

# Influence of the carrier gas on retention factors of gaseous hydrocarbons on polytrimethylsilylpropyne using capillary gas chromatography

V. G. Berezkin,\* A. A. Korolev, I. V. Malyukova, R. G. Mardanov, V. S. Khotimskii, and Yu. P. Yampol'skii

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,  
29 Leninsky prosp., 119991 Moscow, Russian Federation.  
Fax: +7 (095) 230 2224

The retention factor and height equivalent of a theoretical plate for gaseous hydrocarbons  $C_1-C_4$  were studied on capillary columns with the layer of the new polymeric adsorbent polytrimethylsilylpropyne (PTMSP) as functions of the nature and pressure of the carrier gas. The retention factor  $k$  increases in the series helium < nitrogen < carbon dioxide. The  $k$  values depend linearly on the average pressure of the carrier gas in a capillary column with the adsorption PTMSP layer.

**Key words:** gas liquid chromatography, carrier gas, retention factor, polytrimethylsilylpropyne, hydrocarbons.

Search for new adsorbents and the development of techniques for packing and binding adsorbents to the walls of a capillary column are of great interest for capillary gas adsorption chromatography. We have recently<sup>1–5</sup> proposed to use polytrimethylsilylpropyne (PTMSP), a film-forming material, as a chromatographic adsorbent to substantially simplify the procedure for preparation of an adsorption capillary column. We showed that, under the conditions of conventional gas capillary chromatography with the inlet pressure not exceeding 5 atm, the nature of the carrier gas and its pressure have a substantial effect on the retention factors.<sup>1–5</sup>

This work is aimed at studying the influence of the nature of the carrier gas and its pressure on the retention of hydrocarbon gases on PTMSP,<sup>6</sup> whose layer is supported on the inner walls of the capillary column of fused  $SiO_2$ .

## Experimental

The chromatographic parameters of PTMSP (film thickness 0.4  $\mu m$ ) in a capillary column 25 m  $\times$  0.22 mm were studied at 40 °C on an LKhM-8 MD modified gas chromatograph with a flame-ionization detector using helium, nitrogen, and carbon dioxide as carrier gases. The retention time was measured by an I-02 modified integrator with a resolution of 0.1 s. Samples (2–5  $\mu L$ ) of a mixture of hydrocarbon gases  $C_1-C_4$  containing 2–3 vol.% of each component were analyzed. The split ratio was varied from 1 : 75 to 1 : 100.

The dependence of the height equivalent of a theoretical plate (HETP) on the velocity of the carrier gas was studied on the same column but at 31 °C.

The PTMSP sample synthesized in the presence of  $NbCl_5$  as a catalyst was used. According to the  $^{13}C$  NMR spectroscopic data, the sample contained statistically distributed units of the *cis*- and *trans*-configuration in a ratio of 40 : 60. The

sample was characterized by the weighted mean molecular weight  $M_w = 200 \cdot 10^3$ , numerical mean molecular weight  $M_n = 170 \cdot 10^3$ , and polydispersity index  $M_w/M_n = 1.2$ .

The polymer used in this study as the stationary phase was dissolved in toluene and then precipitated with methanol. This purification procedure was repeated twice. According to the elemental analysis data, the content of the catalyst (and products of its decomposition) did not exceed 0.2%. Since the vitrifying temperature of the polymer >300 °C, it should be considered as solid.

The polymer was supported on the column walls by the dynamic method<sup>5</sup> using a 5% solution of PTMSP in chloroform.

## Results and Discussion

Polytrimethylsilylpropyne is a glassy polymer with the unusual complex of properties. It has the highest of all known polymeric materials coefficients of permeability, diffusion, and gas solubility, a very low density (0.7 g  $cm^{-3}$ ), and, correspondingly, a high fraction of free volume (~20%)<sup>7</sup> formed by large cavities.<sup>8,9</sup> Porosity of this polymer is presented by "open" pores<sup>10,11</sup> because cavities inside the polymer film reach the surface. The free volume of the polymer has the bimodal size distribution of cavities, and large cavities (microvolumes) 11–14 Å in diameter predominate. One  $cm^3$  contains<sup>12</sup>  $6 \cdot 10^{19}$  cavities (in polymers, which are not used in membrane technology, the corresponding diameter of cavities does not exceed 5–7 Å).

The chromatographic adsorbent—chromatographed compound system is usually characterized by two groups of parameters: equilibrium values (for example, retention factor  $k$ , relative retention  $\alpha$ , etc.) and kinetic values, which are related to the diffusion of the chromatographic zone (for example, HETP). First let us consider the equilibrium parameters of the PTMSP adsorbent under study.

**Table 1.** Retention factor ( $k$ ) of hydrocarbon gases as a function of the average pressure ( $P_{av}$ ) of the carrier gas for the capillary column packed with PTMSP

Carrier gas	$P_{av}$ /atm	$k$					
		Methane	Ethylene	Ethane	Propylene	Propane	<i>n</i> -Butane
He	1.33	0.0367	0.121	0.196	0.748	1.051	4.44
	1.6	0.0359	0.119	0.193	0.739	1.038	4.39
	9.95	0.0358	0.119	0.192	0.730	1.027	4.34
	2.30	0.0354	0.117	0.190	0.725	1.020	4.32
	2.67	0.0346	0.115	0.187	0.719	1.010	4.28
	1.33	0.0359	0.118	0.191	0.723	1.014	4.25
$N_2$	1.6	0.0354	0.116	0.188	0.712	0.998	4.18
	9.95	0.0350	0.114	0.185	0.701	0.980	4.11
	2.30	0.0344	0.112	0.182	0.688	0.965	4.02
	2.67	0.0336	0.110	0.178	0.677	0.946	3.95
	1.33	0.0338	0.1097	0.175	0.658	0.909	3.75
	1.6	0.0331	0.1069	0.170	0.636	0.877	3.60
$CO_2$	9.95	0.0328	0.1050	0.166	0.615	0.842	3.43
	2.30	0.0313	0.1023	0.159	0.591	0.810	3.27
	2.67	0.0296	0.1014	0.157	0.572	0.799	3.13
	1.33	0.0338	0.1097	0.175	0.658	0.909	3.75
	1.6	0.0331	0.1069	0.170	0.636	0.877	3.60
	9.95	0.0328	0.1050	0.166	0.615	0.842	3.43

Table 1 presents the data illustrating a relation between the experimentally measured retention factors and pressure of various carrier gases (helium, nitrogen, and carbon dioxide). It follows from these data that, on going from He to  $CO_2$ , the retention factor of the chromatographed compounds decreases, and the differences in the  $k$  values increase with an increase in the average pressure of the carrier gas in the column.

Based on our earlier<sup>1</sup> theoretical and experimental works on gas adsorption chromatography, the plot of the carrier gas pressure *vs.*  $k$  value is described by the linear equation in the pressure region below 5 atm

$$k_i(P_{av}) = k_{i0} + k_{i0}b_{mcs}P_{av} = k_{i0} + \lambda_i P_{av}, \quad (1)$$

where  $k_i(P_{av})$  is the retention factor for the  $i$ th sorbate at the average pressure of a specific carrier gas in the column  $P_{av}$ ;  $k_{i0}$  is the retention factor for the  $i$ th sorbate at the "zero" pressure of the carrier gas ( $k_{i0} = \lim k_i(P_{av})$  at  $P_{av} \rightarrow 0$ );  $b_{mcs}$  is the sorption coefficient for a specific carrier gas and specific sorbate, and  $\lambda_i = k_{i0}b_{mcs}$ .

Linear equation (1) satisfactorily describes the experimental data (Table 2). In accordance with the results obtained for other adsorbents,<sup>1,4</sup> the influence of the carrier gas on the retention factors increases in the series He <  $N_2$  <  $CO_2$ . The correlation coefficients  $R$  and estimations of the coefficients of Eq. (1) obtained by the least-squares method<sup>13,14</sup> are presented in Table 2.

The relative retention time is also used widely in analytical practice

$$\alpha_i = k_i/k_{st}, \quad (2)$$

where  $k_{st}$  is the retention factor of the chromatographed compound taken as a standard.

We have previously shown<sup>1,4</sup> that the relative retention time depends linearly on the average pressure of

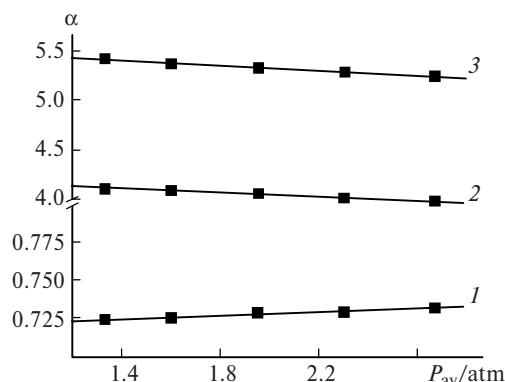
the carrier gas in the column and on the sorption coefficient

$$\alpha_i(P_{av}) = \alpha_{i0} + \alpha_{i0}(b_{mst} - b_{mi})P_{av}, \quad (3)$$

where  $\alpha_{i0} = \lim \alpha_i(P_{av})$  at  $P_{av} \rightarrow 0$ ;  $b_{mst}$  and  $b_{mi}$  are the sorption coefficients for a standard and specific carrier gas, respectively.

**Table 2.** Parameters of linear equation (1)  $k_{i0}$  and  $\lambda_{i0}$  and characteristics of correspondence of this equation to experimental data ( $R$  and  $SD$ )

Sorbate	$k_{i0}$	$\lambda_i$	$R$	$SD$
Carrier gas — He				
Methane	0.0371	-0.0005	0.970	0.0002
Ethylene	0.1271	-0.0045	0.993	0.0003
Ethane	0.2038	-0.0062	0.985	0.0006
Propylene	0.7738	-0.0211	0.985	0.0023
Propane	1.0870	-0.0294	0.988	0.0028
Isobutane	4.5794	-0.1144	0.983	0.0131
<i>n</i> -Butane	6.0722	-0.1524	0.980	0.0189
Carrier gas — $N_2$				
Methane	0.0381	-0.0016	0.993	0.0001
Ethylene	0.1256	-0.0059	0.998	0.0002
Ethane	0.1944	-0.0032	0.998	0.0004
Propylene	0.7677	-0.0342	0.999	0.0009
Propane	1.0313	-0.0169	0.999	0.0010
Isobutane	4.5442	-0.2245	0.999	0.0069
<i>n</i> -Butane	6.0355	-0.3013	0.999	0.0097
Carrier gas — $CO_2$				
Methane	0.0382	-0.0031	0.970	0.0005
Ethylene	0.1173	-0.0062	0.982	0.0007
Ethane	0.1934	-0.0141	0.986	0.0014
Propylene	0.7404	-0.639	0.998	0.0027
Propane	1.0334	-0.0964	0.998	0.0038
Isobutane	4.3481	-0.4630	0.998	0.0192
<i>n</i> -Butane	5.7317	-0.6161	0.997	0.0270



**Fig. 1.** Plots of the relative retention time ( $\alpha$ ) of hydrocarbons  $C_3$  and  $C_4$  vs. average pressure ( $P_{av}$ ) of carrier gas  $CO_2$  for various sorbates: 1, propylene; 2, isobutane; and 3,  $n$ -butane.

Equation (3) can also be presented in the following form:

$$\alpha_i(P_{av}) = \alpha_{i0} + \chi_i P_{av}, \quad (4)$$

where

$$\chi_i = (b_{mst} - b_{mi})\alpha_{i0}. \quad (5)$$

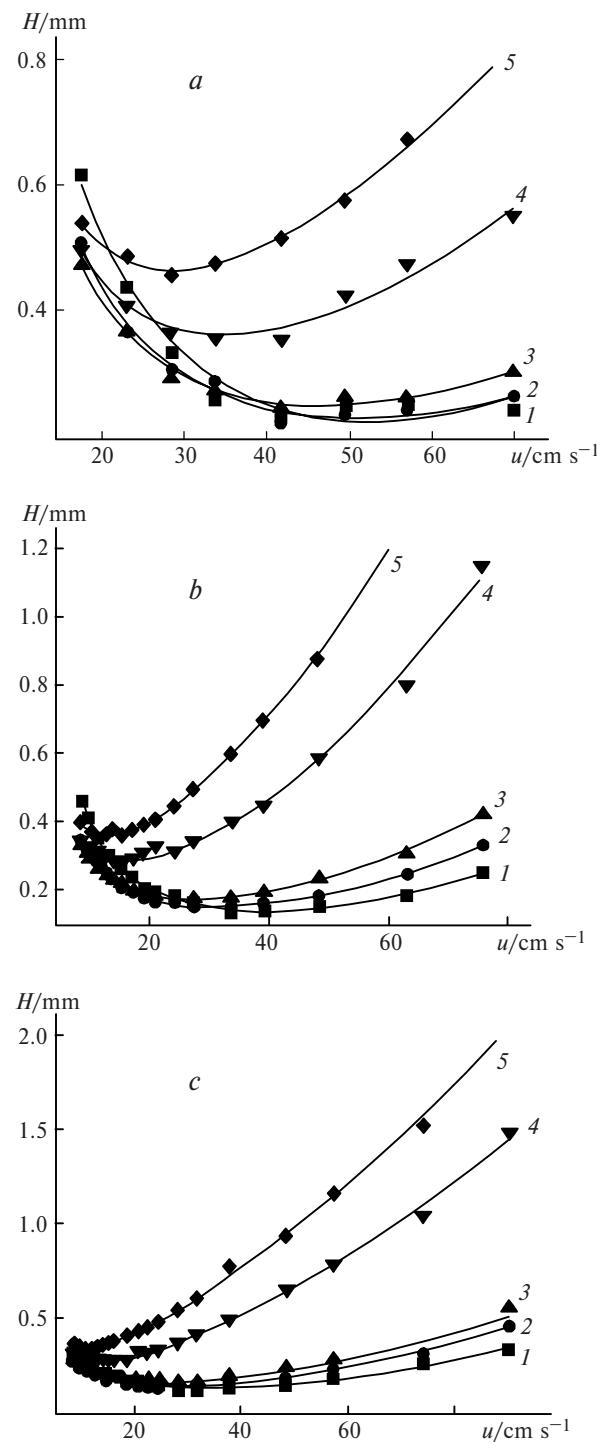
The plots of the relative retention time of hydrocarbons  $C_3$  and  $C_4$  for carbon dioxide as the carrier gas are presented in Fig. 1. As follows from the presented data, the relative retention time changes linearly with an increase in the average pressure of the carrier gas in the capillary column and that corresponds to linear Eqs. (3) and (4).

The carrier gas and adsorbent affect the equilibrium parameters of the chromatographic system and also the degree of diffusion between zones in the chromatographic column (see, e.g., Refs. 4 and 5). Therefore, in this work, we studied the kinetic parameters of the system, which are tightly related to the diffusion of zones of chromatographed compounds.

Based on the experimental plots of HETP vs. velocity of various carrier gases for hydrocarbons  $C_1$ – $C_4$  (Figs. 2 and 3), all studied hydrocarbons can be grouped as "light" ( $C_1$ – $C_3$ ) and "heavy" ( $C_4$ ).

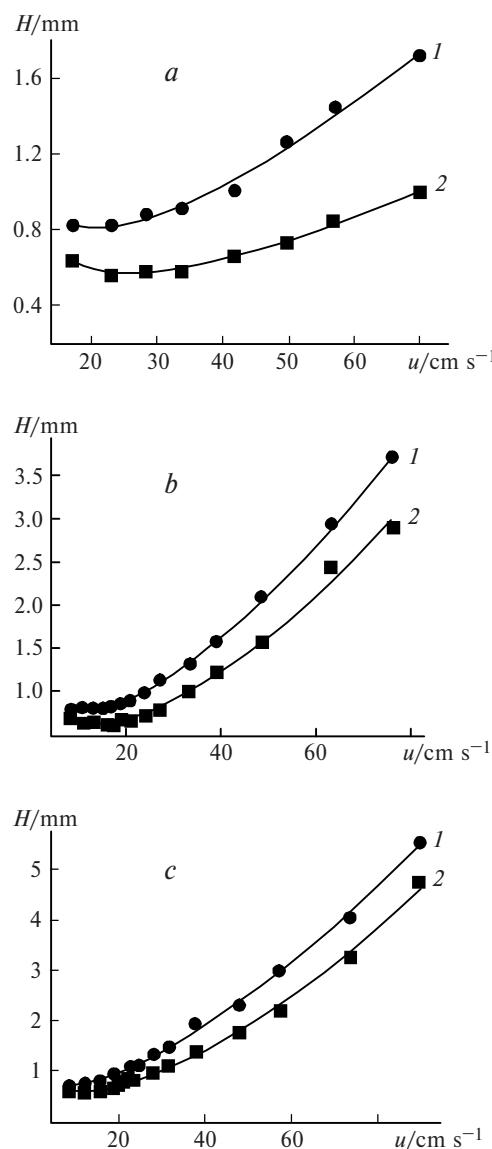
"Light" hydrocarbons are characterized by low HETP values (lower than 1.0 mm), and the HETP value increases with an increase in the molecular weight of the gas. The highest HETP was obtained for propane. In the 30–50  $cm\ s^{-1}$  velocity region, the HETP ratio for propane and propylene is close to 1.5–1.7 and independent of the nature of the carrier gas. This indicates, most likely, that the main reason for diffusion of chromatographic zones lies in high values of resistance to mass transfer in the PTMSP film.

For all carrier gases, the optimum velocity of the carrier gas at which minimum HETP values are achieved decreases with an increase in the molecular weight of the sorbate.



**Fig. 2.** HETP ( $H$ ) as a function of the velocity of various carrier gases ( $u$ ) for hydrocarbons  $C_1$ – $C_3$  at 31 °C: a, helium; b, nitrogen; and c, carbon dioxide. Sorbates: 1, methane; 2, ethylene; 3, ethane; 4, propylene; and 5, propane.

For the group of "heavy" hydrocarbons the HETP value is much higher ( $HETP > 1$  mm) than that for light hydrocarbons  $C_1$ – $C_3$ , and the HETP value for isobutane using any carrier gas exceeds by 2.5–3.5 times HETP



**Fig. 3.** HETP ( $H$ ) as a function of the velocity of carrier gases ( $u$ ) for hydrocarbons  $C_4$  at  $31\text{ }^\circ\text{C}$ : *a*, helium; *b*, nitrogen; and *c*, carbon dioxide. Sorbates: 1, *n*-butane; 2, isobutane.

for *n*-butane. This dependence indicates that when PTMSP is used steric factors due to the shape of the sorbate molecule appear.

The obtained experimental data also show that for all studied carrier gases the slope of the right branch of the Van Deemter curve is much greater for isobutane than for butane. Therefore, isobutane is characterized by much higher resistance to mass transfer. This indicates, in turn, a noticeable influence of the shape of the molecule in mass transfer processes occurring in PTMSP.

In the studied region of velocities of the carrier gas, the nature of the used carrier gas has an insignificant effect on the character of the plot of HETP vs. carrier gas velocity. Thus, the resistance to mass transfer in the

**Table 3.** Calculation of the coefficients in the Goley—Guiochon equation (6)

Sorbate	$B/\text{cm}^2\text{ s}^{-1}$	$C \cdot 10^4/\text{s}$	$D \cdot 10^4$	$\chi^2 \cdot 10^4$
Carrier gas — He				
Methane	11.181	-34.70	0.70	6.40
Ethylene	8.857	-12.30	0.50	1.60
Ethane	8.194	-5.60	0.50	0.80
Propylene	7.761	18.00	0.70	2.70
Propane	7.509	49.80	0.80	0.80
Isobutane	8.918	167.00	0.90	15.80
<i>n</i> -Butane	7.811	91.80	0.60	3.50
Carrier gas — $\text{N}_2$				
Methane	4.058	-7.80	0.40	0.70
Ethylene	3.044	0.80	0.50	0.20
Ethane	2.833	10.60	0.50	0.60
Propylene	2.678	56.30	1.10	4.00
Propane	2.585	107.90	1.40	0.90
Isobutane	5.134	260.20	3.00	8.90
<i>n</i> -Butane	4.581	162.70	3.00	3.00
Carrier gas — $\text{CO}_2$				
Methane	3.145	-2.20	0.40	0.40
Ethylene	2.262	6.00	0.50	0.50
Ethane	2.153	16.50	0.40	9.80
Propylene	1.937	81.10	0.90	3.90
Propane	1.806	143.40	0.90	5.60
Isobutane	3.345	345.50	3.00	3.00
<i>n</i> -Butane	3.799	185.90	3.70	4.28

stationary phase exerts the main effect on the efficiency and, hence, mass transfer processes in a capillary column with the PTMSP layer.

To describe the plot of HETP ( $H$ ) vs. velocity of the carrier gas ( $u$ ), we used the Goley—Guiochon equation<sup>15,16</sup>

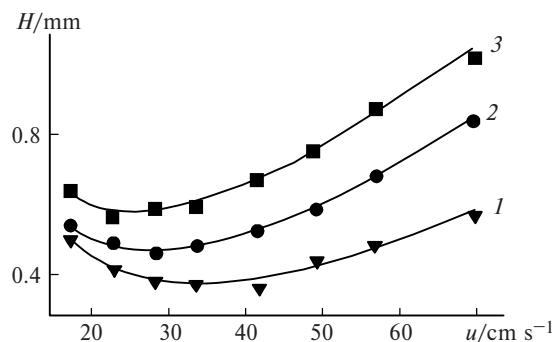
$$H = B/u + Cu + Du^2, \quad (6)$$

where  $B$  is the coefficient of longitudinal molecular diffusion,  $C$  is the coefficient of resistance to mass transfer, and  $D$  is the coefficient that reflects the contribution of the total outer-column diffusion.

The experimental data are well described by Eq. (6). This is also confirmed<sup>17</sup> by analysis of remainders.\* Table 3 contains the estimations of the  $B$ ,  $C$ , and  $D$  coefficients obtained by nonlinear regression. As follows from analysis of the experimental points (Fig. 4) and curves obtained using the coefficients in Eq. (6) (see Table 3). Equation (6) agrees well with the experimental data.

The obtained results (see Table 3) show that, first, the resistance to mass transfer in the stationary phase is the main factor determining the diffusion of the chromatographic zone and, second, for all carrier gases

\* Remainders is the term accepted in mathematical statistics corresponding to the distances from the experimental point to the curve that describes the desired dependence; the study of remainders is efficiently used for the evaluation to which extent this curve agrees with experimental data.



**Fig. 4.** HETP ( $H$ ) as a function of the velocity of the carrier gas ( $u$ ). Points, experiment at 31 °C, helium as carrier gas; lines, plot of type (6) using the calculated coefficients (see Table 3); 1, propylene; 2, propane; and 3, *n*-butane.

studied the resistance to mass transfer for isobutane is by 1.6–1.9 times higher than that for *n*-butane. The resistance coefficient of mass transfer  $C$  (see Eq. (6)) takes negative values only for some "light" sorbates. For example, when He is used as the carrier gas, the negative  $C$  values are observed for methane, ethane, and ethylene, and when nitrogen and CO<sub>2</sub> are used, methane is characterized by the negative  $C$  value. This can be explained by the fact that the Goley–Guiochon equation is most appropriate among equations used for the description of experimental data.<sup>16</sup>

The results obtained show that the behavior of PTMSP is unusual for a chromatographic sorbent. This is manifested, first, in relatively high values of the retention factor  $k$ , which allows the use of this sorbent for the separation of hydrocarbon gases. In addition, this sorbent is characterized by a high selectivity in the separation of mixtures and, finally, a new variety of the "molecular-sieve effect" is observed in the presence of PTMSP. These data confirm that this sorbent is promising to be used in analytical gas adsorption chromatography.

The authors thank V. I. Dvorkin for consulting in experimental data processing.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-3253a).

## References

- V. G. Berezkin and I. V. Malyukova, *Dokl. Akad. Nauk*, 1998, **360**, 1 [*Dokl. Chem.*, 1998 (Engl. Transl.)].
- V. G. Berezkin, I. V. Malyukova, and V. R. Alishoev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 627 [*Russ. Chem. Bull.*, 1996, **45**, 627 (Engl. Transl.)].
- V. G. Berezkin, A. A. Korolev, I. V. Malyukova, V. R. Alishoev, and J. De Zeeuw, *J. High Resol. Chromatogr.*, 1996, **19**, 272.
- V. G. Berezkin and I. V. Malyukova, *Usp. Khim.*, 1998, **67**, 839 [*Russ. Chem. Rev.*, 1998, **67** (Engl. Transl.)].
- B. V. Stolyarov, I. M. Savinov, A. G. Vitenberg, L. A. Kartsova, I. G. Zenkevich, V. I. Kalmanovskii, and Yu. A. Kalambet, *Prakticheskaya gazovaya i zhidkostnaya khromatografija* [Practical Gas and Liquid Chromatography], Izd-vo St. Petersburg Univ., St. Petersburg, 1998, 612 pp. (in Russian).
- V. G. Berezkin, A. A. Korolev, and V. S. Khotimskii, *Dokl. Akad. Nauk*, 2000, **370**, 200 [*Dokl. Chem.*, 2000 (Engl. Transl.)].
- N. Plate and Yu. Yampolskii, in *Polymeric Gas Separating Membranes*, Eds. D. R. Paul and Yu. Yampolskii, CRC Press, Boca Raton, 1994, 155.
- Yu. Yampolskii, V. Shantarovich, F. Chernyahovskii, A. Kornilov, and N. Plate, *J. Appl. Polym. Sci.*, 1993, **47**, 85.
- Yu. Yampolskii, M. Motyakin, A. Wasserman, T. Masudo, M. Teraguchi, V. Khotimskii, and B. Freeman, *Polymer*, 1999, 1745.
- R. Srinivasan, S. R. Anvil, and P. M. Burban, *J. Membr. Sci.*, 1994, **86**, 67.
- M. B. Gokzhaev, Ph. D. (Chem.) Thesis, Institute of Petrochemical Synthesis, RAS, Moscow, 1999, 150 pp. (in Russian).
- V. P. Shantarovich, I. V. Kavdina, Yu. P. Yampolskii, and A. Yu. Alentiev, *Macromolecules*, 2000, **33**, 7453.
- IUPAC 1994 Recommendations*, *Zh. Anal. Khim.*, 1998, **53**, 999 [*Russ. J. Anal. Chem.*, 1998, **53** (Engl. Transl.)].
- A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley, New York, 1972, 534 pp.
- G. Gaspar, R. Annino, C. Vidal-Madjar, and G. Guiochon, *Anal. Chem.*, 1978, **50**, 1512.
- V. G. Berezkin, I. V. Malyukova, and D. S. Avoce, *J. Chromatogr. A*, 2000, **872**, 111.
- G. A. F. Seber, *Linear Regression Analysis*, J. Wiley, New York, 1977.

Received May 17, 2001