Equilibrium chromatographic characteristics of capillary column coated with polytrimethylpropyne for separating polar and non-polar organic compounds by gas capillary chromatography

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The temperature dependence (50—180 °C) of the retention factor for 35 hydrocarbons and their oxygen-containing derivatives was studied using a capillary column coated with a new film-forming polymeric adsorbent polytrimethylsilylpropyne (PTMSP). The heats of adsorption for 24 organic polar and non-polar compounds on PTMSP were determined. They turned out to be lower than the heats of adsorption of the same compounds on Porapak Q widely used in gas chromatography. The new adsorbent PTMSP is characterized by high selectivity suitable for practical application.

Key words: capillary gas adsorption chromatography, organic polymer adsorbents, polytrimethylsilylpropyne (PTMSP), sorption heat.

Organic polymers are widely used in recent years as adsorbents for gas adsorption chromatography.[1—4] The development of new polymeric materials for gas chromatography is pursued currently.[1,5] However, specific restrictions are inherent in many polymeric organic adsorbents used in chromatographic practice. In particular, they are insoluble in organic solvents. This impedes the preparation of capillary columns and considerably increases the cost of capillary columns coated with an organic polymer layer.

To extend the scope of polymeric adsorbents for capillary gas adsorption chromatography, we have previously[6] proposed that the film-forming polymer in the glassy state applied in membrane technology can be used as an adsorbent. On choosing the polymer, special attention was given to such characteristics of polytrimethylsilylpropyne (PTMSP) as high permeability and high vitrifying temperature.[7] This polymer is characterized by a very low density (0.7 g cm^{-3}) and, correspondingly, an unusually high fraction of free volume (~20%).[8] The study of the PTMSP structure by physical tools[9] showed that micropores (diameter 10—15 Å) and submicropores (3—5 Å) prevailed in this polymer, while for polymers not used in membrane technology the pore diameter is 5—7 Å.

The studies allowed the conclusion about the promising application of PTMSP as an adsorbent, in particular, in hollow capillary columns. Previously[6,10] we have shown the advantages of using PTMSP as the chromatographic adsorbent for hydrocarbon gas separation.

This work is aimed at studying the chromatographic characteristics of PTMSP as an adsorbent for separating organic compounds of different classes under the conditions of capillary gas adsorption chromatography.

Experimental

The chromatographic characteristics, *viz.*, retention time, height equivalent to theoretical plate (HETP) at different linear flow rates (u) of the carrier gas, height of the chromatographic peak as a function of the amount of introduced sample, and width of the chromatographic zone, were measured with an updated version of the LKhM-8MD chromatograph (5 model) with a flame-ionization detector ("Khromatograf" plant, Moscow). The temperature in the thermostat of the column was maintained with an accuracy of ±0.5 °C. Helium was used as the carrier gas. The flow split at the inlet of the column was 1 : 20, and the amount of the supplied sample was 0.1 μL.

The relation of the retention factors (k) of organic compounds of various classes on the temperature and other chromatographic characteristics was studied on a capillary column (21 m × 0.22 mm) coated with the polymeric PTMSP adsorbent with an adsorbent layer thickness of 0.4 μm. The relative retention times t_{rel} of the sorbates were calculated using *n*-hexane as the standard.

The relation of k on the height of the chromatographic peak was studied for several organic compounds and showed that the k value remained unchanged with an increase in the amount of the sample injected into a chromatograph.

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Table 1. Retention factor (k) for some low-boiling hydrocarbons as a function of the temperature of the capillary column coated with PTMSP (50—90 °C)

Sorbate	B.p. /°C	k				
		50	60	70	80	90
Isobutane	−11.73	2.172	1.414	1.0	0.522	0.591
Divinyl	−4.4	1.862	2.253	0.818	0.576	0.307
n-Butane	−0.5	2.851	1.816	1.273	0.674	0.727
Isoprene	34.0	9.284	5.379	3.136	2.370	1.421

Results and Discussion

Temperature relation of the retention time for organic compounds. The retention times of low-boiling hydrocarbons were measured at 50—90 °C with a step of 10 °C. The retention characteristics of organic compounds with different structures (boiling from 36.3 to 269 °C) were determined at temperatures from 60 to 180 °C with a step of 20 °C. The retention times for different temperatures were calculated from these values (Tables 1 and 2). The data obtained correspond to the known linear plot[11] of the logarithm of the retention time *vs.* reverse absolute temperature $\log k = A + B/T$ (where A and B are constants).

Based on the temperature relation of k, the heats of adsorption were calculated for all compounds studied (Table 3). The heats of adsorption for compounds of the same homological series increase with the number of C atoms, the behavior being characteristic also of other adsorbents. It was of interest to compare the heats of adsorption on a column coated with PTMSP with the data obtained for the same organic compounds on other adsorbents, *e.g.*, Porapak Q[12] (copolymer of ethylstyrene and divinylbenzene) and graphitized thermal carbon black (GTC)[13] (see Table 3). As follows from the data in Table 3, the heats of adsorption for all studied compounds are higher on Porapak Q than on PTMSP.

For most studied compounds, the heats of adsorption (Q) on PTMSP are higher than those on GTC. This is valid, in particular, for *n*-alkanes (except ethane). Aromatic hydrocarbons (benzene, toluene) are adsorbed on GTC with higher heats than on PTMSP. For oxygen-containing compounds, except methanol and acetone, higher Q values were obtained on PTMSP.

Comparing the Q values on PTMSP for hydrocarbons C_6—C_8, we can conclude that, as a whole, saturated hydrocarbons are adsorbed with higher heats than

Table 2. Retention factor (k) for some organic compounds as a function of the temperature of the capillary column coated with PTMSP (60—180 °C)

Sorbate	B.p. /°C	k						
		60	80	100	120	140	160	180
n-Pentane	36.3	9.081	3.609	1.813	0.918	0.055	—	—
Acetone	56.3	1.701	0.828	0.505	0.309	0.222	—	—
Methyl acetate	57.1	2.747	1.250	0.632	0.350	—	—	—
Hex-1-ene	63.4	—	—	4.479	2.289	1.020	0.587	0.309
Methanol	64.7	—	0.806	0.075	—	—	—	—
n-Hexane	69.0	—	—	6.0	2.742	1.374	0.721	0.40
Ethyl acetate	77.1	10.345	4.196	2.032	1.124	—	—	—
Ethanol	78.4	0.690	0.337	0.20	0.124	0.081	—	—
Methyl ethyl ketone	79.6	—	3.239	1.611	0.876	0.525	—	—
Benzene	80.1	—	—	2.737	1.378	0.780	0.465	0.299
Cyclohexane	80.7	—	—	4.833	2.680	1.263	0.777	—
Hept-1-ene	93.6	—	—	13.615	6.155	2.737	1.433	0.782
Propanol	97.8	3.138	1.370	0.705	0.392	0.242	—	—
n-Heptane	98.4	—	—	20.094	8.092	3.556	1.722	0.909
Methyl propyl ketone	102.0	—	11.370	4.958	2.423	1.263	—	—
Toluene	110.8	—	—	—	4.439	2.170	1.208	0.701
Butanol	117.0	14.575	5.565	2.526	1.258	0.687	—	—
Acetic acid	118.1	7.897	2.348	4.042	0.505	—	—	1.755
Oct-1-ene	121.3	—	—	—	18.031	7.182	3.440	1.037
Butyl acetate	126.5	—	—	—	8.388	3.730	1.922	1.436
Ethylbenzene	136.2	—	—	—	12.599	5.364	2.827	—
Pentanol	137.2	—	20.826	8.516	3.763	1.838	—	1.766
o-Xylene	144.0	—	—	—	15.786	6.340	3.228	1.509
Styrene	145.0	—	—	—	12.880	5.931	2.757	—

Table 3. Heats of adsorption (Q/kcal mol^{-1}) for some organic compounds on PTMSP and other adsorbents

Sorbate	PTMSP, Q	Porapak Q[12]		GTC[13]	
		Q_i	γ_i*	Q_i	γ_i*
Acetylene	3.4	—	—	4.23	19.6
Ethylene	3.8	5.1	25.5	4.30	11.6
Ethane	4.3	6.1	29.5	4.53	5.1
Propylene	5.7	8.1	29.6	—	—
Propane	6.2	8.4	26.2	5.93	−4.55
But-1-ene	5.9	—	—	6.95	15.1
Isobutane	7.5	10.1	25.7	6.95	−7.9
Divinyl	9.0	—	—	—	—
n-Butane	7.8	10.8	27.8	7.21	−8.2
Isoprene	9.2	—	—	—	—
Methanol	3.8	7.4	48.6	5.3	28.3
Ethanol	7.3	9.9	26.3	6.9	−5.8
Acetone	6.4	—	—	8.3	22.9
Propanol	8.7	11.0	20.9	8.1	−7.4
Methyl acetate	8.9	11.1	19.8	7.4	−20.3
Acetic acid	10.5	—	—	8.3	−26.5
Methyl ethyl ketone	8.8	—	—	—	—
n-Pentane	9.8	11.3	13.3	8.9	−10.1
Ethyl acetate	9.3	—	—	—	—
Butanol	10.4	13.0	20.0	9.4	−10.6
Benzene	9.1	14.4	36.8	9.8	7.1
Hex-1-ene	11.3	—	—	—	—
Methyl propyl ketone	10.6	—	—	—	—
Cyclohexane	10.0	13.9	28.1	8.7	−14.9
n-Hexane	11.4	14.7	22.4	10.4	−9.6
Pentanol	11.7	—	—	10.7	−9.3
Toluene	10.9	—	—	11.6	6.0
Hept-1-ene	12.1	—	—	—	—
n-Heptane	13.01	—	—	12.5	−4.5
Butyl acetate	12.4	—	—	—	—
Ethylbenzene	9.3	—	—	—	—
Styrene	11.6	—	—	—	—
o-Xylene	12.6	—	—	—	—
Oct-1-ene	14.0	—	—	—	—
n-Octane	14.3	—	—	13.4	−6.7
Adamantane	14.0	—	—	—	—

* $\gamma_i = (Q_i - Q_{\text{PTMSP}}/Q_i) \cdot 100$.

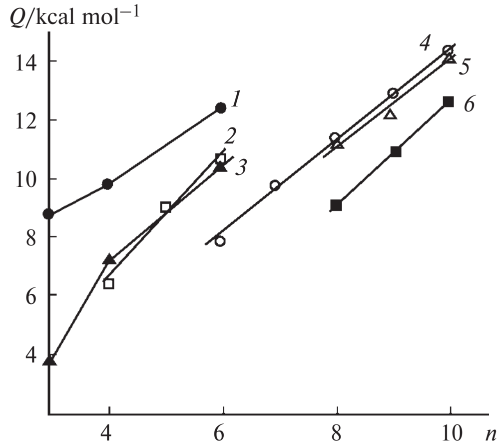

Fig. 1. Plot of the heat of adsorption (Q) on PTMSP for various organic compounds *vs.* number of C atoms in their molecules (n): acetates (*1*), ketones (*2*), normal alcohols (*3*), alkanes (*4*), alkenes (*5*), and aromatic hydrocarbons (*6*).

unsaturated hydrocarbons. However, a much higher heat of adsorption (9.0 kcal mol^{-1}) was obtained for the divinyl (buta-1,3-diene) molecule bearing two double bonds than for *n*-butane (7.8 kcal mol^{-1}). At the same time, the divinyl homologue, *viz.*, isoprene, showed a lower heat of adsorption (9.2 kcal mol^{-1}) than *n*-pentane (9.8 kcal mol^{-1}), probably due to the branched isoprene structure. Comparison of the heats of adsorption for substances different in structure but with the same number of C atoms, for example, in the series *n*-hexane, cyclohexane, and benzene, shows that for benzene the heat of adsorption (9.1 kcal mol^{-1}) is lower than for cycloalkane (cyclohexane, Q = 10.0 kcal mol^{-1}) and *n*-alkane (*n*-hexane, Q = 11.4 kcal mol^{-1}). This difference is most likely associated with the configuration of the sorbate molecule.

It follows from the relations of the heats of adsorption of substances belonging to six different classes on the number of C atoms (n) in their molecules (Fig. 1) that the difference between heats of adsorption, *e.g.*, for *n*-alcohols and acetates with the same number of C atoms in the molecule varies from 2 to 4 kcal mol^{-1}, and the lower n, the greater the difference. Specificity of the organic adsorbent under study is that Q values for the first compounds of the homological series (see methyl acetate and methanol) do not follow a linear relation of Q *vs.* n.

Selectivity of PTMSP. An unusually high selectivity of PTMSP is manifested, in particular, on separating a mixture of aromatic hydrocarbons (benzene, toluene, *o*-xylene, ethylbenzene) and *n*-alkanes C_6—C_8. Aromatic sorbates are eluted much earlier than the corresponding *n*-alkane. For example, benzene is eluted much earlier than *n*-hexane, toluene is eluted earlier than *n*-heptane, and ethylbenzene and *o*-xylene are eluted earlier than *n*-octane. We do not know stationary phases with a similar elution order.

Comparison of the relative retention times (Table 4) on the PTMSP adsorbent and on the non-polar stationary liquid phase (Apiezon L)[14] shows that their values on PTMSP are much lower for all compounds studied except *n*-alkanes.

The relation of the logarithm of the relative retention time ($\log\alpha_i$) on PTMSP to the similar parameter observed on Apiezon L is presented in Fig. 2, *a* for 15 compounds (compounds are numerated in Table 4). For comparison, Fig. 2, *b* the relation of $\log\alpha_i$ for the same compounds on PEG-20M to the similar parameter observed on Apiezon L is presented. In the case of non-

Table 4. Relative retention time ($t_{\rm rel}$) for some organic compounds on columns coated with PTMSP and Apiezon L at 100 °C

Sorbate	$t_{\rm rel}$	
	PTMSP	Apiezon L [14]
n-Pentane (**1**)	0.40	0.46
n-Hexane (**2**)	1.00	1.00
n-Heptane (**3**)	3.01	2.16
Methanol (**4**)	0.15	0.37
Ethanol (**5**)	0.16	0.61
Propanol (**6**)	0.24	0.81
Butanol (**7**)	0.50	2.05
Acetone (**8**)	0.21	0.40
Methyl ethyl ketone (**9**)	0.37	1.05
Methyl propyl ketone (**10**)	0.84	2.09
Hex-1-ene (**11**)	0.78	0.71
Methyl acetate (**12**)	0.23	0.50
Ethyl acetate (**13**)	0.43	0.93
Benzene (**14**)	0.53	2.05
Cyclohexane (**15**)	0.83	1.97

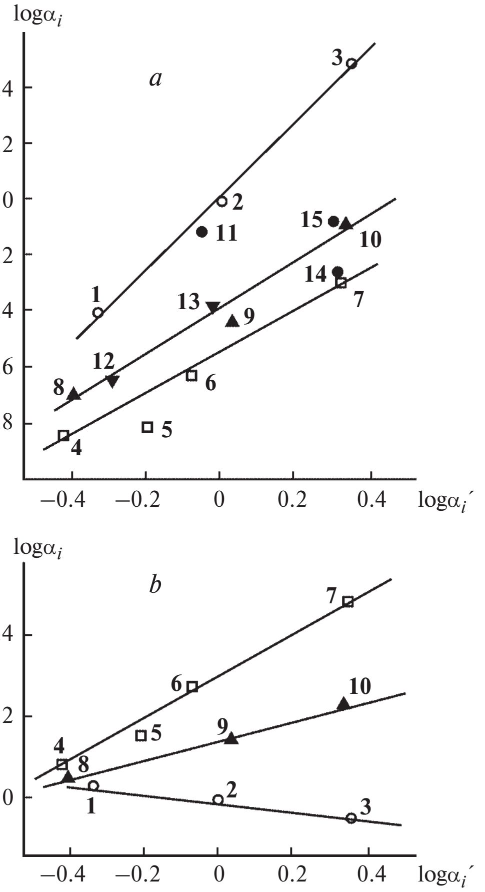

Fig. 2. Plot of the logarithm of the relative retention time ($\log\alpha_i$) on PTMSP (*a*) and PEG-20M (*b*) *vs*. logarithm of the relative retention time on Apiezon L ($\log\alpha_i'$) for some organic compounds (for numeration of compounds, see Table 4).

specific stationary phases, these plots are linear for compounds of the same homological series (see Fig. 2, *b*). However, this is not the case for data in Fig. 2, *a*, and this effect is likely explained by specificity of the stationary phase studied. Evidently, the geometric factor affects the retention values of organic compounds on PTMSP. Molecules with more bulky structures, such as benzene and cyclohexane, are characterized by much lower retention than *n*-heptane ($t_{\rm rel}$ is 0.53, 0.83, and 3.01, respec-

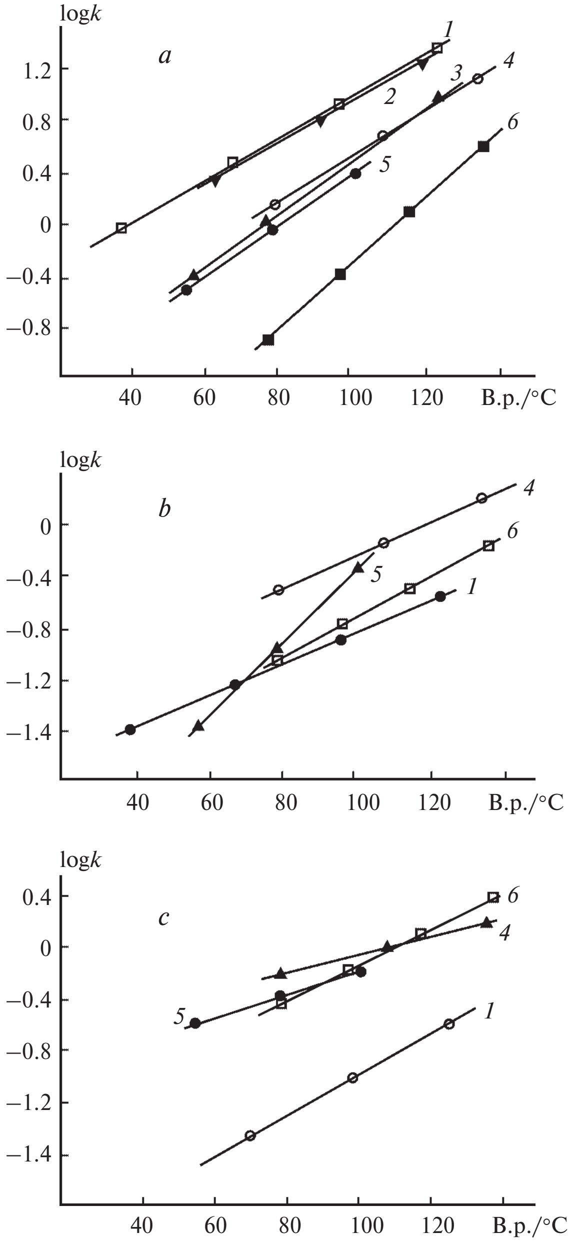

Fig. 3. Logarithm of the retention factor (log*k*) on PTMSP (*a*), SE-30 (*b*), and PEG-20M (*c*) as a function of the boiling point of sorbates for some classes of organic compounds: alkanes (*1*), alkenes (*2*), acetates (*3*), aromatic hydrocarbons (*4*), ketones (*5*), and normal alcohols (*6*).

Table 5. Changes $\Delta\log k = \log k_0 - \log k'$ for hypothetical compounds boiling at the same temperature (77, 87, and 117 °C)

Hypothetical compound	$\Delta\log k$		
	77	87	117
Alkenes	0.02	0.02	0.02
Aromatic hydrocarbons	0.49	0.48	0.41
Acetates	0.61	0.58	0.47
Ketones	0.69	0.64	0.54
Normal alcohols	1.55	1.46	1.15

tively). This suggests that the adsorbent exhibits molecular-sieve effects.

Analysis of the plots of the logarithm of the retention factor (log*k*) for organic compounds of different nature on PTMSP *vs*. boiling point of the sorbates (Fig. 3, *a*) shows that each homological series is characterized by an individual linear function. Similar plots are presented in Fig. 3, *b* and *c* to compare PTMSP with the SE-30 non-polar liquid phase and PEG-20M polar phase, which are most popular in GLC. It follows from the presented results that SE-30 is not selective phase for alcohols and ketones, and the PTMSP phase manifests toward them higher selectivity than the PEG-2M phase, which is usually used for separating oxygen-containing compounds.

For chosen three temperatures (77, 87, and 117 °C) we used the data in Fig. 3, *a* and calculated the changes in the values $\Delta\log k = \log k_0 - \log k'$ (k_0 and k' correspond to the alkane and hypothetical compound, respectively) for the hypothetical compounds boiling at these temperatures. According to the results obtained (Table 5), with the boiling point increase $\Delta\log k$ for alkenes remain unchanged and decrease by the value from 0.08 to 0.15 for the second group of compounds (aromatic hydrocarbons, acetates, and ketones), and this decrease is more significant (0.40) for *n*-alcohols.

Unfortunately, some compounds exhibit noticeably asymmetric broadening of the chromatographic zones. For example, for alcohols, ketones, alkenes, and aromatic and cyclic compounds the asymmetry factor ($A_s = a/b$, where a is the "tail" part and b is the "front" part of the width of the chromatographic zone at the height equal to 0.5 of the peak height) was from 1.2 to 2.2, while for such compounds as *n*-heptane and butyl acetate it was 4.0 and 3.65, respectively.

For PTMSP we studied the characteristics of the broadening of the chromatographic zone for several classes of organic compounds under the conditions of capillary chromatography. For *n*-alkanes, *n*-alcohols, acetates, and ketones on PTMSP we observed relatively high HETP values (from 1.5 to 3 mm) and a sharp increase in the HETP in the field of high flow rates of the carrier gas. To diminish these disadvantages, we developed a procedure for PTMSP modification.[15]

Thus, the study of the equilibrium chromatographic characteristics for organic compounds of different classes allowed us to establish that the selectivity of PTMSP substantially exceeds those of graphitized carbon black, Porapak Q, Apiezon L, and SE-30. Therefore, PTMSP can be characterized as a new selective adsorbent.

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