivities of sorbents are primarily associated with changes in the nature of solute–sorbent interactions (SSI), the quantitative relationship of the contributions of various types of SSI may be considered as a measure of a sorbent's polarity and selectivity.

We have attempted to obtain a quantitative description of the GC properties of adsorbents by dividing the adsorption energies and RI into components describing different types of SSI. This paper deals with a description of adsorption energies. In a subsequent paper the possibility determining the polarity and selectivity of adsorbents by using the same method for RI will be considered.

THEORY

Adsorption energy may be represented as follows (if no charge-transfer complexes form):

$$\Delta U_{\text{ads.}} = \Delta U_{\text{disp.}} + \Delta U_{\text{ind.}} + \Delta U_{\text{or.}} + \Delta U_{\text{hydr.}} \tag{1}$$

The expressions for the first three terms are well known [9,10].
The energy of hydrogen bond formation may be represented by

$$\Delta U_{\text{hydr.}} = Wd_a Wa_s + Wa_a Wd_s \tag{2}$$

where Wa_s and Wd_s are electron-acceptor and electron-donor energetic constants of a sorbate molecule and Wd_a and Wa_a are the same constants of a counterpart (in our case an adsorbent surface) [11]. It is worth noting that the hydrogen bond constants Wa and Wd are related to similar constants for charge-transfer complexes [11]. We assumed that eqn. 2 can be inserted in eqn. 1 to describe in some way donor–acceptor SSI in general.

Substituting the well known expressions for $\Delta U_{\text{disp.}}$, $\Delta U_{\text{ind.}}$ and $\Delta U_{\text{or.}}$ [9,10] and eqn. 2 into eqn. 1 and performing some simplifications, the following equation was obtained:

$$\Delta U = K_1\alpha + K_2(2\mu^2/3kT + \alpha) + K_3 Wa + K_4 Wd + K_5 \tag{3}$$

where α is the polarizability of a sorbate molecule, μ its dipole moment and Wa and Wd its electron-acceptor and -donor constants. The coefficients K_1–K_4 are proportional to athe physico-chemical adsorbent characteristics involved in the expressions for each type of SSI. The term K_5 was included in eqn. 3 to account for neglected SSI. Accordingly, a knowledge of the coefficient values would allow us to establish the ability of an adsorbent to effect certain SSI quantitatively.

Eqn. 3 is applicable to multiple linear regression, in which case desired values of the coefficients for a sorbent may be obtained by using molecular parameters of a set of sorbates and their adsorption energies on the sorbent.

The physico-chemical and topological parameters of sorbate molecules were obtained by the following way. Polarizability was calculated from the Lorentz-Lorenz equation:

$$\alpha = \frac{3}{4\pi L} \cdot V_m \cdot \frac{(n^2 - 1)}{(n^2 + 2)} \tag{4}$$

where V_m is the molar volume and n is the refractive index. Dipole moments were taken from ref. 12 and the constants Wd and Wa for the gas phase were calculated from the data in ref. 11. To take into account steric effects, some topological descriptors were also involved. The molecular connectivity indices (MCI) of the first order were calculated from the expression

$$^1\chi = \sum_{}^{n} (\delta_i \, \delta_j)^{-1/2} \tag{5}$$

where n is the number of valence bonds in a molecule and δ_i and δ_j are the number of atomic valences directed to the adjoining non-hydrogen (e.g., C, O, N) atoms. For cyclic molecules the allowance for a ring of 0.5 was subtracted from the values of $^1\chi$. MCI of the second order were calculated from the expression

$$^2\chi = \sum_{}^{k} (\delta_i \, \delta_j \, \delta_m)^{-1/2} \tag{6}$$

where k is the number of all three atom chains in a molecule (with multiple bonds taken into account). Further details of the theory of MCI can be found elsewhere [13].

EXPERIMENTAL

The method proposed above was used to process literature data on the adsorption energies (ΔU) for the non-polar adsorbent hydrogen treated thermally graphitized carbon black (HT GTCB) (adsorbent I [14]) and for polar $BaSO_4$ modified with NaCl (adsorbent III [15]). Our experimental data for a porous polymer of medium polarity (adsorbent II) were also processed. This adsorbent is a copolymer of ethylene dimethacrylate (EDMA) with epithiopropyl methacrylate (ETPMA) with a specific surface area of 66 m^2/g and containing 11% of suphur [16].

The determination of adsorption energies was performed with a Tswett-165 chromatograph with flame ionization detection. Glass columns (50 cm × 1.2 and 3 mm I.D.) were used. The flow-rate of the carrier gas (helium) was 4–8 cm/s. Before measurements the sorbent was warmed for 6 h in a helium flow at 190°C. The heats of adsorption were measured in the range 135–175°C. Kováts retention indices at 150°C were calculated.

A set of 30 substances was used for regression analyses on the adsorbents studied. It included n-alkanes, n-alkenes, aromatic hydrocarbons, alcohols, ethers, alkylacetates, ketones, nitroalkanes, chloro-substituted compounds and pyridine. Because of the different polarities of the adsorbents, the compositions of the sets of compounds on each adsorbent were slightly different.

We used ref. 17 as the mathematical basis for the multiple linear regression. BASIC programs with matric operators were performed on an Iskra 226 personal computer.

The correlation coefficient r and standard error s were used to evaluate the regression fits.

RESULTS AND DISCUSSION

Discussion of eqn. 3

First the regression analyses were performed in accordance with eqn. 3. The results for each substance on HT GTCB are shown in the first column of Table I, and the integrated results for all adsorbents in the first column of Table II. As HT GTCB is a non-polar adsorbent, all deviations of the calculated ΔU values from the experimental values seem to be connected only with the rough description of dispersion SSI by the $K_1\alpha$ term in eqn. 3. These deviations are probably associated with

TABLE I

REFERENCE VALUES $-\Delta U$ ON HT GTCB [14] AND THEIR DEVIATIONS AGAINST THOSE
CALCULATED WITH EQN. 8 WITH DIFFERENT G

All values in kJ/mol.

No.	Solute	$-\Delta U$ [14]	Deviation without G	G_1	Deviation with G_1	G_2	Deviation with G_2
1	Hexane	39.4	+0.5	0.78	−1.0	0.67	−2.1
2	Heptane	44.0	+0.4	0.82	−1.2	0.70	−2.2
3	Octane	49.4	+0.4	0.86	−0.8	0.73	−2.0
4	Nonane	55.6	−0.3	0.90	−0.8	0.75	−2.7
5	Benzene	36.2	−1.0	0.85	+0.2	0.85	+2.9
6	Toluene	44.4	−3.3	0.93	−0.8	0.81	−1.3
7	Ethylbenzene	47.9	−1.2	0.94	+0.8	0.85	+1.8
8	Fluorobenzene	38.1	−2.1	0.93	+0,5	0.89	+2.6
9	Chlorobenzene	43.8	−1.6	0.93	+0.1	0.85	+1.4
10	Bromobenzene	45.0	+0.3	0.93	+1.5	0.82	+1.9
11	*n*-Propanol	28.6	−1.5	0.71	−1.1	0.77	+0.1
12	Isopropanol	28.0	−0.8	0.79	+1.0	0.68	−1.3
13	*n*-Butanol	34.7	−2.2	0.75	−2.8	0.80	−0.6
14	Isobutanol	31.4	+1.2	0.80	+1.7	0.74	+1.2
15	*sec.*-Butanol	31.6	+0.7	0.80	+1.3	0.75	+0.8
16	*tert.*-Butanol	30.2	+2.7	0.65	−0.4	0.64	−0.4
17	Diethyl ether	31.6	+1.1	0.75	−0.6	0.70	−0.9
18	Di-*n*-propyl ether	41.6	+2.6	0.82	0.0	0.74	−0.1
19	Di-*n*-butyl ether	53.3	+1.1	0.90	−0.5	0.79	−0.8
20	Acetone	26.9	+0.9	0.81	+0.7	0.70	−1.1
21	Methyl ethyl ketone	32.9	+0.2	0.81	−1.3	0.76	−1.1
22	Methyl *n*-propyl ketone	37.7	+0.5	0.85	−0.9	0.78	−0.7
23	Methyl *n*-butyl ketone	42.9	+0.7	0.89	−0.6	0.80	−0.5
24	Ethyl acetate	34.8	−2.1	0.92	+0.2	0.86	+0.4
25	*n*-Propyl acetate	39.9	−1.7	0.96	+0.9	0.86	+0.7
26	*n*-Butyl acetate	44.9	−1.1	1.00	+2.1	0.86	+1.3
27	Dichloromethane	23.9	0.0	0.67	+0.3	0.67	+0.6
28	Chloroform	28.9	+0.6	0.79	+1.9	0.65	−0.4
29	Carbon tetrachloride	30.3	+4.5	0.65	+0.3	0.63	+1.2
30	1,2-Dichloroethane	29.3	+0.5	0.71	−0.6	0.73	+1.4

TABLE II

CORRELATION COEFFICIENTS r AND RELATIVE STANDARD DEVIATIONS s FOR $-\Delta U$
ANALYSES ON THREE SORBENTS WITH EQN. 8 WITH DIFFERENT G

Sorbent	with $G=1$		with G_1		with G_2	
	r	s (%)	r	s (%)	r	s (%)
HT GTCB	0.980	4.7	0.991	3.2	0.984	4.2
EDMA–ETPMA	0.905	5.5	0.952	4.0	0.971	3.1
BaSO$_4$	0.960	9.2	0.970	8.0	0.971	7.8

the fact that large molecules do not contact a surface with all of their atoms. This phenomenon may be taken into account by including in the term $K_1\alpha$ some steric factor ($G \leqslant 1$) for each molecule. Hence the product $K_1 G\alpha$ should have the meaning of the effective polarizability of a molecule for adsorption on a surface.

The steric factor was generated by means of spatial characteristics of a molecule (molar volume and MCI of various orders) in two ways, as follows. Modelling a relatively simple expression for G, providing minimum deviations of ΔU on HT GTCB and further using of G values obtained for adsorption on all other surfaces, we obtained the following expression:

$$G_1 = {}^2\chi/9 - 0.56\ {}^4\chi_c + 0.6 \qquad (0.65 \leqslant G \leqslant 1) \tag{7}$$

(2) It was noted that ratio $Z = {}^1\chi/V_m$ was high for planar or small molecules (carbon dioxide, benzene, pyridine, dioxane, nitromethane) whereas small Z values are characteristic of long-chain molecules with mobile segments (*n*-alkane, *n*-alkenes, ethers) or highly branched molecules (*tert.*-butanol, neopentane,). Assuming that the molecules with maximum Z value have the best contact with a surface, one can assume that relationship $G_2 = Z/Z_{max}$ reflects the degree of engagement of a molecule with a surface. Values of G obtained in such a way were $0.63 \leqslant G_2 \leqslant 1.00$. Both values, G_1 (obtained by the first method) and G_2 (by the second) are given in Table I.

Inclusion of any of these steric factors in eqn. 3 decreases the standard error and increases the correlation coefficient of regression analyses while the number of adjustable terms was invariant (see Table II). However, the use of the steric factor G_2 is preferable because it has a physical meaning and its value has a better correlation with the stereochemistry of molecules (*e.g.*, *n*-butanol 0.80, isobutanol 0.74, *tert.*-butanol 0.64). Therefore, the final form of the eqn. 3 for all adsorbents is

$$\Delta U = K_1 G\alpha + K_2(2\mu^2/3kT + G\alpha) + K_3 Wa + K_4 Wd + K_5 \tag{8}$$

Although eqn. 8 is fairly simple, it involves all kinds of SSI which are of importance in GC [18].

The parameters of sorbate molecules in eqn. 8 are uncorrelated with each other. The correlation matrix is given in Table III.

Results of data processing

The results of the three adsorbent analyses using eqn. 8 are shown in Table IV and in Figs. 1–3. All regression coefficients are given with their standard errors. The significance of every regression coefficient (in this instance it is the significance of a certain type of SSI for adsorption on the adsorbent) may be obtained from Student's *t*-test as ratio of the coefficient to its standard error ($t = K_i/s_i$); t values are given in Table IV.

The t values show that for HT GTCB such sorbent characteristics as dipole moment on the surface and electron-donor and electron-acceptor ability of the surface have negligible deviations from zero. This is in accordance with HT GTCB being a non-polar sorbent and with the absence of any functional groups being able to undergo specific SSI on its surface.

On polymer sorbent II, dispersion SSI are also of most importance. In addition,

TABLE III

CORRELATION MATRIX FOR DESCRIPTORS USED IN EQN. 8

Descriptor	αG	μ^2	Wa	Wd	
αG	1.00	−0.435	−0.587	−0.465	
μ^2		1.000	−0.062	0.164	
Wa			1.000	0.386	
Wd					1.000

TABLE IV

REGRESSION COEFFICIENTS K_i WITH THEIR STANDARD ERROR AND STUDENT'S t-TEST ON THREE SORBENTS OBTAINED WITH EQN. 8 WITH G_2.

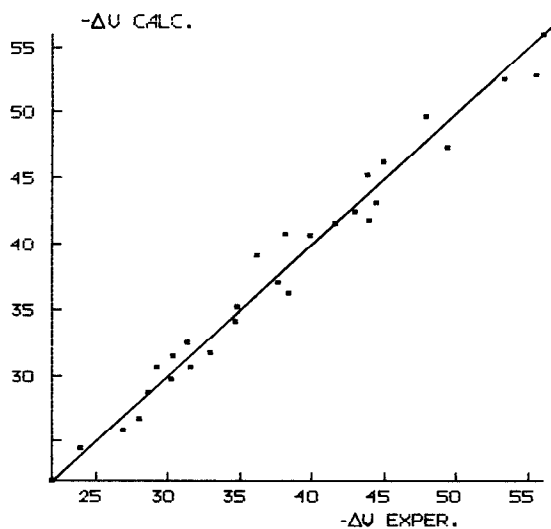| Coefficient	HT GTCB		EDMA–ETPMA		$BaSO_4$	
	K_i	t	K_i	t	K_i	t
K_1	33.1 ± 1.4	23.1	30.9 ± 1.5	20.1	18.1 ± 4.3	4.2
K_2	1.5 ± 1.1	1.0	8.1 ± 0.9	9.3	41.4 ± 3.4	12.3
K_3	1.0 ± 1.4	0.7	13.2 ± 1.2	11.0	35.2 ± 4.1	8.6
K_4	0.1 ± 0.8	0.1	5.2 ± 0.6	8.2	14.2 ± 1.7	8.3
K_5	9.6 ± 1.5	6.5	13.1 ± 1.8	7.2	10.2 ± 5.1	2.0
s (%)	4.2		3.1		7.8	
r	0.984		0.971		0.971	

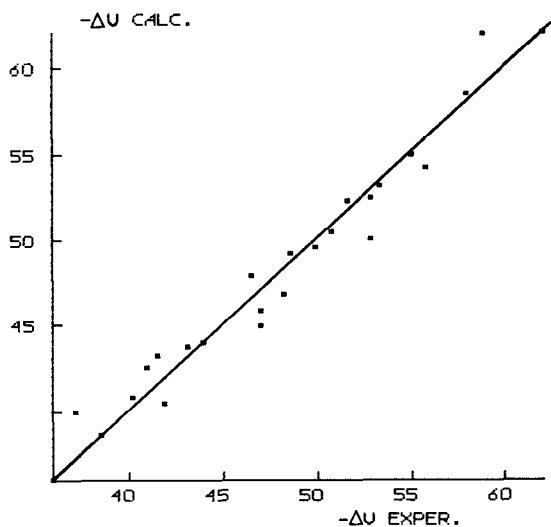Fig. 1. Experimental and calculated values of $-\Delta U$ (kJ/mol) on HT GTCB.

Fig. 2. Experimental and calculated values of $-\Delta U$ (kJ/mol) on EDMA–ETPMA.

the specific SSI induced by carboxy and epithio groups are significant. Some electron-acceptor capability of the surface (K_4) apparently may account for the partial positive charge of the carbon atom in the carboxy group.

As expected, on ionic $BaSO_4$ the orientation SSI caused by the spatial separation of charges on the surface is most significant. The electron-donor capability of SO_4^{2-} and the electron-acceptor capability of Ba^{2+} are also of importance for adsorption. The significance of dispersion SSI on this adsorbent is minimal in comparison with specific SSI.
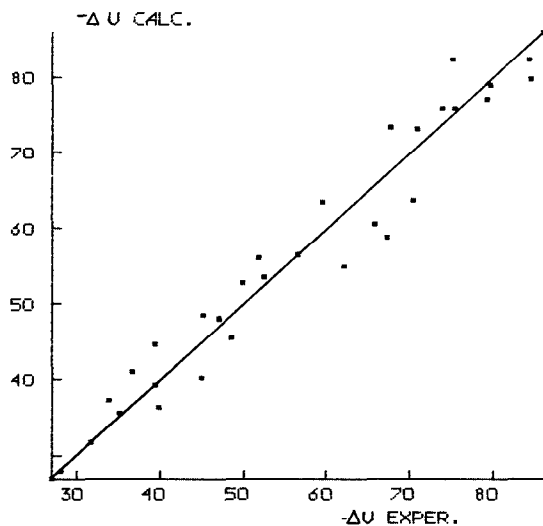

Fig. 3. Experimental and calculated values of $-\Delta U$ (kJ/mol) on $BaSO_4$.

TABLE V

CONTRIBUTIONS OF DIFFERENT KINDS OF SSI TO TOTAL ADSORPTION ENERGY ΔU (%)

Sorbate	Adsorbent	Dispersion	Orientation and induction	Electron acceptor	Electron donor
Benzene	I	100	0	0	0
	II	93	2	0	5
	III	72	0	0	18
n-Propanol	I	96	2	2	0
	II	61	6	20	13
	III	25	20	34	21
Methyl ethyl ketone	I	96	4	0	0
	II	71	17	0	12
	III	28	52	0	20
Nitromethane	I	—	—	—	—
	II	66	27	0	7
	III	—	—	—	—
Pyridine	I	—	—	—	—
	II	—	—	—	—
	III	32	32	0	36

Consideration of the coefficient values for three adsorbents leads to following conclusions. The pronounced decrease in K_1 for transfer from HT GTCB and the porous polymer to $BaSO_4$ represents the change to a surface consisting of hardly polarizable ions instead of molecular structures. The appreciable increasing in K_2 from 8.1 to 41.1 for the pair II–III seems to be connected with the ionic character of the $BaSO_4$ surface. The changes in K_3 and K_4 from zero to certain values indicate the occurrence of electron-donor and electron-acceptor centres on the surfaces.

The polarity of adsorbents calculated on the basis of the "specific" coefficients K_2–K_4 increases considerably in the sequence HT GTCB < EDMA–ETPMA < $BaSO_4$, as expected.

The coefficients K_1–K_5 obtained allow us to calculate different SSI contributions to the total adsorption energy. The contributions correspond to the summands of eqn. 8. As the free term K_5 on all adsorbents was highly correlated with coefficient K_1, K_5 can be assigned to dispersion SSI. All other coefficients were uncorrelated. The correlation matrix is given in Table VI.

TABLE VI

CORRELATION BETWEEN THE REGRESSION COEFFICIENTS

Coefficient	K_1	K_2	K_3	K_4	K_5
K_1	1.00	0.559	0.615	0.253	−0.947
K_2		1.000	0.433	−0.022	−0.627
K_3			1.000	−0.152	−0.581
K_4				1.000	−0.447
K_5					1.000

Contributions calculated in such a manner are given in Table V. The contribution of dispersion SSI is about 100% on HT GTCB for all substances and decreases for polar molecules on polar adsorbents; it is only 25% for *n*-propanol on $BaSO_4$. The orientation contribution on the polymer adsorbent is rather small. On ionic $BaSO_4$ it is predominant for molecules with high dipole moments (*e.g.*, 52% for methyl ethyl ketone). The electron-donor ability of the surface of EDMA–ETPMA or $BaSO_4$ takes effect for the adsorption of alcohols only. With $BaSO_4$ this contribution is predominant (34%). The electron-acceptor capability of the adsorbents surfaces of II and III takes effect for all substances of Rohrschneider's series and reach a maximum for pyridine.

The method developed seems to be of some interest for the determination of adsorbent capability for different kinds of SSI in GC.

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