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RETENTION AND HEATS OF ADSORPTION OF HYDROCARBONS AND ALIPHATIC ALCOHOLS ON CELLULOSE

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SUMMARY

The interaction of methanol, ethanol, *n*-propanol, *n*-butanol, *n*-hexane, *n*-octane, *n*-nonane, *n*-decane, benzene, toluene and ethylbenzene molecules with the surface of microspherical cellulose beads has been studied by gas chromatography. The retention volumes and their dependences on the temperature and molecular parameters of the adsorbate have been determined. The initial differential heats of adsorption have been calculated. The character of interaction of these organic substances has been shown to be determined by the electronic and geometric structures of the molecules.

INTRODUCTION

Polymeric organic sorbents, including those based on polysaccharides, are widely used in liquid column and planar chromatography. Therefore, the macroporous microspherical cellulose (MC), synthesized and studied at the Institute of Macromolecular Chemistry of the ČSSR Academy of Sciences, is of some interest for chromatographic methods[1]. This cellulose was tested in liquid chromatography of dextrans and found to have quite satisfactory properties for the separation of water-soluble biopolymers[2]. It was also proposed for use in gas and liquid adsorption chromatography of low-molecular-weight substances[3,4]. Therefore, an evaluation of the interaction parameters of model organic substances with the cellulose surface is important, *e.g.*, in gas chromatography of organic substances on cellulose columns[3,4].

EXPERIMENTAL

Adsorbent

A sample of microspherical macroporous cellulose was kindly provided by Dr. J. Hradil (Institute of Macromolecular Chemistry, Prague, Czechoslovakia). The preparation of samples of cellulose beads has been described in detail in refs. 1 and 2. The specific surface area of the sample determined by means of the BET method by low-temperature adsorption of nitrogen was equal to 110 m^2/g. The average diameter of the pores determined by the method of small-angle scattering of X-rays was 280 Å.

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Apparatus

A Tswett-104 gas chromatograph (NPO Chimavtomatica, U.S.S.R.) with a flame ionization detector was employed. The column (20 cm × 3 mm I.D.) was packed with 0.3 g cellulose. The diameters of the cellulose beads were 0.2–0.25 mm. Helium was used as the carrier gas at a flow-rate of 30 cm^3/min. The sample vapours were introduced into the column by a heated injection port, using a microsyringe (1 μl). Methane was used as the non-adsorbed gas. Prior to chromatographic measurements, the cellulose beads in the column were dried in the carrier gas stream at 110°C for 2 h.

In order to calculate the retention volumes, V, and then the adsorption heats, $-\Delta\bar{U}$, the corrected retention times of the vapours of adsorbed substances were determined from the maxima of chromatographic peaks from series of injections at very low concentration. The values of V were calculated according to

$$V = \frac{t_R w P T_c}{T P_o} \cdot \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{1}$$

where t_R = corrected retention time in min, w = the flow-rate of carrier gas in ml/min, P_i, P_o, P are the pressures at the inlet and outlet of the column and that corrected for the presence of water vapour in the flow-meter, respectively, T_c and T are the temperatures of the column and of the flow-meter, respectively. The absolute retained volume, V_A, was calculated according to[5]

$$V_A = V/ms \tag{2}$$

where m is the mass of cellulose in the column and s its specific surface area. The retention values for each adsorbate were calculated from at least ten chromatographic peaks at each temperature. The accuracy was 5%.

The values of the differential adsorption heats were calculated on the basis of the dependence of the experimental values of the retention volumes on the temperature:

$$-\Delta\bar{U} = R \, \mathrm{d} \ln (V/T)/\mathrm{d}(1/T) \tag{3}$$

RESULTS

Fig. 1 shows chromatograms of *n*-alkanes (a) and aromatic hydrocarbons (b). The peaks are symmetrical, and the retention times do not depend on the amount of vapour injected over a range of one order of magnitude. Fig. 1c shows examples of the separation of a mixture of three substances: namely, *n*-heptane, toluene and *n*-propanol, *i.e.*, substances with similar boiling points (100–110°C). The separation of these substances in a chromatographic column proceeds due to specific interaction of molecules with different chemical structures with the cellulose surface.

Fig. 2 shows the dependences of log V/T on $1/T$ for hydrocarbons and alcohols. These graphs allow us to calculate the values of the differential adsorption heats, and are practically linear over the temperature range of 60–110°C.

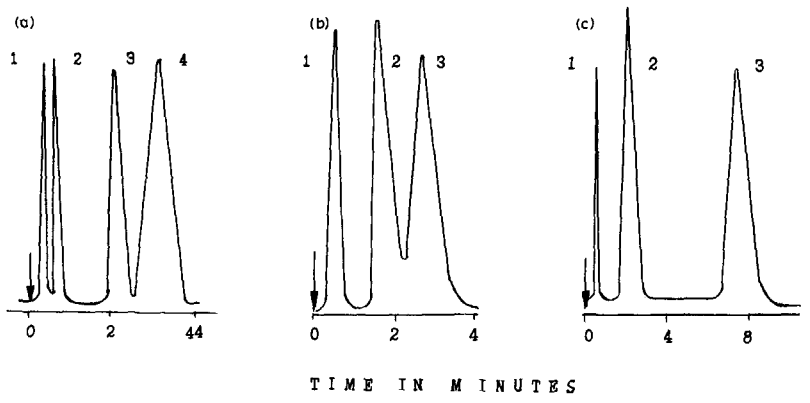

Fig. 1. Gas chromatograms on microspherical cellulose at 100°C. (a) *n*-Alkanes: 1 = *n*-hexane; 2 = *n*-heptane; 3 = *n*-octane; 4 = *n*-nonane. (b) Aromatic hydrocarbons: 1 = benzene; 2 = toluene; 3 = ethylbenzene. (c) 1 = *n*-Heptane; 2 = toluene; 3 = *n*-propanol.

DISCUSSION

Table I gives the values of the retention volumes, V_A, of *n*-alkanes, aromatic hydrocarbons and aliphatic alcohols on microspherical cellulose at 100°C, as well as the differential adsorption heats of these substances calculated from the chromatographic data. For comparison, the Table gives the values $-\Delta\bar{U}$ on C-120 silochrome[6], graphitized carbon black[5] and immobilized polymeric sorbent polyarylate[7]. The V_A

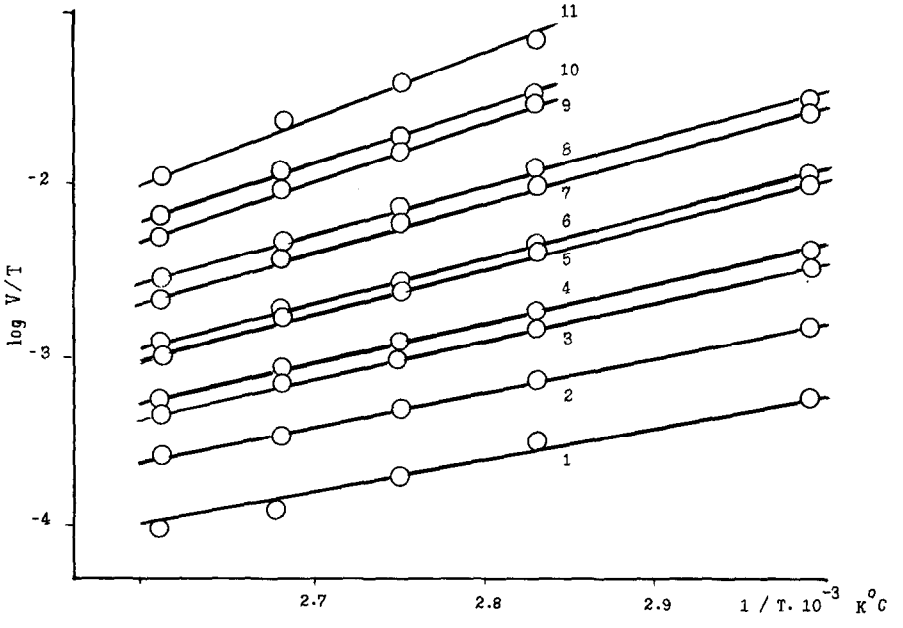

Fig. 2. Dependence of log V/T on $1/T$ for *n*-pentane (1), *n*-hexane (2), benzene (3), *n*-heptane (4), toluene (5), *n*-heptane (6), ethylbenzene (7), *n*-nonane (8), *n*-propanol (9), *n*-decane (10) and *n*-butanol (11).

TABLE I

VALUES OF V_A AT 100°C AND OF $-\Delta\bar{U}$ FOR ORGANIC SUBSTANCES UPON INTERACTION WITH CELLULOSE (MC), C-120 SILOCHROME[6], GRAPHITIZED CARBON BLACK[5] AND POLYARYLATE[7]

Adsorbate	V_A *(cm³/m²) MC*	$-\Delta\bar{U}$ *(kJ/mol)*			
		MC	*C-120*	*Carbon black*	*Polyarylate*
n-Pentane	0.067	33.5	–	37.4	–
n-Hexane	0.12	37.1	37.3	43.7	55.4
n-Heptane	0.27	42.4	41.1	52.5	64.0
n-Octane	0.62	48.1	–	56.3	72.8
n-Nonane	1.4	52.4	48.8	62.2	80.4
n-Decane	3.5	57.9	53.1	70.1	–
Benzene	0.21	41.1	41.1	41.2	62.3
Toluene	0.61	46.1	45.5	48.7	71.3
Ethylbenzene	1.3	53.3	49.3	53.3	–
Methanol	1.9	61.9	35.9	–	41.3
Ethanol	1.7	61.7	37.8	29.0	51.7
n-Propanol	3.4	70.3	39.7	34.0	59.1
n-Butanol	7.2	75.5	–	39.5	68.1

values at low concentrations of the adsorbate at equilibrium appear to be the Henry constants which characterize the adsorbent–adsorbate system at a given temperature[5]. Table I shows that, in the interaction of normal hydrocarbon molecules with the surface of microspherical cellulose, the Henry constant $K = V_A$ and $-\Delta\bar{U}$, characterizing the change in the internal energy of adsorption, increase in the homologous series with an increase in the molar volume and average polarizability of the molecules. However, the effect of the molar volume becomes less pronounced due to differences in the geometric and electronic structures of the molecules of the sorbates studied.

The molecules of toluene and ethylbenzene have volumes close to those of *n*-heptane and *n*-octane, respectively, but they are retained in the column 2–2.5 times longer. Alcohol molecules having a free electron pair at the oxygen atom are retained much longer than *n*-alkanes, though their molar volume is smaller.

A comparison of $-\Delta\bar{U}$ values shows that the heats of adsorption of *n*-alkanes on the MC surface are lower than those for graphitized carbon black, approximately equal to $-\Delta\bar{U}$ values for C-120 and considerably less than those for polyarylate. Initial adsorption heats of alcohols on the cellulose surface exceed $-\Delta\bar{U}$ values for all the sorbents, and this appears to be characteristic of the cellulose sorbent.

Fig. 3 shows the dependence of $-\Delta\bar{U}$ for homologous series of *n*-alkanes, alkylbenzenes and *n*-alcohols on the polarizability of the molecules. These dependences are linear to a first approximation. The $-\Delta\bar{U}$ values of aromatic compounds and alcohols capable of specific interaction exceed those of *n*-alkanes having the same numbers of carbon atoms. The values $\Delta(-\Delta\bar{U})$ calculated from these dependences show a contribution of the specific interaction of the molecules of alcohol and alkylbenzenes with the surface hydroxyl groups of cellulose. In the case of aromatic compounds, the $\Delta(-\Delta\bar{U})$ values are on average equal to 7–9 kJ/mol; in the case of

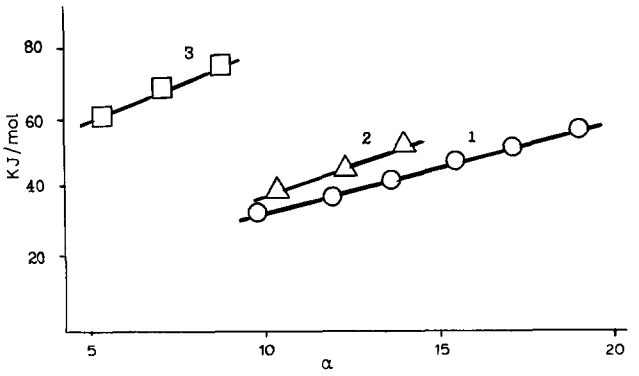

Fig. 3. Dependence of differential adsorption heats, $-\Delta\bar{U}$, of *n*-alkanes (1), alkylbenzenes (2) and *n*-alcohols (3) on the average polarizability of the molecules. α in Å.

alcohols they are equal to 42–45 kJ/mol. The concentrated electron density at the periphery of the π-bonds in aromatic molecules and at the oxygen atom of alcohol molecules is responsible for the specific interaction of these molecules with the partly protonized hydrogen atoms of the hydroxyl groups of the cellulose surface. The specific interaction of the alcohol molecules exhibits an higher energy than that of the alkylbenzene molecules, probably due to the formation of hydrogen bonds between the alcohol molecules and the cellulose hydroxyl groups, the bond strength being equal

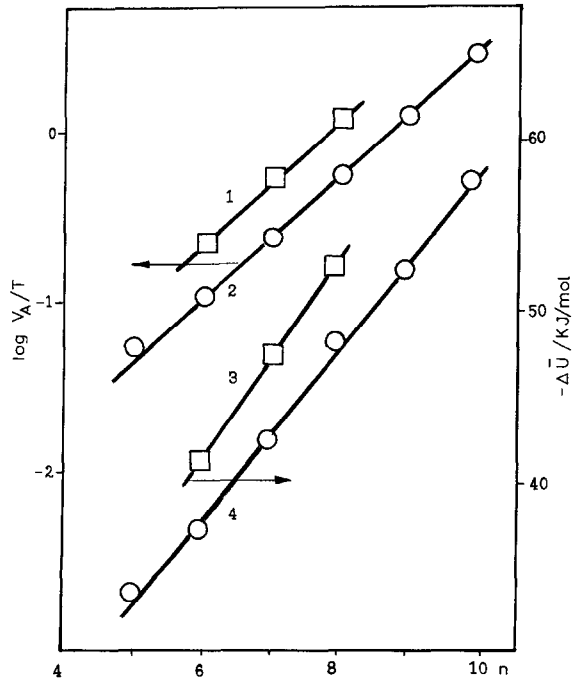

Fig. 4. Dependences of log V_A and $-\Delta\bar{U}$ on the number of carbon atoms, *n*, in *n*-alkanes and aromatic hydrocarbons.

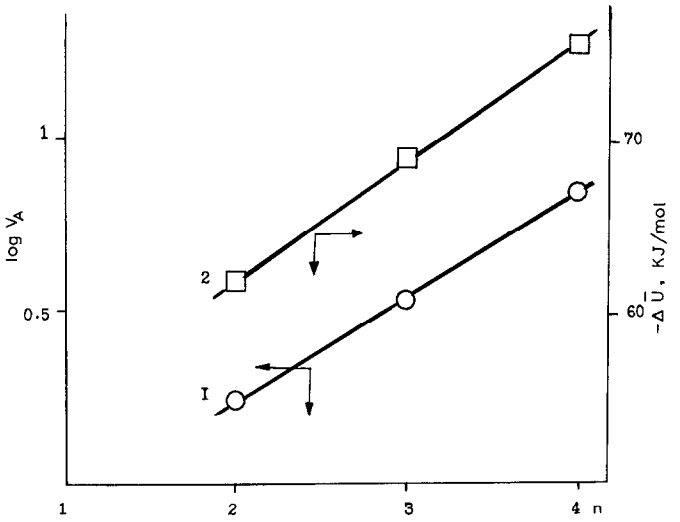

Fig. 5. Dependences of log V_A and $-\Delta\bar{U}$ on the number of carbon atoms, n, in alcohols.

to 40 kJ/mol. The strength of the adsorption interaction of alcohols with the surface of microspherical cellulose particles is determined by the energy of the hydrogen bond formation. The heat of adsorption also depends on the structure of the adsorbent pores.

The dependences of log V_A and $-\Delta\bar{U}$ on the number of carbon atoms, n, in the n-alkanes, aromatic hydrocarbons (Fig. 4) and alcohols (Fig. 5) were plotted on the basis of the chromatographic data. These dependences are satisfactorily described by the equations $\log V_A = a + bn$ and $-\Delta\bar{U} = \bar{a} + \bar{b}n$. This allows one to predict retention and the $-\Delta\bar{U}$ values for individual members of homologous series as well as to evaluate the contributions of the specific interaction of functional groups or bonds and the increments due to CH_2 groups in retention and the heat of adsorption on cellulose. Table II gives the values of the coefficients in these equations for the adsorption of n-alkanes, aromatic hydrocarbons and alcohols with the surface of microspherical cellulose. The increment in $-\Delta\bar{U}$ for non-specific interaction by one CH_2 group is equal to 6.1 kJ/mol for n-alkanes, 6.9 kJ/mol for n-alcohols and 5.2

TABLE II
VALUES OF THE COEFFICIENTS OF a AND b IN THE EQUATIONS FOR ADSORPTION ON CELLULOSE (MC) AND CHROMOSORB 101

Adsorbates	$\log V_A = a + bn$		$-\Delta\bar{U} = \bar{a} + \bar{b}n$			
	MC		*MC*		*Chromosorb 101*	
	a	b	$\bar{a}$	$\bar{b}$	$\bar{a}$	$\bar{b}$
n-Alkanes	−3.14	0.37	7.6	6.1	11.7	6.4
Alkylbenzenes	−2.76	0.37	6.0	5.2	—	
n-Alcohols	−0.09	0.31	54.6	6.9	29.5	6.4

kJ/mol for aromatic hydrocarbons. The data[8] for Chromosorb 101 are given for comparison. The values of the increment are on average similar for these polymers. However, the coefficients a and b seem to change with a change in the type of homologous series and chemical nature of the adsorbent surface.

CONCLUSIONS

The interaction of n-alkanes, aromatic hydrocarbons and alcohols with a sample of microspherical cellulose has been studied by means of gas chromatography. The values of the retention volume, V_A, of these organic substances were determined at 60, 80, 90, 100 and 110°C. Using the temperature dependence of V_A, the differential adsorption heats $-\Delta\bar{U}$, characterizing the adsorption energy of the molecules of the adsorbates studied upon interaction with the surface of microspherical cellulose have been calculated. The contribution of the specific interaction to the total heat of adsorption of aromatic hydrocarbons and alcohols upon interaction with the cellulose surface has been evaluated. It has been shown that microspherical cellulose can be used as an adsorbent in gas chromatography. In accordance with the classification of molecular interactions proposed by Kiselev and Yashin[5], this adsorbent can be classified as Type II, *i.e.*, a specific sorbent.

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