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Thermodynamic and adsorption properties of semiinterpenetrating polymer networks based on polybenzimidazoles and polyaminoimide resin

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Thermodynamic characteristics of adsorption of organic compounds on semiinterpenetrating networks based on polybenzimidazoles and polyaminoimide resin with different compositions were studied at small coverages using inverse gas chromatography. The following characteristics were determined: adsorption equilibrium constants (specific retention volumes) of substances of different classes (*n*-alkanes, aromatic hydrocarbons, ethers, ketones, alcohols, and nitrogen- and halogen-containing compounds), appropriate changes in differential molar internal energy and Helmholtz potential, and changes in standard molar entropy of the sorbates. The contributions of the molecular fragments to the heat of adsorption were calculated. The adsorption properties of the semiinterpenetrating networks based on polybenzimidazoles and polyaminoimide resin differ from those of the starting polymeric materials and their physical mixtures with the similar composition. Unlike graphitized thermal carbon black (nonspecific adsorbent), the network and starting materials manifest the specific properties (electron-donating and electron-accepting). The difference in the thermodynamic characteristics of adsorption on the semiinterpenetrating polymeric networks with different compositions is determined by the size and geometry of interphase regions.

Key words: inverse gas chromatography, adsorption, semiinterpenetrating polymer networks, polybenzimidazoles, polyaminoimide resin, polymer-polymer mixtures, thermodynamic characteristics.

Much attention is presently given to the synthesis and study of semiinterpenetrating polymeric networks (SIPN), which are complex networks consisting of the three-dimensional and linear polymers, which are not chemically bound but inseparable due to mechanical interlacing of chains. The development of various methods for the preparation of polymer-polymer mixtures (polymerization, mixing, disintegration, precipitation, *etc.*) formed a basis for the intense study of the physicochemical properties of SIPN,[1] which are determined, to a great extent, by the nature of their functional groups and interactions between them. The studies of intermolecular interactions of these groups with substances of different classes can substantially contribute to the investigation of the physicochemical properties of SIPN. Inverse gas chromatography (IGC) was found to be an informative and convenient method for studying the adsorption of organic molecules,[2—10] because it allows one to determine the adsorption equilibrium constants and changes in the differential standard entropy of adsorption and to calculate the heat of adsorption.[11—15]

An additional characteristic of the interaction of sorbents with those or other groups of organic molecules is the contributions from different molecular groups or fragments of molecules to these interactions. Knowledge of these contributions makes it possible to refine the mechanism of adsorption.[16,17]

In this work, IGC was used to study SIPN based on aromatic polyheteroarylenes. An interest in such mixtures is caused, first of all, by a combination of the thermal and chemical stabilities with high mechanical characteristics. The thermodynamic characteristics of adsorption of organic compounds on the surface of the SIPN synthesized with different compositions were determined, and these characteristics were compared for the starting polymers and their physical mixtures. We also attempted to reveal and explain the difference in the properties determining their use in practice.

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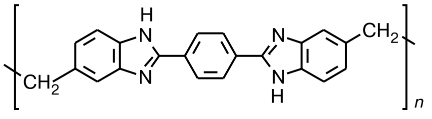
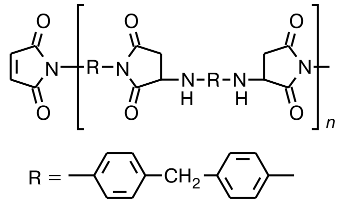
Table 1. Characteristics of the starting polymers (M_r is the molecular weight, ρ is density, T_p is the limiting temperature of thermal stability, and η_{red} is the reduced viscosity)

Polymer	M_r	Composition	ρ/g cm^{-3}	T_p/°C	η_{red}/dL g^{-1}
PBI	30000—35000	 (VTU-PBI-IF-76)	0.90—0.95	400	0.94
PBI	20000		0.85—0.90	400	0.57
PAIR	3000—3500	 (TU 09-06-173-73)	0.82—0.80	350	—

Experimental

Polybenzimidazoles (PBI) with different molecular weights, polyaminoimide resin (PAIR), and related SIPN were chosen as objects for the study. The characteristics of the starting polymers are presented in Table 1.

The starting polymeric materials were deposited on the support surface (Chromaton N-AW-DMCS) with the inert and small specific surface area (particle size 0.160—0.200 mm) (Table 2). For this purpose, 2% solutions of the starting polymers in DMF (the volume corresponded to the content of 5—10 wt.% of the support weight) were prepared. A weighed amount of the support was added to the prepared solution, and the resulting mixture was stored for 5—7 days with periodical stirring (for the adsorption of the polymer and formation of the uniform coating of the support by the polymer). Then the solvent was removed with continuous stirring by slow evaporation first at an atmospheric pressure and then on a rotary evaporator.

Table 2. Characteristics of columns (m_s is the weight of the support, m_p is the weight of the polymer, l is the column length, ΔT is the temperature interval, d is the thickness of the polymer film on the support surface determined using Eq. (2), and $S_{sp}{}^p$ is the specific surface of the polymer film on the support)

Blend	m_s/g	m_p/g	$x \cdot 10^{-2}$	l/cm	ΔT/°C	d/nm	$S_{sp}{}^p$/m^2 g^{-1}
Chromaton N-AW-DMCS	1.7125	—	0.00	150	56—100	—	0.6
100% PAIR	3.5986	0.1799	5.00	300	55—110	107—110	—
100% PAIR	1.6859	0.8430	5.00	300	55—110	107—110	—
100% PBI^a	3.6145	0.1807	5.00	300	55—110	97—103	—
100% PBI^a	1.7648	0.8824	5.00	300	55—110	97—103	—
100% PAIR	3.5865	0.2699	7.00	300	60—106	153—157	1.2
100% PAIR	1.4125	0.1063	7.00	150	57—127	153—157	1.2
100% PBI^a	3.6204	0.2725	7.00	300	62—107	140—148	0.4
100% PBI^a	1.8348	0.1381	7.00	150	56—121	140—148	0.4
100% PBI^b	3.2098	0.2416	7.00	300	61—108	132—140	—
100% PBI^b	1.8467	0.1390	7.00	150	56—120	132—140	—
90% PBI + 10% PAIR	3.6044	0.2713	7.00	300	60—105	—	0.6
90% PBI + 10% PAIR	1.5797	0.1189	7.00	150	56—135	—	0.6
70% PBI + 30% PAIR	3.2922	0.2478	7.00	300	60—106	—	0.8
70% PBI + 30% PAIR	1.5956	0.1201	7.00	150	55—134	—	0.8
100% PAIR	3.5899	0.3590	10.00	300	63—106	226—231	—
100% PAIR	1.7667	0.8834	10.00	300	63—106	226—231	—
100% PBI^a	3.6185	0.3618	10.00	300	65—106	206—218	—
100% PBI^a	1.7912	0.8956	10.00	300	65—106	206—218	—

Note. $x = m_p/(m_p + m_s)$.

[a] $\eta_{red} = 0.57$ dL g^{-1}.

[b] $\eta_{red} = 0.94$ dL g^{-1}.

The columns with different amounts of the polymeric phase (PAIR or PBI) on the support surface in the 5—10 wt.% interval were thus prepared.

The SIPN films on the inert support were obtained as follows. The PBI—PAIR blends were prepared by mixing 2% solutions of the starting polymers in DMF taken in different proportions: PAIR was dissolved in DMF at ~20 °C, PBI was dissolved at 150 °C for 40 min in a nitrogen atmosphere; an insoluble precipitate (0.20 wt.%) was filtered off. The content of PAIR in the blend was 10 and 30 wt.%. The resulting solutions containing two polymeric components were deposited on the sorbent similarly to the method described above. After the solvent was removed, PAIR was structured on the matrix of linear PBI (reduced viscosity $\eta_{\text{red}} = 0.57$ dL g^{-1}) for 8 h at 230 °C in argon. The following blends of polymers with the SIPN structure were thus prepared: 90 wt.% PBI + 10 wt.% PAIR (90 : 10) and 70 wt.% PBI + 30 wt.% PAIR (70 : 30). The content of the SIPN phase on the support surface was 7 wt.% (related to the support weight).

The polymeric adsorbents prepared and dried to a constant weight were placed in a chromatographic column, which was preliminarily washed with ethanol and dried, and conditioned in a argon flow for 8 h at 200 °C. The characteristics of the column prepared are presented in Table 2.

Chromatographic studies were carried out on Perkin—Elmer 900 and Tsvet-560 gas chromatographs with flame-ionization detectors. Nitrogen was used as the carrier gas, its flow rate in experiment being 30 mL min^{-1}. Methane served as a nonsorbed component for the estimation of the dead time of the chromatograph. Stainless steel chromatographic columns 300 and 150 cm long with an inner diameter of 0.2 cm were used. The accuracy of temperature control of the columns in the thermostats was ±0.2 °C. The pressure at the inlet to the chromatographic column was detected using a standard pressure gauge, and these data were used to correct retention volumes.

n-Alkanes, aromatic hydrocarbons, ethers, ketones, alcohols, and halogen- and nitrogen-containing substances were used as adsorbates. Molecules of these substances have different electronic structures and belong to different groups by their ability to specific and nonspecific intermolecular interactions.[11] All adsorbents used were reagent grade "for chromatography." The main characteristics of the sorbates are presented in Table 3. Gaseous samples were injected manually using a Hamilton gas-proof syringe. To achieve the critical dilution, an adsorbate vapor—air mixture (0.5—20 mL) was introduced.

The retention times of the adsorbates were determined from the position of the chromatographic peak maximum. Four to five measurements were carried out at each temperature. The specific retention volume ($V_{m,1}$) was calculated from the mean retention time. The retention factors of the sorbates used on the polymeric materials were determined at five—six temperatures.

The changes in the differential molar internal energy ($-\Delta\bar{U}^0{}_1$) equal to the heat of adsorption, entropy ($\Delta\bar{S}^0{}_{1,c}$), and Helmholtz potential ($\Delta\bar{F}^0{}_{1,c}$) were determined from the plots of $\ln V_{m,1}$ *vs.* $1/T$.[12]

The contributions of different functional groups to the thermodynamic characteristics of adsorption were determined[16,17] assuming that the contributions of the same groups in different compounds to the thermodynamic characteristics of adsorption from the gas phase are equal. Accepting the additive scheme, the heat of adsorption of compounds $\bar{q}_1$ can be presented as the sum of the contributions to the heat of different groups

$$\bar{q}_1 = \sum_i \bar{q}_i n_i, \tag{1}$$

where $\bar{q}_i$ is the contribution to the heat of adsorption from the *i*th group, and n_i is the number of groups of the same type.

The thickness of the polymeric films (d) on the support surface was calculated using the equation[19]

$$d = x/(\rho S_{\text{sp}}{}^{\text{s}}(100 - x)), \tag{2}$$

where x is the content of polymer in the packing (wt.%), $S_{\text{sp}}{}^{\text{s}}$ is the specific surface area of the support, and ρ is the density of the polymeric phase.

The specific surface area of the polymeric materials was determined using the thermal desorption of argon.[20]

Electronic microscopic studies of the polymeric films were carried out with a Tesla BS-350 scanning autoemission electron microscope with a voltage on the electron tubes of 16 kV. In order to obtain microphotographs of good quality and to form the conducting layer, the film samples (PAIR, PBI, and SIPN with different compositions) were covered with a thin gold layer using thermal sputtering in a vacuum followed by the condensation of Au atoms on the support covered with the samples.

Results and Discussion

The gas chromatographic experiment can be carried out in two different concentration intervals, depending on the amount of the adsorbate introduced into the chromatographic column: under conditions of the ultimate concentration and at infinite dilution of the sorbate. We performed the IGC study under conditions of infinite dilution because, in this case, the interaction between the sorbate molecules can be neglected and the retention time depends only on the presence of active sites in the polymers under study. In addition, the chromatographic equilibrium is fairly rapidly established under these conditions.[11,21]

For each of the sorbates and columns used in the work, we found the limiting temperatures (see Table 2), below which the retention volumes depend on the flow rate of the carrier gas and the amount of the sample introduced. Inside these temperature ranges the values of $V_{m,1}$ and thermodynamic characteristics of sorption were measured: from the bottom they are restricted by the low rate of diffusion of the sorbates to the polymeric phase film, and from the top they are restricted by the small retention times of the sorbate, due to which the different in retention times of the sorbate and methane becomes too small and the accuracy of measurement decreases. In addition, the temperature interval was chosen in such a way that the chromatographic peaks for each adsorbate were symmetrical and their retention times were independent of the amount of the sample (in the temperature region where Henry´s law is valid). Under these conditions, the reten-

Table 3. Characteristics of sorbates (boiling points, dipole moments μ, and polarizabilities α) and their specific retention volumes ($V_{m,1}$) at 100 °C on PAIR, PBI, SIPN with the composition 70 : 30 and 90 : 10, and graphitized thermal carbon black (GTC) (the $V_{m,1}$ values for the physical blend were calculated using Eq. (5))

Adsorbate	B.p./°C	μ^{20}/D	α/Å^3	$V_{m,1}$/cm^3 g^{-1}						
				PAIR	PBI	PBI + PAIR (70 : 30)		PBI + PAIR (90 : 10)		GTC
						physical mixture	SIPN	physical mixture	SIPN	
				Saturated, unsaturated, and cyclic hydrocarbons						
n-Hexane	68.74	0	11.9	0.52	1.14, 1.13 [a]	0.09	0.96	1.05	1.11	319 [b]
n-Heptane	98.43	0	13.7	1.04	1.84, 1.84 [a]	1.55	1.67	1.74	1.82	1395 [b]
Hept-1-ene	93.64	0.3	13.35	1.40	2.01	1.81	1.93	1.94	2.03	940 [b]
Isooctane	99.24	0	—	0.79	1.35	1.15	1.23	1.28	1.34	—
n-Octane	127.67	0	15.6	2.66	3.06, 3.07 [a]	2.94	3.13	3.02	3.16	379
n-Nonane	150.8	0	17.48	6.23	5.05	5.38	5.70	5.16	5.37	1695
n-Decane	174	0	19.15	13.6	8.25	9.58	10.5	8.67	9.03	7093
Cyclohexane	81.4	0.3	11	0.42	1.02	0.78	0.84	0.93	0.97	—
				Aromatic hydrocarbons						
Benzene	80.09	0	10.4	1.26	2.08, 2.08 [a]	1.79	1.97	1.97	2.05	223 [b]
Toluene	110.63	0.4	12.4	2.03	3.71, 3.72 [a]	3.10	3.29	3.49	3.67	90
Ethylbenzene	136.15	0.4	—	3.78	6.36	5.44	5.81	6.04	6.3	425
Isopropylbenzene	152.39	0.4	—	6.30	8.94	8.04	8.76	8.63	9.03	426
o-Xylene	144.41	0.5	14.5	4.76	7.54	6.57	7.10	7.2	7.54	—
				Ethers						
Dibutyl ether	140.9	1.2	15.35	14.2	9.03	13.9	26.1	10.4	12.2	—
Diisopropyl ether	68.5	1.2	—	37.7	2.46, 2.44 [a]	4.16	8.0	2.93	3.42	—
1,4-Dioxane	101.4	0.4	—	14.2	12.2	19.3	36.6	14.2	16.4	5.78
				Halogen-containing compounds						
o-Fluorotoluene	114	—	—	2.66	4.44	3.81	19.5	4.22	4.39	—
Chlorobenzene	132	1.6	13.9	65.4	7.24	14.0	8.17	9.03	9.21	81.9
CH_2Cl_2	40.1	1.58	—	17.5	4.18	6.42	6.75	4.82	4.95	—
$CHCl_3$	61.2	1.1	8.23	14.2	3.39	5.20	11.4	3.91	3.97	4.98
1,2-Dichloroethane	83.7	1.8	—	24.3	5.26	8.32	6.69	6.13	6.42	4.27
CCl_4	76.9	0	10.5	20.9	2.32	4.48	2.21	2.89	3.13	7.39
				Ketones						
Acetone	56.24	2.86	6.32	35.5	5.93	10.2	15.3	7.09	7.61	2.49
Methyl ethyl ketone	79.6	2.8	8.2	46.5	8.85	14.6	27.7	10.44	12.18	—
				Alcohols						
Ethanol	78.37	1.7	5.6	178	65.4	88.2	130	72.2	104	1.25
Propan-2-ol	82.4	1.7	—	69.4	86.5	81.0	122	84.6	124	2.23
Propan-1-ol	97.2	1.7	7.3	354	117	163	254	130	196	2.49
Butan-2-ol	99.5	1.7	—	117	159	145	225	154	235	6.76
Butan-1-ol	117.5	1.7	9.5	652	221	306	480	247	380	9.79
Isobutanol	107	1.7	—	219	176	188	242	180	226	6.76
Hexan-1-ol	157.2	1.7	—	2592	750	1095	1735	857	1330	134
Phenol	182	1.6	—	4629	1451	2054	3287	1629	2592	118
				Nitrogen-containing compounds						
Acetonitrile	82	3.5	4.4	1572	180	344	579	223	368	—
1-Nitropropane	132	2.98	—	215	102	127	227	109	192	—
Nitrobenzene	210.9	4.21	12.92	10301	428	1112	2109	589	1073	552
Pyridine	115.4	2.3	11.1	728	228	323	538	256	414	18.7

[a] Obtained for PBI with η_{red} = 0.94 dL g^{-1}.

[b] Obtained at 200 °C on the carbon black covered by pyrocarbon.[18]

tion factor for a small sample (at the infinite dilution of the sorbate) is equal to the adsorption equilibrium constant in the equation of the Henry isotherm.[11,12]

In addition, no hysteresis was observed when the measurements were carried out in the mode of successive heating and cooling. Finally, the $V_{m,1}$ values were found to be independent of the amount of the sorbate sample. The above data suggest that the thermodynamic parameters obtained characterize the conditions of infinite dilution of the sorbate or the initial regions of the adsorption isotherms.

The retention times of alcohols and nitrogen-containing sorbates were determined on the columns with l = 150 cm, because in longer columns these substances are irreversibly retained. The retention factors of all other sorbates (saturated, unsaturated, cyclic, and aromatic hydrocarbons, ethers, halogen-containing compounds, and ketones) were determined on the columns with l = 300 cm (see Table 2).

Thus, the temperature interval (ΔT) and the length of the chromatographic column (l) varied for different sorbates. However, the common temperature interval was 55—135 °C (see Table 2).

Sorbate molecules can be retained by polymer as a result of both adsorption on the external pellet surface due to nonspecific and specific interactions with different adsorption sites and adsorption and diffusion into the polymer bulk. In addition, diffusion of the molecules into the cavity of the polymer and adsorption on the inner surface of these cavities are also possible.

Researchers of the thermodynamic properties of polymers by IGC deal with relatively thin polymeric films on a solid support. Naturally, the characteristics determined by this method for polymeric phases with different structures can depend on both the support nature and thickness of the supported polymeric film.[21]

We studied the influence of the amount of the polymeric phase (PBI with η_{red} = 0.57 dL g^{-1} and PAIR) carried by the inert support (Chromaton) on the retention volume of the sorbate (Table 4). The retention of some sorbates on the noncovered support was studied to obtain a more clear chromatographic pattern. It is noteworthy that the chromatographic peaks on the noncovered supports for the polar sorbates (chlorobenzene, pyridine, acetone, toluene) are asymmetric, and the retention time of the sorbate depends on the volume of the introduced sample. Nevertheless, the latter differs insignificantly from the retention time of the nonsorbed substance (methane). The nonpolar sorbates (*n*-heptane, *n*-hexane, benzene, *etc.*) are not virtually retained in the column, and their retention times differ insignificantly. Thus, it can be concluded that the contribution of adsorption on the solid support is negligible.

Table 4. Dependence of the specific retention volumes ($V_{m,1}$) of sorbates on the content of the polymeric phase (x) at 100 °C

Sorbate	$x \cdot 10^{-2}$ (%)		
	5	7	10
	PAIR		
n-Hexane	0.79	0.69	0.53
n-Heptane	1.25	1.17	1.06
Benzene	1.42	1.38	1.27
Chlorobenzene	69.2	68.4	66.0
Pyridine	769.0	758.0	732.0
Acetone	39.4	38.5	36.4
Dibutyl ether	49.8	47.7	39.8
	PBI		
n-Hexane	1.24	1.20	1.15
n-Heptane	1.96	1.94	1.87
Benzene	2.23	2.17	2.09
Chlorobenzene	7.49	7.42	7.26
Pyridine	242.0	238.0	232.0
Acetone	6.29	6.21	6.07
Dibutyl ether	9.44	9.28	9.10

The $V_{m,1}$ values for some sorbates obtained at different concentrations of the polymeric phase (PAIR and PBI) on the support surface are presented in Table 4. It is seen that beginning from the 5% content, in particular, PAIR, on Chromaton (this corresponds to d = 107—110 nm, see Table 2) the $V_{m,1}$ values of all sorbates presented increase. However, the increase in the content of the PAIR phase from 7 to 10 wt.% has a smaller effect on $V_{m,1}$. The increase in $V_{m,1}$ with a change in the polymeric phase on the support from 5 to 10 wt.% is also observed for PBI, although it is less significant. In turn, this agrees with the results of studying the specific surface area of the supported polymeric film $S_{sp}{}^{p}$ (see Table 2). For example, for PAIR, which is characterized by the formation of the three-dimensional polymeric network, the specific surface area is greater than that for PBI. Therefore, we can conclude that diffusing sorbate molecules penetrate into a greater depth of the polymeric phase in the case of PAIR as compared with PBI.

It is most likely that the increase in the specific retention volume caused by the change of the polymeric phase content on the support surface from 5 to 10% indicates that the volume sorption contributes to $V_{m,1}$. Diffusion of small sorbate molecules to the polymeric phase at temperatures lower than the vitrification temperature is determined by the density of packing of polymeric chains rather than by their mobility. A minor change in $V_{m,1}$ with an increase in x can be ascribed to the increase in the contribution of sorption, which occurs due to the diffusion of the sorbate molecules to the polymeric phase bulk. However, compared to the contribution of adsorption to the mechanism of sorbate retention, the fraction of the volume sorption is small (see Table 4). Since the contribution of the latter at x = 10% becomes almost minimum, all further studies of the adsorption properties of the polymeric films were carried out at this x.

The physical and physicomechanical properties of polymers depend substantially on the molecular weight.[22] For example, we studied the dependence of $V_{m,1}$ of some sorbates on the molecular weight (M_r), in particular, for PBI with $\eta_{red} = 0.57$ and 0.94 dL g^{-1} (see Table 1). The data presented in Table 3 indicate that $V_{m,1}$ is independent of M_r for PBI. This agrees with the data of the thermomechanical and thermogravimetric studies of PBI with different molecular weights. Beginning from $M_r = 15000$ ($\eta_{red} = 0.43$ dL g^{-1}), the temperature interval of softening achieves its maximum and remains virtually unchanged with the further increase in the molecular weight.[22] Thus, the relation between $V_{m,1}$ and M_r of PBI is observed in the region of lower molecular weights ($M_r < 15000$), *i.e.*, in the region where the polymeric properties only begin to form. In addition, the molecular weight of the polymer has a slight effect on the diffusion rate and permeability of the sorbates to the polymeric phase.[23] For further chromatographic studies, we used PBI with $M_r = 20000$ because of its higher solubility.

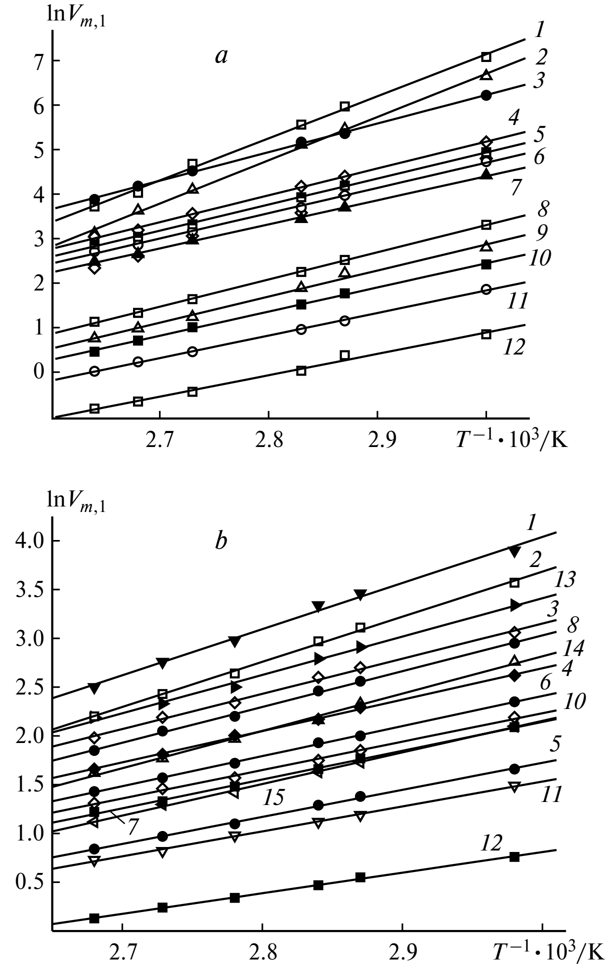


Fig. 1. Plots of $\ln V_{m,1}$ *vs.* inverse temperature on PAIR (*a*) and PBI (*b*) for some adsorbates: 1,4-dioxane (*1*), diethyl ether (*2*), chlorobenzene (*3*), 1,2-dichloroethane (*4*), CCl_4 (*5*), CH_2Cl_2 (*6*), CH_3Cl (*7*), ethylbenzene (*8*), *n*-octane (*9*), toluene (*10*), benzene (*11*), *n*-hexane (*12*), isopropylbenzene (*13*), *n*-nonane (*14*), and *n*-heptane (*15*).

A comparison of the behavior of compounds of different classes in the chromatographic experiment makes it possible to understand what functional groups of the polymers, which determine the mechanism of sorption and properties of the polymeric materials under study, are involved in intermolecular interactions. For example, the plots of $\ln V_{m,1}$ *vs.* $1/T$ for some sorbates on the polymeric films in the temperature intervals under study (see Table 2) are presented in Figs. 1 and 2. These plots are linear, indicating that no transformations associated, *e.g.*, with phase transitions capable of changing the mechanism of

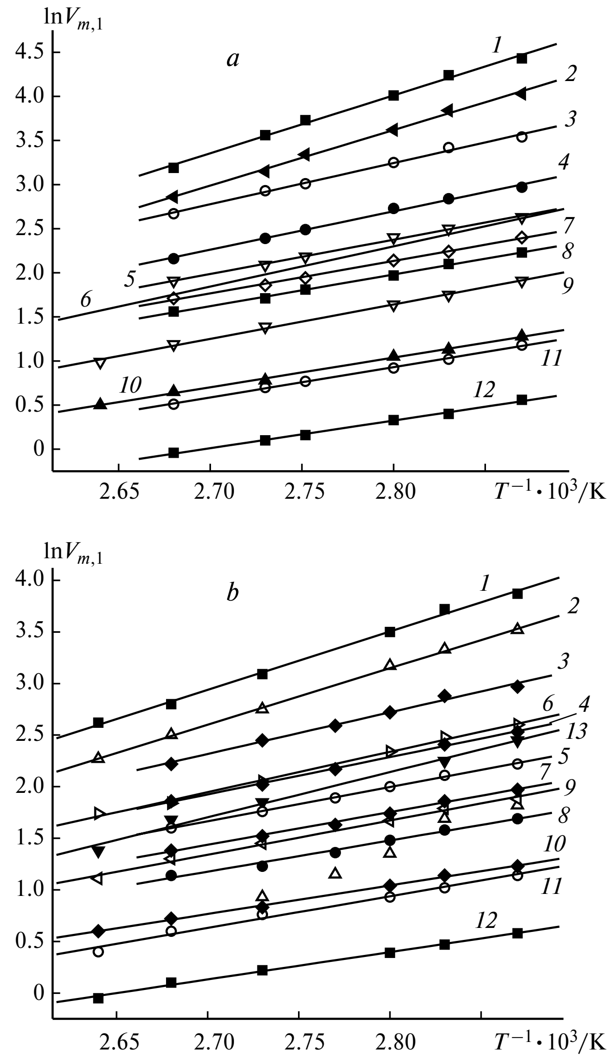


Fig. 2. Plots of $\ln V_{m,1}$ *vs.* inverse temperature on SIPN with the compositions 70 : 30 (*a*) and 90 : 10 (*b*) for some adsorbates: 1,4-dioxane (*1*), diethyl ether (*2*), chlorobenzene (*3*), 1,2-dichloroethane (*4*), CH_2Cl_2 (*5*), ethylbenzene (*6*), CH_3Cl (*7*), CCl_4 (*8*), toluene (*9*), benzene (*10*), *n*-heptane (*11*), *n*-hexane (*12*), and *n*-nonane (*13*).

sorption of these substances, occur in the polymeric structure.

The adsorption equilibrium constants (specific retention volumes) of the sorbates obtained on the polymeric films at 100 °C and their physicochemical properties are presented in Table 3.

Tables 5 and 6 contain the correlation coefficients r and coefficients A and B in the linear equation

$$\ln V_{m,1} = A + B/T. \qquad (3)$$

The $-\Delta\bar{U}^0{}_1$, $\Delta\bar{S}^0{}_{1,c}$, and $\Delta\bar{F}^0{}_{1,c}$ values calculated from Eq. (3) are also presented in Tables 5 and 6.[12]

All polymeric films studies exhibit the linear dependence of $-\Delta\bar{U}^0{}_1$ on the number of C atoms (n_C) in molecules of the sorbates of different classes of organic compounds. Table 7 contains the coefficients in the linear equation

$$-\Delta\bar{U}^0{}_1 = a + bn_C. \qquad (4)$$

The b coefficient, which determines the slope of these lines, is equal to the increment of the energy of the CH_2 group. It is approximately the same for all adsorbates on the polymeric materials under study.

Sometimes it is difficult to determine the specific features and adsorption mechanism based on the adsorption interaction of molecules with different functional groups, because an increase in the contribution to the interaction of one group can be compensated by a decrease in the contribution of another group. Therefore, it is important to determine the contributions of different functional groups to the thermodynamic characteristics of adsorption and to consider its mechanism according to these data. The contributions of different functional groups to the heat of adsorption ($\bar{q}_1$) calculated using Eq. (1) are presented in Table 8. It is seen from these data that the contributions of the polar groups (electron-donating and electron-accepting) to $\bar{q}_1$ are greater for adsorption on the polymeric sorbents than on graphitized thermal carbon black (GTC), while the contributions of the methyl, methylene, and other nonpolar groups for adsorption on the polymeric sorbents are smaller than for adsorption on the GTC surface. It is noteworthy that the contributions of the methyl groups are greater than those of the methylene groups, which is probably related to their higher mobility. In addition, for all polymeric sorbents studied, the contribution of the OH group to the heat of adsorption is maximum. This indicates that both electron-donating and electron-accepting properties are manifested in this case. Thus, the contributions to the heat of adsorption for PAIR, PBI, and SIPN differ basically from those for GTC, and the adsorption properties of SIPN approach the properties of PBI.

Unlike GTC,[11] the polymeric films are capable of specific interactions (see Table 3). The presence of π-electrons in molecules of unsaturated and aromatic hydrocarbons contributes noticeably to the intermolecular interactions of these compounds with the functional groups on the polymer surface. For example, unsaturated hydrocarbons are eluted before saturated hydrocarbons on the column with GTC (according to the polarizability of their molecules), whereas for PAIR, PBI, and SIPN they are eluted behind saturated hydrocarbons, although the boiling points of unsaturated hydrocarbons are lower (see Table 3). Benzene is also eluted on all polymeric films after *n*-hexane, while on GTC *n*-hexane (with a higher electron polarizability than benzene) is eluted behind benzene.[11]

A substantial increase in the retention factors and $-\Delta\bar{U}^0{}_1$ values on PAIR (see Tables 3, 5, and 6) in the series benzene—toluene—chlorobenzene—pyridine—nitrobenzene fully agrees with an increase in the polarities of these molecules. On the one hand, pyridine, whose boiling point is lower than that of chlorobenzene, is eluted after chlorobenzene. On the other hand, although the polarities of phenol and chlorobenzene are the same, the first compound is retained on PAIR ~70 times as strong as the second compound apparently due to the presence of the OH group capable of hydrogen bonding with the functional groups of this polymer. Acetonitrile, whose polarity is higher and the boiling point is lower than those of pyridine, leaves the column after pyridine. Such a behavior of the sorbates on PAIR is determined, most likely, by the presence of the NH and C=O groups and the partially protonated amide group in the polymer molecule.

A similar elution order of the substance is observed on PBI and SIPN. Aromatic hydrocarbons are more strongly retained on the linear PBI surface, because the interaction of the planar aromatic rings of the benzene molecule and its analogs with the linear polymer occurs much more easily than that with PAIR (three-dimensional polymeric network). This can explain, most likely, why the linear molecules of normal paraffins are retained on PBI 1.3—2 times as long as on PAIR. As should be expected, the entropy factor plays a remarkable role in this case: the $\Delta\bar{S}^0{}_{1,c}$ values for PBI are much lower than those for PAIR (see Tables 5 and 6).

A comparison of the data in Tables 3 and 8 shows that the retention of the corresponding *n*-alkanes on GTC is higher than that on the polymeric sorbents. This indicates that the adsorption potential of the surface of the latter is lower than the potential of the planar graphite surface. However, alcohols, ketones, ethers, and nitrogen-containing sorbates are much weaker retained on GTC, *i.e.*, in the case of the polymeric sorbents, the electron-donating and electron-accepting properties are more strongly manifested compared to the GTC surface.

In order to compare the experimental retention volumes of the sorbates on SIPN with the compositions 90 : 10 and 70 : 30, we calculated[23] the $V_{m,1}$ values corre-

Table 5. Correlation coefficients *r*, coefficients in Eq. (3), and characteristics $-\Delta\bar{U}^0{}_1 = \bar{q}_1$ (kcal mol^{-1}), $\Delta\bar{S}^0{}_{1,c}$ (cal mol^{-1} K^{-1}), $\Delta\bar{F}^0{}_{1,c}$ (kcal mol^{-1}) for PAIR and PBI

Adsorbate	PAIR						PBI					
	$A\cdot10^3$	$-B$	r	$\bar{q}_1$	$-\Delta\bar{S}^0{}_{1,c}$	$-\Delta\bar{F}^0{}_{1,c}$	$A\cdot10^3$	$-B$	r	$\bar{q}_1$	$-\Delta\bar{S}^0{}_{1,c}$	$-\Delta\bar{F}^0{}_{1,c}$
Saturated, unsaturated, and cyclic hydrocarbons												
n-Hexane	4.7982	13.505	0.9913	9.5	28.8	−0.5	2.1121	5.5261	0.9988	4.2	13	0.1
n-Heptane	5.3753	14.306	0.9976	10.7	30.4	0	2.6815	6.5858	0.9936	5.3	15.1	0.5
Hept-1-ene	5.5774	14.515	0.9942	11.1	30.8	0.3	2.7692	6.7202	0.9967	5.5	15.3	0.5
Isooctane	5.1100	13.92	0.9898	10.2	29.6	−0.2	2.1936	5.5991	0.9947	4.4	13.1	0.2
n-Octane	5.8540	14.694	0.9935	11.6	31.2	0.7	3.194	7.4269	0.9978	6.3	16.7	0.8
n-Nonane	6.2912	14.993	0.9926	12.5	31.8	1.4	3.8292	8.6703	0.9958	7.6	19.2	1.2
n-Decane	6.8003	15.589	0.996	13.5	33.0	1.9	4.3577	9.5706	0.999	8.7	21	1.6
Cyclohexane	4.5717	13.128	0.9937	9.1	28.1	−0.6	1.9964	5.3352	0.9907	4	12.6	0
Aromatic hydrocarbons												
Benzene	5.0823	13.41	0.9992	10.1	28.6	0.2	2.5676	6.1707	0.9976	5.1	14.2	0.5
Toluene	5.4420	13.879	0.9984	10.8	29.6	0.5	2.9021	6.472	0.9984	5.8	14.8	1.0
Ethylbenzene	6.1374	15.106	0.9997	12.2	32.0	1.0	3.6601	7.9476	0.9994	7.3	17.8	1.4
Isopropylbenzene	6.6198	15.909	0.9983	13.2	33.6	1.4	3.9039	8.297	0.999	7.8	18.5	1.6
o-Xylene	6.2484	15.199	0.9996	12.4	32.2	1.2	3.7473	8.0275	0.999	7.4	17.9	1.5
Ethers												
Dibutyl ether	9.2302	21.131	0.9947	18.3	44.0	2.7	4.6157	10.16	0.9985	9.2	22.2	1.6
Diisopropyl ether	7.7654	18.117	0.9934	15.4	38.0	2.0	3.9395	9.6314	0.9947	7.8	21.1	0.7
1,4-Dioxane	9.4477	21.201	0.9971	18.8	44.1	3.0	4.7224	10.125	0.9943	9.4	22.1	1.9
Halogen-containing compounds												
o-Fluorotoluene	5.5446	13.891	0.997	11.0	29.6	0.7	3.0427	6.6924	0.9966	6	15.3	1.1
Chlorobenzene	6.4543	13.133	0.9956	12.8	28.1	3.1	3.6423	7.7625	0.9984	7.2	17.4	1.5
CH_2Cl_2	5.7051	12.406	0.9982	11.3	26.6	2.1	3.1152	6.9262	0.992	6.2	15.7	1.1
$CHCl_3$	5.4325	11.894	0.9977	10.8	25.6	2.0	2.9799	6.787	0.9977	5.9	15.5	0.9
1,2-Dichloroethane	6.0655	13.014	0.9986	12.1	27.8	2.4	3.2724	7.1154	0.9994	6.5	16.1	1.2
CCl_4	5.8851	12.717	0.992	11.7	27.3	2.3	2.7993	6.6637	0.995	5.6	15.2	0.6
Ketones												
Acetone	6.9562	15.093	0.994	13.8	32.0	2.6	5.7989	13.751	0.9989	11.5	29.3	1.3
Methyl ethyl ketone	7.5217	16.306	0.999	14.9	34.4	2.8	6.0338	14.009	0.9983	12	29.8	1.6
Alcohols												
Ethanol	5.0108	8.2538	0.9996	10	14.4	3.8	4.2055	7.0896	0.9989	8.4	12.1	3.1
Propan-2-ol	4.3084	7.3068	0.9976	8.6	12.5	3.1	4.3225	7.1279	0.9985	8.6	12.2	3.3
Propan-1-ol	5.4788	8.814	0.9984	10.9	15.5	4.4	4.5182	7.3504	0.9979	9	12.6	3.5
Butan-2-ol	4.7677	8.012	0.9963	9.5	13.9	3.5	4.6441	7.3715	0.9988	9.2	12.7	3.8
Butan-1-ol	5.7568	8.9468	0.9993	11.4	15.8	4.8	4.792	7.4474	0.998	9.5	12.8	4.0
Isobutanol	5.1283	8.3517	0.9967	10.2	14.6	4.0	4.6849	7.3886	0.9994	9.3	12.7	3.8
Hexan-1-ol	7.2869	11.537	0.9987	14.5	20.9	5.8	5.2835	7.5377	0.9985	10.5	13	4.9
Phenol	7.5758	11.716	0.9977	15.1	21.3	6.3	5.5376	7.5654	0.9992	11	13	5.4
Nitrogen-containing compounds												
Acetonitrile	5.1874	6.5376	0.9987	10.3	11.0	5.5	2.8387	2.4149	0.9985	5.6	2.8	3.8
1-Nitropropane	3.9277	5.1557	0.9985	7.8	8.3	4.0	2.1423	1.1205	0.9984	4.3	0.2	3.4
Nitrobenzene	6.0595	6.9961	0.9995	12.0	11.9	6.9	3.6589	3.7453	0.9976	7.3	5.5	4.5
Pyridine	4.4047	5.2117	0.9981	8.8	8.4	4.9	3.0456	2.7283	0.9973	6.1	3.4	4.0

sponding to the physical mixtures of PAIR and PBI with similar compositions

$$\ln V_{m,1} = \frac{m_{\text{PAIR}}}{m_{\text{tot}} \ln V^{\text{PAIR}}_{m,1}} + \frac{m_{\text{PBI}}}{m_{\text{tot}} \ln V^{\text{PBI}}_{m,1}}, \qquad (5)$$

where m_{PAIR} is the weight of PAIR for the column packed with SIPN with the corresponding composition, m_{PBI} is the weight of PBI for the same column, and m_{tot} is the total weight of the polymeric film.

The data found using Eq. (5) can be obtained experimentally. For this purpose, the column is needed that consists of 90 (70)% PBI and 10 (30)% PAIR. In this case, both polymer should separately be deposited on the support surface.

The experimental $V_{m,1}$ values for the 90 : 10 and 70 : 30 SIPN and the $V_{m,1}$ values for the physical mixture of PBI and PAIR calculated using Eq. (5) are presented in table 3. The plots of $\ln V_{m,1}$ *vs.* SIPN composition for

Table 6. Correlation coefficients r, coefficients in Eq. (3), and characteristics $-\Delta\bar{U}^0{}_1 = \bar{q}_1$ (kcal mol^{-1}), $\Delta\bar{S}^0{}_{1,c}$ (cal mol^{-1} K^{-1}), $\Delta\bar{F}^0{}_{1,c}$ (kcal mol^{-1}) for SIPN with compositions 90 : 10 and 70 : 30

Adsorbate	SIPN 90 : 10						SIPN 70 : 30					
	$A \cdot 10^3$	$-B$	r	$\bar{q}_1$	$-\Delta\bar{S}^0{}_{1,c}$	$-\Delta\bar{F}^0{}_{1,c}$	$A \cdot 10^3$	$-B$	r	$\bar{q}_1$	$-\Delta\bar{S}^0{}_{1,c}$	$-\Delta\bar{F}^0{}_{1,c}$
Saturated, unsaturated, and cyclic hydrocarbons												
n-Hexane	2.6518	7.0285	0.996	5.3	12	0.1	3.1181	8.4055	0.9967	6.2	18.7	0
n-Heptane	3.0681	7.6532	0.997	6.1	13.2	0.4	3.455	8.7439	0.9989	6.9	19.4	0.4
Hept-1-ene	3.0602	7.4956	0.9989	6.1	12.9	0.5	3.5872	8.936	0.9968	7.1	19.7	0.5
Isooctane	2.5628	6.6118	0.9973	5.1	11.2	0.2	3.2308	8.4686	0.9982	6.4	18.8	0.2
n-Octane	3.7644	8.9641	0.995	7.5	15.8	0.8	4.1506	9.9808	0.9991	8.2	21.8	0.8
n-Nonane	4.3874	10.143	0.9899	8.7	18.2	1.2	4.6544	10.748	0.9954	9.2	23.3	1.3
n-Decane	4.8874	10.904	0.995	9.7	19.7	1.6	5.3055	11.874	0.9989	10.5	25.6	1.7
Cyclohexane	2.2723	6.1107	0.9989	4.5	10.2	0	2.9599	8.1312	0.9978	5.9	18.1	–0.1
Aromatic hydrocarbons												
Benzene	2.7696	6.7125	0.9978	5.5	11.4	0.5	3.3499	8.3445	0.9975	6.7	18.6	0.5
Toluene	3.3168	7.6151	0.9986	6.6	13.1	1.0	3.9058	9.2948	0.9973	7.8	20.5	0.9
Ethylbenzene	3.9058	8.5988	0.9977	7.8	15.1	1.4	4.555	10.454	0.9988	9.1	22.8	1.3
Isopropylbenzene	4.2225	9.1319	0.999	8.4	16.2	1.6	4.8691	10.932	0.9982	9.7	23.7	6
o-Xylene	4.0812	8.9252	0.999	8.1	15.7	1.5	4.6492	10.932	0.9993	9.2	23.7	1.4
Ethers												
Dibutyl ether	5.4738	12.179	0.9994	10.9	22.2	1.8	6.3229	14.092	0.9973	12.6	30	2.1
Diisopropyl ether	4.7382	11.478	0.9978	9.4	20.8	0.9	5.3391	12.639	0.9981	10.6	27.1	1.2
1,4-Dioxane	5.6545	12.33	0.9984	11.2	22.5	2.1	6.598	14.471	0.9965	13.1	30.7	2.4
Halogen-containing compounds												
o-Fluorotoluene	3.4503	7.8122	0.9967	6.9	13.5	1.1	4.1571	9.7579	0.9967	8.3	21.4	1.0
Chlorobenzene	4.0347	8.5763	0.9962	8	15.1	1.6	4.6587	9.7996	0.9949	9.3	21.5	2.0
CH_2Cl_2	3.3064	7.2887	0.9989	6.6	12.5	1.2	3.8581	8.4333	0.9988	7.7	18.7	1.4
$CHCl_3$	3.169	7.1194	0.9985	6.3	12.2	1.0	3.6631	8.1216	0.9979	7.3	18.1	1.3
1,2-Dichloroethane	3.6078	7.8157	0.9991	7.2	13.5	1.4	4.3207	9.4107	0.9976	8.6	20.7	1.6
CCl_4	3.0206	6.9797	0.9903	6	11.9	0.8	3.6056	8.1146	0.998	7.2	18.1	1.2
Ketones												
Acetone	6.0785	14.25	0.9975	12.1	26.3	1.5	6.3976	14.737	0.9993	12.7	31.3	1.8
Methyl ethyl ketone	6.3848	14.662	0.9943	12.7	27.1	1.8	6.6143	14.839	0.9983	13.1	31.5	2.2
Alcohols												
Ethanol	4.7088	7.4869	0.9996	9.4	12.9	3.8	4.5797	7.3209	0.9997	9.1	12.6	3.7
Propan-2-ol	4.3131	7.2479	0.9978	8.6	12.4	3.2	4.3359	7.2471	0.9978	8.6	12.4	3.2
Propan-1-ol	5.2847	8.3233	0.9971	10.5	14.6	4.4	5.1075	8.056	0.9971	10.1	14	4.2
Butan-2-ol	4.5921	7.4633	0.9988	9.1	12.8	3.6	4.7209	7.7222	0.9987	9.4	13.4	3.7
Butan-1-ol	5.6173	8.6231	0.9994	11.2	15.1	4.8	5.4386	8.3419	0.9998	10.8	14.6	4.6
Isobutanol	5.0875	8.2146	0.9979	10.1	14.3	4.0	4.9999	8.01	0.9985	9.9	13.9	4.0
Hexan-1-ol	6.3216	9.1504	0.9953	12.6	16.2	5.8	6.3017	9.2888	0.9991	12.5	16.5	5.6
Phenol	7.137	10.665	0.9983	14.2	19.2	6.3	6.7818	9.9472	0.9989	13.5	17.8	6.1
Nitrogen-containing compounds												
Acetonitrile	4.9459	6.036	0.9982	9.8	10	5.4	4.4775	5.1956	0.9988	8.9	8.3	5.0
1-Nitropropane	3.7428	4.667	0.9983	7.4	7.3	4.0	3.3886	3.8472	0.9987	6.7	5.7	3.9
Nitrobenzene	5.7529	6.4244	0.9992	11.4	10.8	6.7	5.3396	5.9328	0.9996	10.6	9.8	6.2
Pyridine	4.2684	4.894	0.9985	8.5	7.7	4.8	3.9947	4.3693	0.9988	7.9	6.7	4.7

some sorbates are shown in Fig. 3. In the whole region of the composition studied (see Table 3 and Fig. 3) the experimental $V_{m,1}$ and $\ln V_{m,1}$ values for SIPN lie above the additive values. The additive dependence (see Fig. 3, dotted line) corresponds to the simple physical mixture of the polymers. It should be noted that the $V_{m,1}$ value alters in different manners with the changing composition of SIPN. For example, the difference between $\ln V_{m,1}$ of the physical mixture and 90 : 10 SIPN for all sorbates studied is lower than that for 70 : 30 SIPN (see Fig. 3). In addition, for the polar sorbates this difference is much higher than that for the nonpolar sorbates. Thus, for the polar sorbates the active sorption fragments of the SIPN structure become more accessible. Moreover, an increase in the specific retention volume with an increase in the fraction of PAIR in SIPN indicates an increase in the incom-

Table 7. Coefficients (*a* and *b*) in Eq. (4) for PAIR, PBI, and SIPN

Sorbate	PAIR		PBI		SIPN			
					90 : 10		70 : 30	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
n-Hydrocarbons	3.0	1.1	–2.5	1.1	2.0	1.2	–0.8	1.1
Aromatic hydrocarbons	3.8	1.0	1.6	1.1	1.4	1.2	–0.5	1.2
Ethers	6.7	1.4	3.6	0.7	4.9	0.8	4.6	1.0
Halogen-containing compounds	10.5	0.8	5.9	0.3	6.0	0.6	6.8	0.9
Ketones	10.5	1.1	10.0	0.5	10.3	0.6	10.5	0.5
Primary alcohols	7.5	1.1	7.4	0.5	8.0	0.8	7.5	0.8
Secondary alcohols	5.9	0.9	6.8	0.6	7.1	0.5	6.2	0.8

Table 8. Contributions of different functional groups to the heat of adsorption ($\bar{q}_i$/kcal mol^{-1}) for PAIR, PBI, SIPN, and GTC

Group	PAIR	PBI	SIPN		GTC
			90 : 10	70 : 30	
—Me	2.1±0.1	1.3±0.4	1.2±0.2	1.2±0.3	2.2±0.3
$=CH_2$	1.1±0.3	0.7±0.3	0.8±0.2	1.0±0.2	1.4±0.1
—Cl	5.1±0.1	2.7±0.2	2.8±0.1	3.4±0.1	2.6±0.2
—O—	6.3±0.4	3.3±0.3	3.8±0.3	4.4±0.1	0.5±0.3
=C=O	4.5±0.3	7.7±0.6	8.5±0.6	6.2±0.2	2.3±0.4
—OH	7.6±0.1	10.4±0.3	10.3±0.3	9.8±0.4	2.6±0.1
$—NO_2$	2.2±0.3	2.8±0.5	3.6±0.1	3.2±0.6	4.1±0.3
≡N	0.3±0.1	2.6±0.2	2.5±0.3	2.4±0.3	2.8±0.2
≡CH	1.7±0.1	0.7±0.1	0.9±0.2	1.1±0.3	1.9±0.1
≡C—	0.3±0.1	0.2±0.1	0.9±0.2	1.2±0.2	0.9±0.4

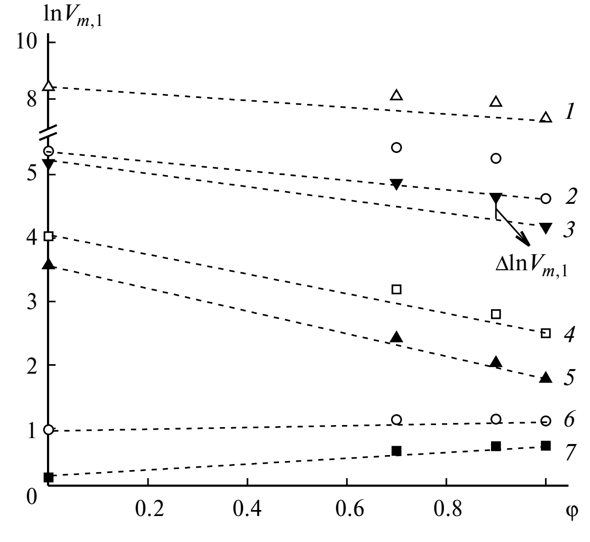


Fig. 3. Additive dependences of $\ln V_{m,1}$ on the composition of SIPN (content of PBI φ) for phenol (*1*), 1-nitropropane (*2*), ethanol (*3*), 1,4-dioxane (*4*), acetone (*5*), *n*-octane (*6*), and benzene (*7*) (points arranged above the additive line correspond to SIPN, and points lying on the additive line correspond to the physical mixture of PAIR and PBI).

patibility of the individual polymers in SIPN, which, in its turn, affects the phase structure of SIPN. The electronic photographs of the PBI and PAIR films and the 90 : 10 and 70 : 30 SIPN films are presented in Figs. 4 and 5. The phase structure of SIPN with both compositions is characterized by the presence of spherical PAIR domains in the PBI matrix. However, the phase structure of 70 : 30 SIPN (see Fig. 5) is characterized by larger PAIR domains than those in 90 : 10 SIPN. It should be mentioned that the structure of the starting polymers (PBI and PAIR) (see Fig. 4) is characterized by phase uniformity.

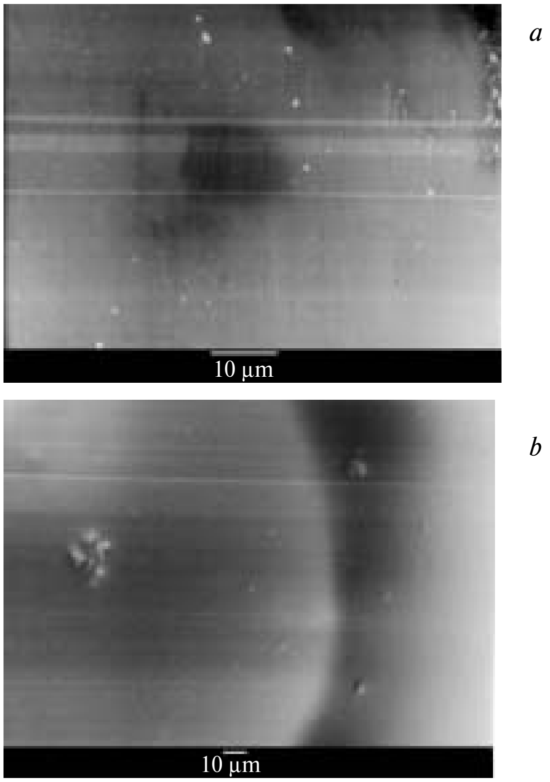


Fig. 4. Electronic microphotographs of the PAIR (*a*) and PBI (*b*) films.

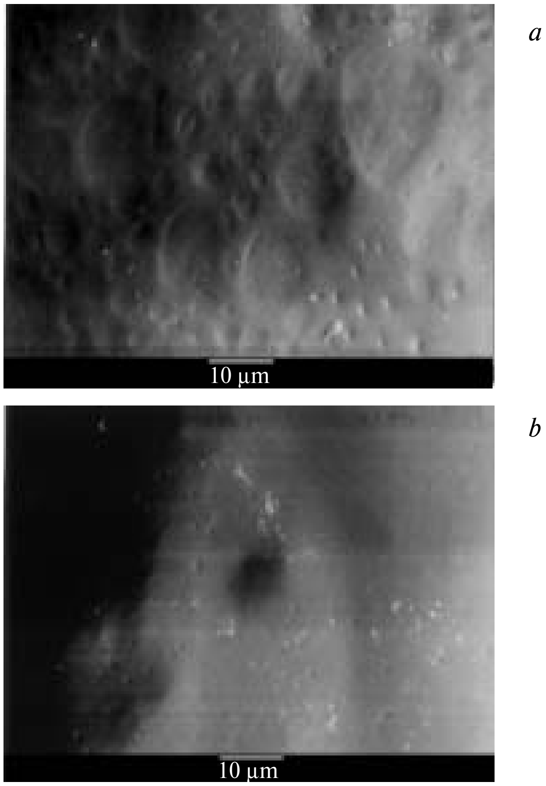


Fig. 5. Electronic microphotographs of the SIPN films with the composition 70 : 30 (*a*) and 90 : 10 (*b*).

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