Polytrimethylsilylpropyne as adsorbent for separation of gases

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Polytrimethylpropyne supported on a solid substrate was proposed as a chromatographic adsorbent for the separation of hydrocarbon gases. The heats of adsorption of hydrocarbon gases were determined. The efficiency of application of this sorbent for the selective separation of C_1—C_4 hydrocarbon gases in packed columns was demonstrated.

Key words: gas chromatography, hydrocarbon gases, adsorbent, selectivity, heat of adsorption

The use of organic adsorbents is of substantial interest for solving the problem of analysis of hydrocarbon gases.[1] High selectivity of these adsorbents can be controlled by varying their composition and structure. In addition, the sorption surface is more uniform for organic adsorbents than for inorganic ones. Only a limited range of adsorbents of this type are used currently in gas chromatography, mainly in capillary chromatohraphy.[2]

Several publications describe the use of packed columns filled with carbon molecular sieves. An example of determination of impurities in pure 1,3-butadiene using a column (5 m × 1.5 mm) packed with modified Carbopack B (carbon molecular sieves) containing 4.94% picric acid has been reported.[3] The C_1—C_4 hydrocarbons were separated on this column over a period of 20 min at 46 °C, although ethane and ethylene were eluted together. A column (1.8 m × 3.2 mm) with the carbon molecular sieves Carbosphere (grain size 80—100 mesh) provided separation of all the C_1—C_2 hydrocarbons at 225 °C; acetylene was eluted ahead of ethylene or ethane.[4a] Ten C_1—C_4 compounds were separated over a period of 3.5 min at 40 °C using a micropacked column (1.7 m × 0.28 mm) with the Sterling MT adsorbent (graphitized black) with a grain diameter of 0.08 mm.[5] Unfortunately, the separation characteristics are incomplete because the mixture contained neither ethylene nor acetylene. The Alltech catalogue cites examples of application of commercial packed columns with a porous polymer of the Haye Sep trademark[4b] for the separation of light hydrocarbon gases. Thus a stainless-steel column (3 m × 1.6 mm) with the Haye Sep S polymer (grain size 100—120 mesh) provided efficient separation of the C_1—C_2 group of hydrocarbons at 60 °C (3 min) and programmed heating to 90 °C. However, the difference between the retentions of ethylene and acetylene in this column is slight and acetylene is eluted after ethylene, which markedly restricts the scope of application of this polymer for determination of an acetylene impurity in ethylene.

Polymeric sorbents that provide elution of acetylene before ethylene or ethane from packed columns [6] appear to be especially promising for the separation of gaseous hydrocarbons. Previously,[7] it has been proposed to use capillary columns with polytrimethylsilylpropyne (PTMSP) for this purpose. In this work, we studied the use PTMSP in packed columns, which are distinguished by high stability and steadiness of operation.

Experimental

The retention times were measured using an LKhM-8MD chromatograph (design 5) with a flame ionization detector (Khromatograph, Moscow). The temperature of the column thermostat was maintained with an accuracy of ±0.5 °C. Helium at a flow rate of 35 mL $\min^{-1}$ was used as the carrier gas.

The temperature dependence of the retention times of saturated and unsaturated C_1—C_4 hydrocarbons on the adsorbent with the PTMSP polymer phase was studied on a stainless-steel packed column (6 m × 3 mm). The relative retention times of the sorbates were calculated using propane as the standard. The size of gaseous samples did not exceed 0.5—1 μL. The root-mean-square error of the measurement of retention values was 0.054.

A polymer sample sufficient for the preparation of the sorbent with 10% (w/w) PTMSP on a solid support was dissolved in chloroform (chemically pure grade, for spectroscopy), and the solution was supported on Chromosorb W (Supelco) with a grain size of 80—100 mesh using a standard procedure.[6]

Results and Discussion

The retention times of hydrocarbon gases from methane to *n*-butane were measured at several temperatures (from 55 to 130 °C both under isothermal conditions (75 °C) and with programmed heating). The corresponding chromatorams are presented in Fig. 1, *a*—*c*. The degree of separation attained indicates a high selectivity of PTMSP, which ensures a clear group separation. Tables 1 and 2 present the retention factors (k) and the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 225—228, February, 2001.

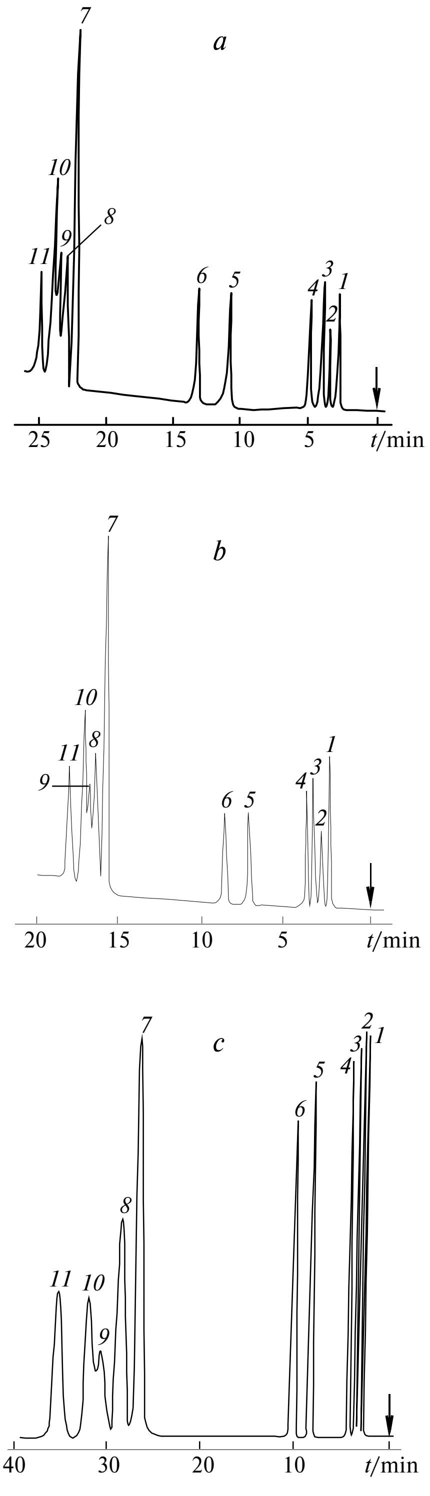

Fig. 1. Chromatogram of a mixture of C_1—C_4 hydrocarbon gases: (*1*) methane, (*2*) acetylene, (*3*) ethylene, (*4*) ethane, (*5*) propylene, (*6*) propane, (*7*) but-1-ene, (*8*) isobutane, (*9*) isobutylene, (*10*) *trans*-but-2-ene, (*11*) *n*-butane. A 6 m × 3 mm stainless-steel column; 10% PTMSP on Chromosorb W (80—100 mesh) as the sorbent; column temperature from 55 °C (6 min) to 155 °C (4 K min^{-1}) (*a*); from 75 °C (5 min) to 135 °C (4 K min^{-1}) (*b*); 75 °C (*c*); He as the carrier gas, 35 mL min^{-1}; flame ionization detector.

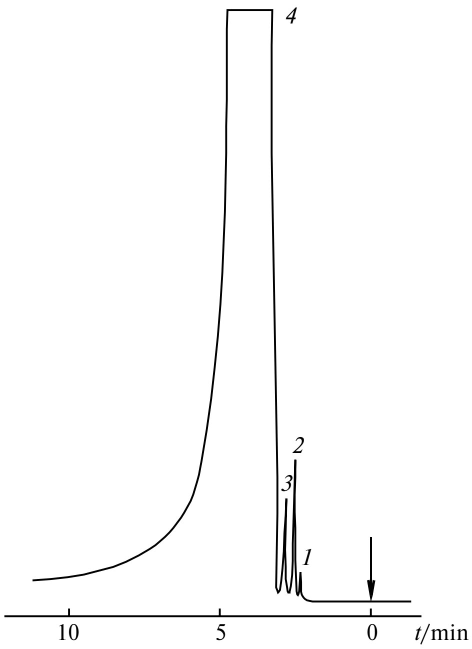

Fig. 2. Chromatogram of the impurities in ethylene; (*1*) methane, (*2*) acetylene, (*3*) unidentified, (*4*) ethylene. A 6 m × 3 mm stainless-steel column; 10% PTMSP on Chromosorb W (80—100 mesh) a the sorbent; column temperature 65 °C; He as the carrier gas, 35 mL min^{-1}; flame ionization detector.

relative retention values (α), together with the *k* and α values calculated from the data obtained on a capillary column with PTMSP.[7] The possibility of separating gaseous hydrocarbons of the C_2 group is of special interest because acetylene is eluted from this adsorbent ahead of ethylene; in the analysis of impurities in ethylene, the acetylene peak is clearly resolved from the

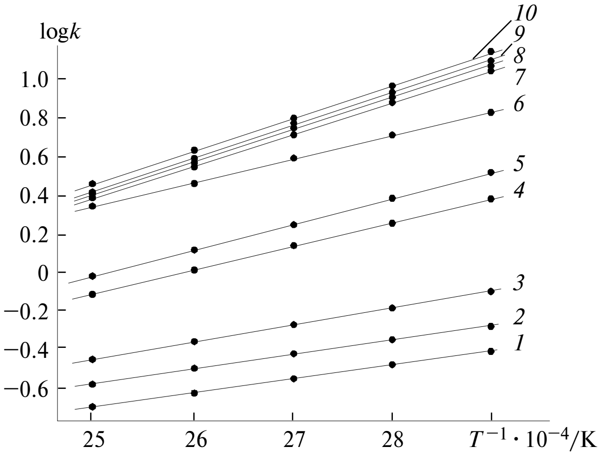

Fig. 3. log*k* *vs.* $1/T$ for C_1—C_4 hydrocarbon gases: (*1*) methane, (*2*) acetylene, (*3*) ethylene, (*4*) ethane, (*5*) propylene, (*6*) propane, (*7*) but-1-ene, (*8*) isobutane, (*9*) isobutylene, (*10*) *trans*-but-2-ene, (*11*) *n*-butane. A 6 m × 3 mm column with 10% PTMSP on Chromosorb W (80—100 mesh); *T*/°C, 75, 95, 107, 120, and 130; He as the carrier gas, 35 mL min^{-1}; flame ionization detector.

ethylene macrozone (Fig. 2). Figure 3 shows the variation of the logarithm of the retention factor k *vs.* reciprocal temperature (T^{-1}) plotted for the sorbates studied here. From the temperature dependence of the retention factor k, the heats of adsorption of these compounds can be determined (Table 3). The adsorption heats found on a capillary adsorption column (10 m × 0.53 mm) with Porabond G (Chrompack) with the layer thickness d_f = 10 μm (helium as the carrier gas, flow rate 39 cm s^{-1}) and the published data[8] for the heats of adsorption on graphitized black are given for comparison. It follows from Table 3 that the greatest heats of adsorption of hydrocarbon gases (Q/kcal mol^{-1}) are found for the Porabond Q sorbent, which suggests that this adsorbent differs appreciably from PTMSP or graphitized black. Comparison of the Q values on PTMSP and graphitized black reveals the following regularity: for hydrocarbons of the C_2 group, the heats of adsorption are greater on PTMSP, whereas for hydrocarbons of the C_3 and C_4 groups, they are greater on the chromatographic adsorbent proposed here than on the graphitized black. The only exception to this rule is but-1-ene, the adsorption heat of which on graphitized black is substantially (by 1.05 kcal mol^{-1}) lower than that on PTMSP. According to our views, the mechanisms of sorption of gaseous hydrocarbons on graphitized black and on PTMSP are different.[7] Examination of the adsorption heats (see Table 3) for hydrocarbons of the C_2 and C_3 groups shows that in each group, the adsorption heat is greater for the saturated hydrocarbon (ethane and propane) than for the unsaturated one (ethylene and propylene). Apparently, the adsorption heats are affected by the decrease in the number of H atoms, which decreases the energy of interaction and by the change in the molecular geometry and the valence state of the C atom.[8] Carbon chain branching in the isomeric molecules of both alkanes (for example, isobutane) and alkenes (for example, isobutylene) brings about a decrease in the adsorption heats relative to those of *n*-butane and but-1-ene; apparently, this is related to the decrease in the number of units in the sorbate molecule contacting with the adsorbent molecule.

For the new sorbent, the kinetic characteristics of chromatographic band broadening under conditions of gas chromatography were studied. Figure 4 presents the dependence of the HETP on the linear velocity of the carrier gas (u) for the three sorbates with different retention factors k at the same temperature. For isobutane and propylene on the adsorbent proposed here, the curves of HETP *vs.* u are located higher and the slope of the right branch for them is greater than that for ethylene. Since isobutane and propylene have higher molecular weights (58.12 and 42.08, respectively) and, hence, much lower molecular diffusion coefficients than ethylene (28.05), the observed differences in the variations of the HETP and u can be due to the different intradiffusion mass exchange parameters.

Table 1. Dependence of the retention factors k for hydrocarbon gases on temperature

Sorbate	Column at T/°C					
	Packed					Capillary[7],
	75	95	107	120	130	31
Methane	0.21	0.17	0.15	0.14	0.12	0.030
Acetylene	0.38	0.30	0.26	0.22	0.19	0.047
Ethylene	0.55	0.41	0.34	0.29	0.25	0.073
Ethane	0.81	0.57	0.47	0.40	0.34	0.114
Propylene	2.43	1.50	1.15	0.94	0.76	0.431
Propane	3.22	1.93	1.47	1.16	0.94	0.681
But-1-ene	7.06	4.25	3.36	2.59	2.15	—
Isobutane	10.68	5.65	4.06	3.02	2.32	2.81
Isobutene	11.83	6.02	4.40	3.10	—	—
trans-But-2-ene	12.33	6.30	4.66	3.22	2.50	—
n-Butane	13.16	6.93	4.90	3.61	2.74	3.82

Table 2. Dependence of the relative retention α of hydrocarbon gases on temperature

Sorbate	Column at T/°C					
	Packed					Capillary[7],
	75	95	107	120	130	31
Methane	0.07	0.09	0.10	0.12	0.13	0.07
Acetylene	0.12	0.15	0.17	0.19	0.20	0.08
Ethylene	0.17	0.21	0.23	0.26	0.27	0.12
Ethane	0.25	0.30	0.32	0.35	0.36	0.18
Propylene	0.75	0.78	0.79	0.80	0.81	0.68
Propane	1.0	1.0	1.0	1.0	1.0	1.0
But-1-ene	3.12	2.75	2.33	2.23	2.11	—
Isobutane	3.44	2.93	2.54	2.52	2.48	4.54
Isobutene	3.60	3.15	2.60	2.60	—	—
trans-But-2-ene	3.83	3.34	2.75	—	—	—
n-Butane	4.17	3.59	3.32	3.09	2.93	6.18

Table 3. Adsorption heats of C_1—C_4 hydrocarbon gases

Sorbate	Q/kcal mol^{-1}			Q = = ($Q_{\text{PTMSP}} - Q_{\text{black}}$)
	I	II	III	
Acetylene	3.4	—	4.23	−0.83
Ethylene	3.8	5.1	4.30	−0.50
Ethane	4.3	6.1	4.53	−0.23
Propylene	5.7	8.1	—	—
Propane	6.2	8.4	5.93	+0.27
But-1-ene	5.9	—	6.95	−1.05
Isobutane	7.6	10.1	6.95	+0.65
Isobutene	8.0	—	—	—
trans-But-2-ene	7.9	—	7.29	+0.61
n-Butane	7.8	10.8	7.21	+0.59

Note. I is 10% PTMSP on Chromosorb W; II is CP-Porabond Q; III is graphitized black.

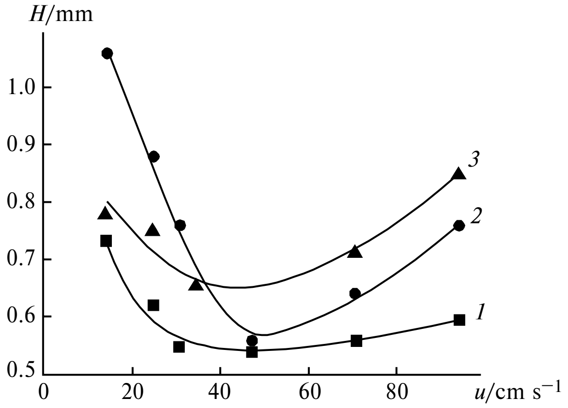

Fig. 4. HETP *vs.* the linear velocity of the carrier gas (helium) for ethylene (*1*), propylene (2), and isobutane (*3*).

Thus, by applying a layer of the PTMSP polymer on a solid support, we obtained a polymeric adsorbent for gas chromatography. A packed column with this polymeric adsorbent is highly selective and has a relatively low HETP (~0.53 mm). In the separation of gaseous hydrocarbons of the C_2 group, acetylene is eluted before ethylene, which is of interest regarding determination of acetylene admixtures in ethylene.

This work was supported by the Russian Foundation for Basic Research (Project No. 00-03-32-53a).

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Received in July 20, 2000;
in revised form October 19, 2000