Estimation of cellulose polarity by gas chromatography

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ABSTRACT

   The interaction between bead cellulose and methanol, ethanol, acetonitrile, nitromethane, acetone, 2-butanone, chlorobenzene and tetrahydrofuran during gas chromatography has been studied. From the specific retention volumes, initial differential heats of adsorption and the contributions of the specific interaction energies of molecules adsorbed to the cellulose surface to the total adsorption energy have been estimated. The calculated Kováts' indices and Rohrschneider's equation constants have been employed for comparison of the polarity and selectivity of the cellulose surface with various polymer sorbents.

INTRODUCTION

   The number of stationary phases has increased considerably in recent times. The important role in these is that of the polymeric sorbents. The most important advantage provided by these phases is the surface reactivity, allowing numerous changes in surface properties and porosity, and thus polymer sorbents are the most universally used. Up to now, there has been no comprehensive study which deals with intermolecular interactions between organic molecules and the polymer, and with the thermodynamics of these reactions.

   This study is concerned with the adsorption of low-molecular-weight compounds on bead cellulose at different temperatures and compares many known polymer sorbents.

EXPERIMENTAL

   Macroporous cellulose beads were synthesized by a procedure described elsewhere [1–4]. The sorbent particle size was 0.25–0.50 mm, the specific surface area in the dry state 110 m²/g as determined with an Areatrone analyser (Strolein, Germany), mean pore size 50 nm and pore volume 1.18 ml/g.

   Retention time was measured with a set of organic compounds within the temperature range 60–100°C by means of a Tswet 102 chromatograph with a flame

ionization detector. The cellulose sorbent was heated for 2 h at 100°C in a flow of helium (30 ml/min) prior to chromatographic measurements. The dead retention volume was determined by methane.

From the experimental retention times the corrected retention volumes, V_R, were calculated. The differential heat of adsorption, $-\Delta U$, was determined from the temperature dependence of retention volume [5]. Kováts' indices were used as relative retention parameters [6]. The classification of Rohrschneider [7,8], in a modified version by Supina [9], was used for polarity estimation of bead cellulose and some other polymer sorbents.

RESULTS AND DISCUSSION

Our results permit comparison of adsorption interactions of different molecules with polymer adsorbents and cellulose. Recently the linear dependence of logarithm of retention volume on the number of carbon atoms and molecular polarizibility α was revealed for homologous series of *n*-alkanes and aromatic compounds. The molecular non-specific interaction energy is approximately proportional to α/r^6, where r is the distance between interacting molecules. The contribution of specific interactions to the total adsorption energy is then estimated as the difference between retention data (Kováts' indices) of *n*-alkanes and organic compounds bearing functional groups. Kováts' indices, I, calculated from retention volumes of polar compounds, are summarized in Table I. Fig. 1 illustrates the relation of Kováts' indices to molecular polarizability, and the actual values are given in Table I. The highest difference is observed with alcohols, nitromethane and acetonitrile. The retention of alcohols is determined by the ability to form hydrogen bonds with the surface hydroxyl groups of the cellulose. High retention of the strongly polarized acetonitrile ($\mu = 3.96$ D) and nitromethane ($\mu = 3.44$ D) occurs owing to the specific dipole–dipole interaction with

TABLE I

RETENTION DATA OF ORGANIC COMPOUNDS ON CELLULOSE SORBENT AT COLUMN TEMPERATURE 100°C

Adsorbate	$\alpha(\text{Å}^3)^a$	$\mu(D)^b$	$\log V_R{}^c$	I^d	I^e
Methanol	3.23	1.65	2.15	935	700
Acetonitrile	4.4	3.96	2.09	919	700
Ethanol	5.06	1.7	2.10	921	670
Acetone	6.32	2.73	1.72	819	520
1-Propanol	6.89	1.66	2.35	984	640
Nitromethane	7.2	3.44	2.11	924	570
2-Butanone	8.2	2.8	1.96	885	500
Tetrahydrofuran	10.0	1.63	1.83	747	240
Benzene	10.3	0	1.28	671	170
Chlorobenzene	12.3	1.72	1.86	861	240

[a] Polarizability.
[b] Dipole moment.
[c] Retention volume.
[d] Kovats' index.
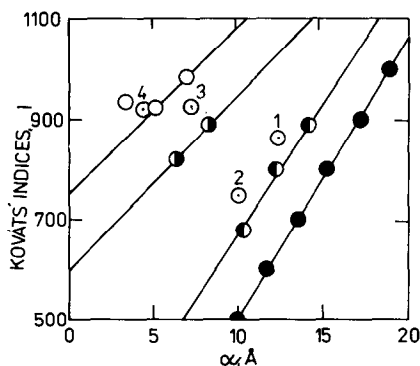[e] Kovats' index differences between sorbate and alkane.

Fig. 1. Effect of polarizability, α (Å^3), on Kovats' indices, I. ● = Alkanes; ◑ = aromatic hydrocarbons; ◐ = ketones; ○ = alcohols; 1 = chlorobenzene; 2 = tetrahydrofuran; 3 = nitromethane; 4 = acetonitrile.

the polar cellulose surface. The retention data of polar compounds indicates extensive specific interactions and suggests that the cellulose may be classified as polar sorbent of the second type according to the sorbent classification of Kiselev and Yashin [5].

For polarity relations of various adsorbents and stationary phases the chromatographic polarity scale developed by Rohrschneider [7,8] is traditionally used. Comparison of retention indices, I, of polar compounds on different sorbents facilitates calculation of the relative polarity of cellulose. If squalane is considered to be the most non-polar stationary phase, with polarity defined as $P = 0\%$ then the opposite extreme is β,β'-dicyandiethylene, $P = 100\%$. Thus the polarity of cellulose with respect to benzene is 5%. This approach provides a tool to compare various sorbents using Kováts' scale relating retention indices for 2-butanone. As a base, the index for retention of 2-butanone on Chromosorb 106 was defined as $I = 0$. The upper limit of the scale was chosen as the index achieved on the copolymer methyl methacrylate–acrylonitrile with the highest retention value and was defined as 100%. All other sorbents fit into this scale very well (Fig. 2).

Any sorbent may be described by its retention of selected compounds of different polarity. The original Rohrschneider approach uses Kováts' indices and relates them to squalane [9]. Table II lists the data acquired for cellulose and some other sorbents. From Table II it can be seen that the cellulose sorbent exhibits strong specific adsorption due to the donor–acceptor intermolecular interaction with molecules such as alcohols, nitromethane or ketones. The polarity of the cellulose surface is high even in comparison with commercial sorbents with attached polar groups, e.g. Chromosorb 104 with nitril groups or Polysorb N with a free electron pair on nitrogen in the pyridine ring.

The mechanism of retention of various compounds in polymeric sorbents is not clearly understood. It is expected that, due to the dependence of retention on the temperature and chemical nature of the sorbent surface, the interaction proceeds between solvent and adsorbent or between free solvent and fixed solvent [11]. We studied the relation between retention of polar compounds at low concentrations and low temperatures (60–100°C) and the thermodynamic characteristics for the cellulose. The data for differential internal energy $(-\Delta U)$ determined from the retention
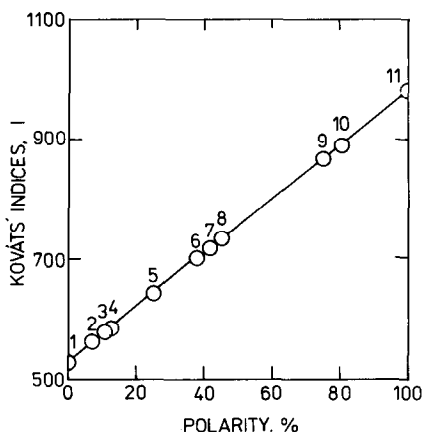
Fig. 2. Scale of polarity of adsorbents calculated on 2-butanone at 100°C. 1 = Chromosorb; 2 = Porapak QS; 3 = Chromosorb 102; 4 = Chromosorb 105, Porapak Q and Porapak S; 5 = Chromosorb 101 and Chromosorb 107; 6 = copolymer methyl methacrylate (MMA)–ethylene dimethacrylate (EDMA) (10:90); 7 = Porapak T; 8 = copolymer MMA–methyl methacrylate with 2-hydroxyethyl methacrylate (HEMA)–EDMA (8:32:60); 9 = Chromosorb 104; 10 = Cellulose; 11 = copolymer HEMA–acrylonitrile (AN)–EDMA (55:6:39).

diagram of ketones and alcohols sorbed on cellulose indicate a high polarity for the cellulose surface.

Table III lists values of $-\Delta U$ obtained for the temperature range 60–100°C and the values, $\Delta(-\Delta U)$, of the contribution of the specific interaction to the total adsorption energy —calculated as a difference between heat of adsorption of polar molecules and *n*-alkanes interpolated to equal polarizability.

Table III shows that cellulose is the most selective sorbent when it interacts with alcohols accompanied by the formation of hydrogen bonds between the hydroxyl of

TABLE II

RETENTION ROHRSCHNEIDER INDICES FOR DIFFERENT POLYMERIC SORBENTS

Adsorbent	Func-tional group	Tempera-ture (°C)	Rohrschneider index				Ref.
			Benzene	Ethanol	Methyl ethyl ketone	Nitro-methane	
Cellulose	OH	100	0.22	5.37	3.54	4.67	—
Chromosorb 104	CN	100	1.67	1.66	2.62	4.32	12
Polysorb N	Pyridine	100	1.24	3.44	2.14	3.53	12
Spheron S 90F	OH	150	0.26	1.29	0.82	1.96	12
Synachrome E5	Phenyl	150	0.40	0.21	0.36	0.38	12
Copolymers:							
GMA–EDMA (60:40)	Epoxy	150	0.18	2.33	1.89	2.81	15
MMA–HEMA–EDMA (8:32:60)	OH	150	1.40	2.80	2.24	3.54	14
HEMA–AN–EDMA (55:6:39)	OH, CN	150	3.58	5.05	4.38	4.24	14
Porapak Q	Phenyl	150	0.52	1.15	0.93	1.37	12
Porapak T	EDMA	150	1.30	2.60	2.21	3.34	12

TABLE III

DIFFERENTIAL INTERNAL ENERGIES OF ADSORBENTS (kJ/mol)

Adsorbate	Cellulose		Chromosorb 101 [13],	Chromosorb 102 [13],	Chromosorb 104 [13],
	$-\Delta U$	$\Delta(-\Delta U)$	$-\Delta U$	$-\Delta U$	$-\Delta U$
Methanol	61.9	44	35.9	38.1	47.8
Ethanol	62	40	42.3	44.7	54.2
1-Propanol	73.3	42	48.7	51.3	60.6
Acetone	54.0	32	41.2	35.3	52.8
2-Butanone	57.2	27	47.6	41.9	59.2
Hexane	37.1	—	50.1	51.3	50.4

alcohol and hydroxyl located at the cellulose surface. The mean energy is -42 ± 2 kJ/mol for alcohols and -29 ± 3 kJ/mol for ketones. The extent of $\Delta(-\Delta U)$ for aromatic hydrocarbons is insignificant and results from weak specific intermolecular interactions with the non-specific interaction energy are 4–13 kJ/mol [10]. Fig. 3 depicts the polarity scale of various sorbents compared using the $-\Delta U$ data for ethanol and 2-butanone. Zero is defined as $-\Delta U$ for ethanol on the polar polymeric sorbent Chromosorb 101, with 100% being ethanol on cellulose. The selectivity of other sorbents toward ethanol is located within these limits. For 2-butanone the relation is partly distorted. The highest energy belongs to the interaction with Chromosorb 104, the smallest to Chromosorb 102. The extent of $-\Delta U$ of 2-butanone for cellulose is lower than for ethanol. This consideration results in the data given in Table IV where the conventional chromatographic polarity of cellulose is compared with some other polymer sorbents using Kovats' indices at 100°C or differential internal energies calculated according to method applied in Fig. 1.

The suggested polarity scale, as well as Rohrschneider's scale, allows estimation of quantitative data on specific interactions with polar molecules. The advantages of
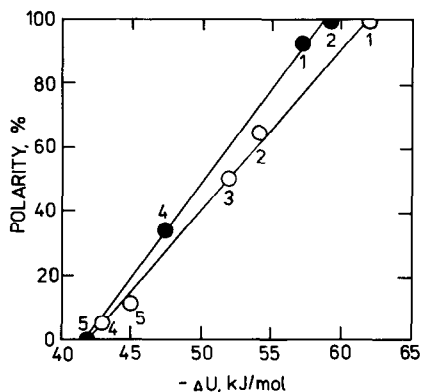

Fig. 3. Scale of polarity according to differential internal energy $(-\Delta U)$ of ethanol (○) and 2-butanone (●) adsorption. 1 = Cellulose; 2 = Chromosorb 104; 3 = Porapak T; 4 = Porapak Q; 5 = Chromosorb 102.

TABLE IV

RELATIVE POLARITY (*P*) OF ADSORBENTS ACCORDING TO KOVATS' INDICES (*I*) AND
DIFFERENTIAL ENERGY ($-\Delta U$)

Adsorbent	*P*(%)		
	I (2-butanone)	$-\Delta U$ (kJ/mol)	
		Ethanol	2-Butanone
Cellulose	100	100	90
Chromosorb 104	95	65	100
Porapak Q	15	35	5
Chromosorb 102	10	–	10
Chromosorb 106	0	–	–
Chromosorb 101	–	0	0

the proposed conventional scale which uses $-\Delta U$ are the comparison of energy values
and the insignificant effect of temperature.

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