ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2019, Vol. 93, No. 9, pp. 1796–1803. © Pleiades Publishing, Ltd., 2019.
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Thermodynamics of the Adsorption of Isomeric Dipyridyls and Their Derivatives from Water–Organic Solutions on HYPERCARB™ Porous Graphitic Carbon

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Received December 28, 2018; revised February 8, 2019; accepted February 14, 2019

Abstract—High-performance liquid chromatography is used under near-equilibrium conditions to study the adsorption of isomeric dipyridyls and their derivatives from water–acetonitrile, water–methanol, and water–isopropanol solutions onto Hypercarb™ graphite-like carbon material in the region of Henry's law. Hypercarb™ graphite-like carbon material exhibits high adsorption selectivity in separating the investigated isomeric dipyridyl and its derivatives. It is shown that the possibility of forming strong intramolecular C–H–N'-hydrogen bonds in a molecule of 2,2'-dipyridyl or its derivatives strengthens the adsorption bonding of adsorbate molecules and the surface of the graphite-like material due to stabilization of their planar conformation. Destabilizing this intramolecular hydrogen bond by adding substituents in different positions of the pyridine rings enhances the specific intermolecular interaction between adsorbate molecules and the solvent's components and distorts the planar conformation of dipyridyls, weakening their retention on the Hypercarb™ material. Positive adsorption from the water–organic medium on the carbon adsorbent is observed for all of the investigated dipyridyls, with the exception of 2,2'-dipyridyl-*N*,*N*'-dioxide, which is adsorbed weaker than the solvent components. Anomalous medium–property dependences are found for the thermodynamic characteristics of the adsorption of dipyridyls on porous graphitic carbon, and are attributed to the predominance of adsorbate–adsorbent π–π interactions over hydrophobic ones and the resolvation of adsorbate molecules with acetonitrile in proportion to lowering the content of water in the bulk solution.

Keywords: adsorption, chromatography, carbon, graphite, thermodynamics, dipyridyls

DOI: 10.1134/S0036024419090218

INTRODUCTION

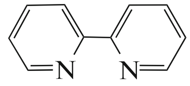
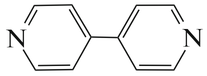
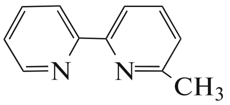
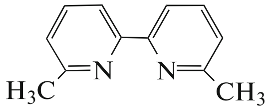
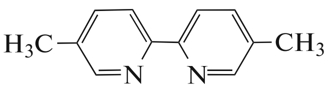
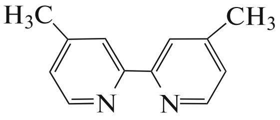
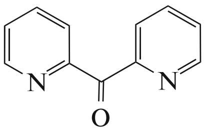
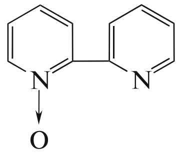
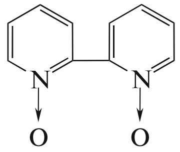
Micro- and mesoporous carbons are of interest to researchers as promising materials used in adsorption gas-accumulation systems; as components of semiconducting, photoactive, and electrode materials; as carriers for heterogeneous catalysis; and as adsorbents in processes of concentration and separation [1–7]. Notable among them are graphite-like structures with a unique selectivity in the adsorption separation of substances with similar molecular structure [8–10].

Hypercarb™ carbon material, which is produced through the pyrolytic decomposition and subsequent graphitization of phenol-formaldehyde oligomer in pores of mesoporous silica, is used in chromatography [11–13]. Porous graphitic carbon (PGC) exhibits high selective adsorption ability in the separation of compounds with different spatial molecular structures (including isomers) via high-performance liquid chromatography (HPLC) [14–18]. In addition, using PGC as a stationary phase for HPLC allows the separation of hard-to-split mixtures whose molecules have similar spatial structures but differ in their numbers of π-electrons [15–18].

At the same time, the mechanism of adsorption onto PGC during liquid-phase separation is not yet fully understood. Almost no data are available on the effect the quantitative and qualitative composition of the liquid phase has on the thermodynamic characteristics of the adsorption (TCA) of different classes of compounds on PGC. We also have no reliable information on the contribution from the specific and dispersive interactions of adsorbate molecules with PGC surfaces for different compositions of the bulk solution. It is therefore difficult to optimize the conditions for separating complex multifunctional organic compounds (including isomers) on PGC by means of HPLC.

The aim of this work was to determine the TCA for isomeric dipyridyls and some of their derivatives on Hypercarb™ graphite-like carbon material from water–organic solutions in the region of Henry's law by means of HPLC, and to determine the TCA depen-

Table 1. Structural formulas of the adsorbates

Adsorbate	Name	Structural formula
1	2,2'-Dipyridyl	
2	4,4'-Dipyridyl	
3	6-Methyl-2,2'-dipyridyl	
4	6,6'-Dimethyl-2,2'-dipyridyl	
5	5,5'-Dimethyl-2,2'-dipyridyl	
6	4,4'-Dimethyl-2,2'-dipyridyl	
7	Di(2-pyridyl)ketone	
8	2,2'-Dipyridyl-*N*-oxide	
9	2,2'-Dipyridyl-*N*,*N*'-dioxide	

dence on the adsorbate's molecular structure, along with the composition and the nature of the liquid phase.

EXPERIMENTAL

Isomeric dipyridyls and their derivatives were purchased from Sigma Aldrich (Table 1) and used as adsorbates. Chromatographic measurements confirmed the purity of the investigated compounds.

Commercial Hypercarb™ PGC (Thermo Scientific, United States) with a specific surface area of $S_{sp} = 120$ m^2/g was used as the adsorbent. The size of the adsorbent particles was 5 μm. A stainless steel chromatography column 50 mm long with an internal diameter of 2.1 mm was used. The mass of adsorbent in the column was $g = 0.2$ g.

Binary water–organic mixtures were used as mobile phases. Organic components were acetonitrile (MeCN), methanol (MeOH), and isopropanol (*i*-PrOH), all of HPLC grade. Deionized water was prepared with a DME-1/B membrane deionizer system (BMT, Russia). MeCN concentration Φ_{MeCN} was varied from 0.40 to 0.90 volume fractions in increments of 0.10. The concentrations of MeOH and *i*-PrOH were held constant at $\Phi_{\text{MeOH}} = \Phi_{i\text{-PrOH}} = 0.70$ volume fractions.

TCA measurements of isomeric dipyridyls from solutions were made under the conditions of a dynamic adsorption experiment using chromatographic equipment. The initial chromatographic data were obtained on an Agilent 1100 Series liquid chromatograph equipped with a diode bar detector, a mobile phase deaerator, and a Rheodyne sampling valve with a sample loop of 20 μL. The elution of 10^{-4} M solutions of individual adsorbate samples was conducted in the isocratic mode. The volume flow rate of the mobile phase was 1 mL/min. The proper Gaussian shape of chromatographic peaks indirectly confirmed the proximity of the experimental conditions to the region of Henry's law. Temperature T of the column was varied from 313 to 333 K with steps of 10 K. The column was thermostatted for 30 min prior to the dynamic adsorption of dipyridyls.

The initial experimental chromatographic data were used to determine the values of the Henry constant ($K_{1,c}$, μL/m^2), the standard differential molar changes in the Gibbs energy ($\Delta_a G°$, kJ/mol), the enthalpy ($\Delta_a H°$, kJ/mol), and the entropy ($\Delta_a S°$, J/(mol K)) for adsorption as described in [18]. The calculated TCA values corresponded to the harmonic mean temperature of the investigated range of temperatures: $T_{av} = 323$ K. The values of the dead volume ($V_M = 270$ μL), the volume of the adsorption phase ($v_a = 61$ μL), and the thickness of the adsorption layer ($t = 2.54$ nm) were used in calculating the TCA. Tables 2–4 present the TCA data calculated for isomeric dipyridyns and their derivatives.

The molecular geometry of the investigated compounds were optimized, and the corresponding dipole moments were calculated with the Gaussian 09 software [19], based on the density functional theory (DFT) with hybrid functional B3LYP and basis set 6-31+G(*d*,*p*). The calculations were performed for molecules in a vacuum.

RESULTS AND DISCUSSION

The data from Tables 2 and 4 demonstrate the strong influence the molecular structure of the dipyridyls had on the Henry constants of their adsorption $K_{1,c}$ and the standard differential molar changes in the

Table 2. Henry adsorption constants ($K_{1,c}$, μL/m^2) and standard differential molar changes in Gibbs energy ($\Delta_a G^\circ$, kJ/mol) upon the adsorption of dipyridyls and their derivatives on PGC from solutions of MeCN–H$_2$O with different volume fractions Φ_{MeCN} at T_{av} = 323 K

Adsorbate	$\Phi_{MeCN} = 0.40$		$\Phi_{MeCN} = 0.50$		$\Phi_{MeCN} = 0.60$		$\Phi_{MeCN} = 0.70$		$\Phi_{MeCN} = 0.80$		$\Phi_{MeCN} = 0.90$	
	$K_{1,c}$	$-\Delta_a G^\circ$	$K_{1,c}$	$-\Delta_a G^\circ$	$K_{1,c}$	$-\Delta_a G^\circ$	$K_{1,c}$	$-\Delta_a G^\circ$	$K_{1,c}$	$-\Delta_a G^\circ$	$K_{1,c}$	$-\Delta_a G^\circ$
1	156.1	11.1	96.9	9.8	69.0	9.0	52.4	8.3	43.1	7.8	36.8	7.4
2	31.8	7.0	20.7	5.9	15.8	5.3	14.8	5.1	14.6	5.1	16.5	5.4
3	352.6	13.3	206.9	11.8	136.3	10.7	98.7	9.9	76.1	9.2	59.3	8.6
4	1067.7	16.2	590.8	14.6	362.7	13.3	245.2	12.3	174.8	11.4	126.7	10.6
5	1948.2	17.8	1024.7	16.1	614.0	14.7	423.9	13.8	316.1	13.0	241.4	12.3
6	938.8	15.9	504.3	14.2	310.8	12.9	218.5	12.0	167.0	11.3	131.3	10.6
7	21.6	6.0	14.1	5.0	10.1	4.3	8.0	3.8	6.7	3.5	6.2	3.3
8	12.3	4.7	9.7	4.2	9.1	4.1	10.2	4.3	11.6	4.6	16.3	5.4
9	–0.9	–1.2	–0.7	–0.8	–0.9	–1.2	–0.5	–0.5	–0.6	–0.7	0.5	0.5

Table 3. Standard differential molar changes in enthalpy ($\Delta_a H^\circ$, kJ/mol) and entropy ($\Delta_a S^\circ$, J/(mol K)) upon the adsorption of dipyridyls and their derivatives on PGC from MeCN–H$_2$O solutions with different volumetric fractions Φ_{MeCN} at T_{av} = 323 K

Adsorbate	$\Phi_{MeCN} = 0.40$		$\Phi_{MeCN} = 0.50$		$\Phi_{MeCN} = 0.60$		$\Phi_{MeCN} = 0.70$		$\Phi_{MeCN} = 0.80$		$\Phi_{MeCN} = 0.90$	
	$-\Delta_a H^\circ$	$-\Delta_a S^\circ$	$-\Delta_a H^\circ$	$-\Delta_a S^\circ$	$-\Delta_a H^\circ$	$-\Delta_a S^\circ$	$-\Delta_a H^\circ$	$-\Delta_a S^\circ$	$-\Delta_a H^\circ$	$-\Delta_a S^\circ$	$-\Delta_a H^\circ$	$-\Delta_a S^\circ$
1	10.9	–0.5	11.0	3.8	14.2	16.4	13.3	15.5	13.1	16.5	14.7	22.7
2	6.1	–2.8	5.1	–2.8	7.8	7.7	6.3	3.6	7.1	6.2	8.0	8.1
3	13.5	0.7	13.9	6.2	14.9	12.7	15.5	17.5	16.1	21.2	17.4	27.3
4	15.6	–2.0	15.2	1.7	16.8	10.6	18.0	17.7	18.8	22.9	20.1	29.4
5	16.6	–4.1	15.7	–1.4	16.8	6.2	17.5	11.5	17.8	14.9	20.0	24.1
6	15.5	–1.0	15.3	3.2	15.98	9.2	16.6	14.2	17.4	19.1	20.2	29.4
7	5.48	–2.1	5.9	2.7	5.9	4.8	8.9	15.6	9.1	17.3	10.1	21.1
8	0.4	–13.5	1.2	–9.5	2.9	–3.6	4.7	1.3	8.0	10.5	8.4	9.4
9	4.5	17.5	–	–	–	–	–	–	–	–	–	–

Table 4. Thermodynamic characteristics of the adsorption of dipyridyls and their derivatives on PGC from water–alcohol solutions with volume fractions $\Phi_{i\text{-}PrOH} = \Phi_{MeOH} = 0.70$ of the organic component at T_{av} = 323 K

Adsorbate	*i*-PrOH–H$_2$O				MeOH–H$_2$O			
	$K_{1,c}$, μL/m^2	$-\Delta_a G^\circ$, kJ/mol	$-\Delta_a H^\circ$, kJ/mol	$-\Delta_a S^\circ$, J/(mol K)	$K_{1,c}$, μL/m^2	$-\Delta_a G^\circ$, kJ/mol	$-\Delta_a H^\circ$, kJ/mol	$-\Delta_a S^\circ$, J/(mol K)
1	14.7	5.1	–	–	104.4	10.0	20.2	31.4
2	3.7	2.4	–	–	59.5	8.6	21.3	39.3
3	32.8	7.1	9.6	7.9	223.0	12.0	21.4	28.7
4	88.4	9.6	11.0	4.2	589.2	14.6	24.1	29.2
5	128.6	10.6	10.1	–1.4	1298.1	16.8	27.7	34.0
6	68.7	8.9	8.1	–2.8	580.3	14.6	25.2	32.7
7	1.8	1.4	–	–	25.3	6.4	17.2	33.2
8	2.1	1.6	–	–	18.4	5.7	12.9	22.5
9	–2.5	–11.0	–	–	0.2	0.2	–	–

Gibbs energy Δ_aG° when they were adsorbed from the solutions on the PGC surface. Upon moving from 2,2'-dipyridyl (substance **1**) to 4,4'-dipyridyl (substance **2**), the magnitude of $K_{1,c}$ fell by approximately 500% for adsorption from the solutions with low volumetric contents of MeCN (Φ_{MeCN} = 0.40–0.60), by approximately 400% for adsorption from the MeCN–H_2O solution with Φ_{MeCN} = 0.70, and by approximately 300% for adsorption from the mixture MeCN–H_2O with the higher volume content Φ_{MeCN} = 0.80–0.90 of the organic component.

It should be noted that the molecules of both isomers are nonpolar for both adsorbates, as quantum-chemical calculations show: μ = 0.000 D. The stronger adsorption of 2,2'-dipyridyl (substance **1**) compared to 4,4'-dipyridyl (substance **2**) was in our opinion due to the molecules of substance **1** having a planar geometry (Tables 2, 4). The planar conformation of 2,2'-dipyridyl is strongly stabilized by two intramolecular C–H–N' hydrogen bonds between the hydrogen atom at position 3 of one pyridyl radical, the nitrogen atom of the adjacent cycle, and the π–π-conjunction between pyridine cycles. As a result, the nitrogen atoms in the 2,2'-dipyridyl molecule are opposite each other [20, 21]. The *anti*-conformer of 2,2'-dipyridyl is 27 kJ/mol more stable than the *cis*-conformer [21]. According to [20], complexing in a solution with the nitrogen atoms of 2,2'-dipyridyl can destroy existing intramolecular C–H–N' hydrogen bonds, resulting in possible changes of the *trans*-orientation of nitrogen atoms in 2,2'-dipyridyl while its molecule acquires nonplanar geometry. However, the stronger adsorption of 2,2'-dipyridyl (substance **1**) from water-organic media relative to 4,4'-dipyridyl (substance **2**) on the PGC surface (Tables 2 and 4) indicates there is no such complexing, so it appears that 2,2'-dipyridyl in these solutions solvates through van der Waals interactions with the solvent.

Lowering the content of MeCN in the solution from which adsorption proceeds reduces the difference between the Henry constant of the adsorption of 2,2'-dipyridyl (substance **1**) and 4,4'-dipyridyl (substance **2**), which reflects the weakening of the system's selectivity of adsorption toward these isomers. At the same time, the difference between the magnitudes of $K_{1,c}$ of these two isomeric dipyridyls is enough even at Φ_{MeCN} = 0.90 for their complete separation by HPLC when using PGC as the stationary phase (Tables 2 and 4). The adsorption bonding of 4,4'-dipyridyl (substance **2**), for which the angle between the cycles is 37.2° [22], and the PGC surface is weaker than for 2,2'-dipyridyl (substance **1**). This is likely due to its molecule not having planar geometry, which cannot be acquired from the π–π conjunction between aromatic cycles.

Adding one methyl radical at position 6 of the 2,2'-dipyridyl molecule further reinforces the adsorption bonding of adsorbate molecules with the PGC surface (Tables 2 and 4). The value of $K_{1,c}$ for 6-methyl-2,2'-dipyridyl (substance **3**), whose molecules have weak polarity (μ = 0.536 D), is almost twice that of its unsubstituted nonpolar analog. This results from the increased number of contacts between adsorbate molecules and the graphite-like surface of the carbon material after adding a methyl group, and the elevated electron density on the nitrogen atom of the substituted ring, which is due to the methyl's electron-donor properties. The elevated electron density promotes the formation of intramolecular C–H–N' hydrogen bonds and thus stabilizes the planar conformation of this adsorbate. Adding a second methyl group at position 6' of the adjacent pyridine ring upon the transition to 6,6'-dimethyl-2,2'-dipyridyl with μ = 0.000 D, (substance **4**) almost triples the magnitude of $K_{1,c}$ (Tables 2 and 4), another result of the increased number of contacts between the adsorbate molecules and the carbon adsorbent, and the stabilization of the molecular flat geometry in favor of a planar orientation during adsorption on the graphite-like surface.

The transition from 6,6'-dimethyl-2,2'-dipyridyl (substance **4**) to its structural isomer 5,5'- dimethyl-2,2'-dipyridyl, for which μ = 0.000 D (substance **5**), almost doubles the retention on the PGC. As with the isomeric 2,2' and 4,4'-dipyridyls, the increased concentration of MeCN in the mobile phase somewhat reduces the difference between the $K_{1,c}$ values of isomeric dimethyl-2,2'-dipyridyls but does not prevent their full separation in columns with PGC under HPLC conditions (Tables 2 and 4). The doubled adsorption bonding of 5,5'-dimethyl-2,2'-dipyridyl and PGC compared to 6,6'-dimethyl-2,2'-dipyridyl is perhaps due to the presence of two methyl groups at the meta-positions relative to the carbon atoms at positions 3 and 3' of the pyridine rings enhancing the electron-donor properties of the hydrogen atoms in the vicinity of these carbon atoms. This contributes to the strengthening of the intramolecular C–H–N' hydrogen bonds, which stabilizes the planar conformation of the 5,5'-dimethyl-2,2'-dipyridyl molecule.

In contrast, Tables 2 and 4 show that another isomer, 4,4'-dimethyl-2,2'-dipyridyl, for which μ = 0.094 D, (substance **6**), adsorbs on the PGC surface a bit more weakly than 6,6'-dimethyl-2,2'-dipyridyl (substance **4**). In our opinion, this is because the two methyl groups at positions 4 and 4' slightly reduce the electron-acceptor properties of the hydrogen atoms occupying the positions 3 and 3', respectively. This weakening could be due to the positive inductive effect of methyl radicals and the hyperconjugation effect. As a result, it prevents the formation of strong intramolecular C–H–N' hydrogen bonds stabilizing the planar conformation of the 4,4'-dimethyl-2,2'-dipyridyl molecule. This adsorbate with the nonplanar geometry is thus not retained on PGC as well as 6,6'-dimethyl-2,2'-dipyridyl (see Tables 2 and 4).

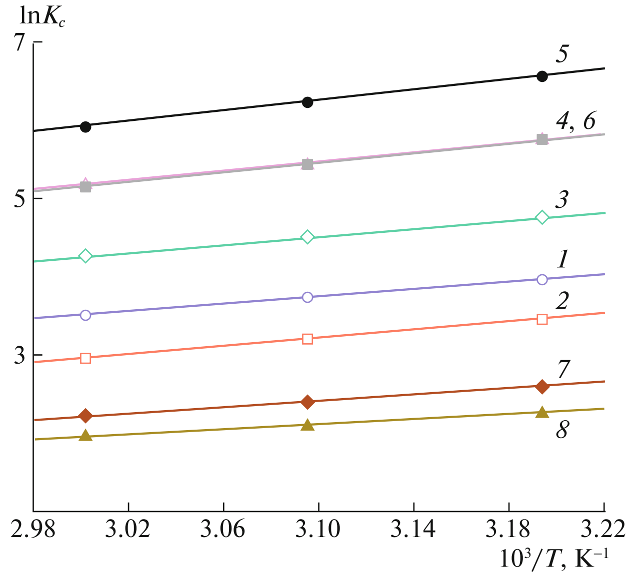


Fig. 1. (Color online) Logarithm of the distribution constant of the investigated dipyridyls versus the reciprocal temperature upon their adsorption in PGC from the solution of MeOH–H$_2$O with Φ_{MeOH} = 0.70; below, the numbers on the curves correspond to those of the substances listed in Table 1.

Important factors that determine the character of adsorption of isomeric dipyridyls and their substituted analogs from water–organic solutions on Hypercarb™ carbon material are thus the geometry of adsorbate molecule and the number of its possible contacts with the graphite-like PGC surface. The presence of substituents in the adsorbing molecule that stabilize the planar conformation greatly enhances the adsorption bonding of dipyridyls and the PGC surface. The main factor that allows the adsorption bonding of dipyridyl molecules and PGC is in this case the possibility of almost complete contact between its atoms and the graphite-like surface. We thus have adsorbate–adsorbent π–π interactions and additional electrostatic forces between the molecules with flat geometry and the flexible π-electron system of graphite-like PGC surface, rather than interaction between the polar centers of adsorbate molecules and the residual polar functional groups of the graphite sheet, as is observed for graphitized thermal black [23, 24].

The latter point is confirmed by the weak adsorption of molecules with a nonplanar geometry. For example, Tables 2 and 4 show that di(2-pyridyl)ketone (substance **7**) is adsorbed on PGC from water–organic media much more weakly than its closest analog, 2,2'-dipyridyl (substance **1**). 2,2'-Dipyridyl-*N*-oxide and 2,2'-dipyridyl-*N*,*N*'-dioxide (substances **8** and **9,** respectively), which contain semi-polar bonds, are also adsorbed weakly on PGC. Molecules of di(2-pyridyl)ketone and 2,2'-dipyridyl-*N*,*N*'-dioxide have dipole moments (μ = 4.299 and 2.048 D, respectively), so they participate in strong orientation interactions with polar solvent molecules. At the same time, the 2,2'-dipyridyl-*N*,*N*'-dioxide molecule has no dipole moment, and it cannot interact with the solvent through orientation forces. These adsorbates are likely solvated not only through a mechanism of van der Waals interactions with the polar solvent but also through the formation of intermolecular hydrogen bonds between the basic pyridine nitrogen atoms of the adsorbate molecules and the acid centers of the solvent components. Along with the nonplanar geometry of these adsorbates, such solvation results in their fast elution from a column under the conditions of dynamic adsorption.

The presented values of $\Delta_a G°$ show that the adsorption equilibrium shifts toward the formation of adsorption complexes of adsorbate molecules with the PGC surface (Tables 2 and 4). The only exception is 2,2'-dipyridyl-*N*,*N*'-dioxide (substance **9**), the molecule of which is nonpolar and contains two semi-polar bonds. Due to the combination of weak adsorption bonding with the graphite-like surface and strong solvation through the water–organic solvent, this substance is adsorbed more weakly than the solvent itself; i.e., it is characterized by negative adsorption on the PGC surface from water–organic solutions. This is apparent from its negative values of $K_{1,c}$ and the positive values of $\Delta_a G°$ (see Tables 2 and 4), which show a shift of adsorption equilibrium in the case of 2,2'-dipyridyl-*N*,*N*'-dioxide (substance **9**) toward the breakdown of adsorbate–adsorbent adsorption complexes.

Figure 1 shows the dependences of the logarithm of the distribution constants for the investigated dipyridyls on the reciprocal temperature upon their adsorption on the PGC surface from an MeOH–H$_2$O solution with Φ_{MeOH} = 0.70. As with the adsorption of dipyridyl from MeCN–H$_2$O and *i*-PrOH–H$_2$O media, these dependences are functions that grow linearly, reflecting the exothermic character of the liquid-phase adsorption of the investigated substances on the PGC surface. For example, Tables 3 and 4 demonstrate the variations in the standard differential molar changes in enthalpies $\Delta_a H°$ and entropies $\Delta_a S°$ during adsorption. It is seen from these data that the liquid phase adsorption of all the investigated compounds is characterized by negative values of $\Delta_a H°$, regardless of the nature and composition of the bulk solution from which adsorption proceeds. This is due to the predominant gain in energy caused by the interaction between adsorbate molecules and the PGC surface over the energy costs of overcoming the solvation interactions between adsorbate molecules and the solvent, and the desorption of preliminarily adsorbed solvent molecules on the PGC surface. In addition, however, the adsorption of most of the investigated substances is characterized by negative values of $\Delta_a S°$ that reflect the predominance of losses in the degrees of freedom of the adsorption system, caused by the adsorption

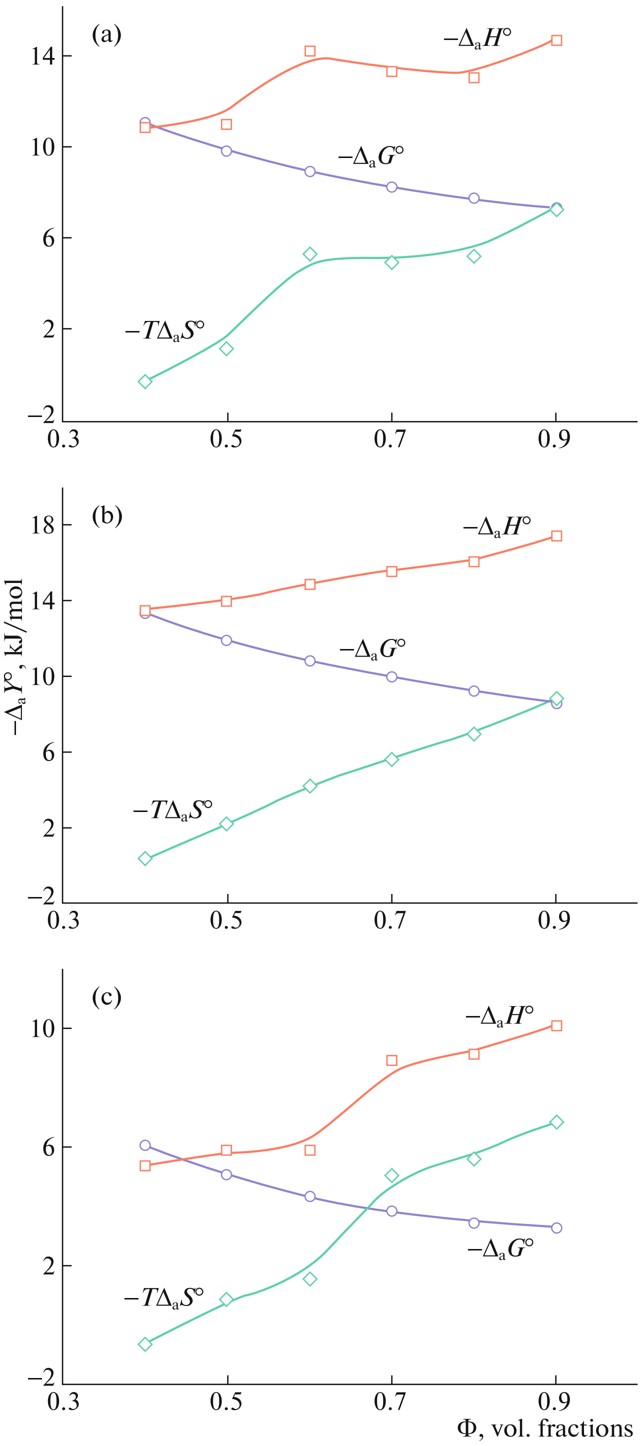


Fig. 2. (Color online) Dependences of the thermodynamic characteristics of the adsorption of (a) 2,2'-dipyridyl, (b) 6-methyl-2,2'-dipyridyl, and (c) di(2-pyridyl)ketone in PGC from solutions of MeCN–H_2O on volume fraction Φ_{MeCN}.

bonding of adsorbate molecules and the PGC surface, over the release of additional degrees of freedom caused by solvent molecules being added to the bulk solution due to degradation of the solvation spheres of adsorbate molecules and the desorption of preliminarily adsorbed solvent. An exception is the adsorption from the maximally watered-down MeCN–H_2O solutions and from the *i*-PrOH–H_2O solution, where positive variations in entropy are observed when a molecule moves from the bulk solution into the surface layer (Tables 3 and 4).

The maximum absolute magnitudes of $\Delta_aH°$ and $\Delta_aS°$ are characteristic of the adsorption from the MeOH–H_2O solutions of the investigated dipyridyls on the PGC surface. Intermediate values of $\Delta_aH°$ and $\Delta_aS°$ are observed for adsorption from the MeCN–H_2O solutions, and minimal changes in the absolute magnitude of TCA are observed for adsorption from the *i*-PrOH–H_2O solutions (Table 4). The values of $K_{1,c}$ and the absolute magnitudes of $\Delta_aG°$ of the investigated dipyridyls fall in the same way upon moving from the MeOH–H_2O solutions to the MeCN–H_2O media, and then to the binary solvents *i*-PrOH–H_2O (Tables 2 and 4). As is known from [18], this is due to the strong association between the MeOH–H_2O mixtures resulting in more effective displacement of adsorbate molecules from the MeOH–H_2O media onto the nonpolar surface. This sequence of the reduction of TCA absolute magnitudes upon varying the nature of the water–organic solvent results from the higher concentration of preliminarily adsorbed acetonitrile on the nonpolar surface, compared to methanol [18].

Along with the nature of organic component of the bulk solution from which adsorption proceeds, the composition of the binary solvent has a strong impact on the TCA values of dipyridyls (Tables 2 and 3). At the same time, we can see from the dependences of different TCA values of the investigated dipyridyls on the volumetric fraction of acetonitrile in the mobile phase shown in Fig. 2 that as expected, the absolute values of $\Delta_aG°$ fall monotonically when content Φ_{MeCN} of acetonitrile in the solution is raised. This weakening of adsorption bonding in most of the investigated dipyridyls is associated with the enhanced solvating of their molecules by acetonitrile and the reduced hydrophobic interactions resulting from the destruction of the network hydrogen bonds in the bulk solution. The specified drop in the absolute magnitudes of $\Delta_aG°$ upon an increase in Φ_{MeCN} is characteristic of almost all dipyridyls (Figs. 2a–2c). An exception is 2,2'-dipyridyl-*N*-oxide, for which absolute magnitude $\Delta_aG°$ falls slightly as Φ_{MeCN} grows. In contrast, it then rises somewhat to values exceeding $\Delta_aG°$ in absolute magnitude, which are typical of adsorption from watered-down solvents (Table 2). This is apparently a result of the initial rise in the concentration of acetonitrile in the solution enhancing the solvation of the pyridine rings of this adsorbate and thus weakening its retention. In contrast, a further increase in the volume content of acetonitrile probably prevents the specific

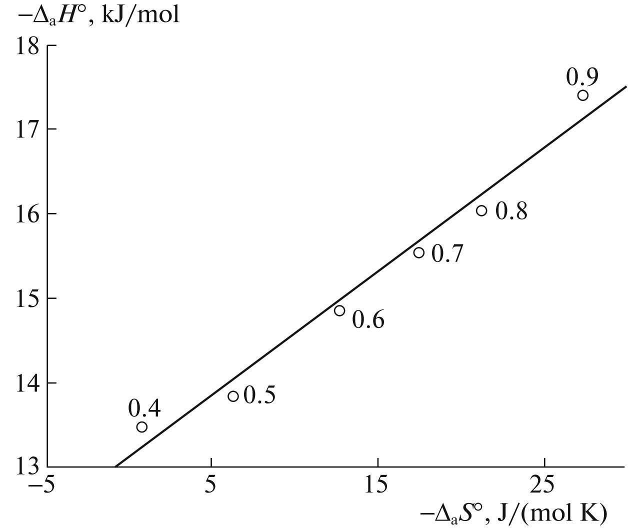


Fig. 3. Correlation between the changes in standard differential molar enthalpy and entropy, measured upon the adsorption of 6-methyl-2,2'-dipyridyl on PGC from solutions of MeCN–H_2O with different volume fractions Φ_{MeCN}.

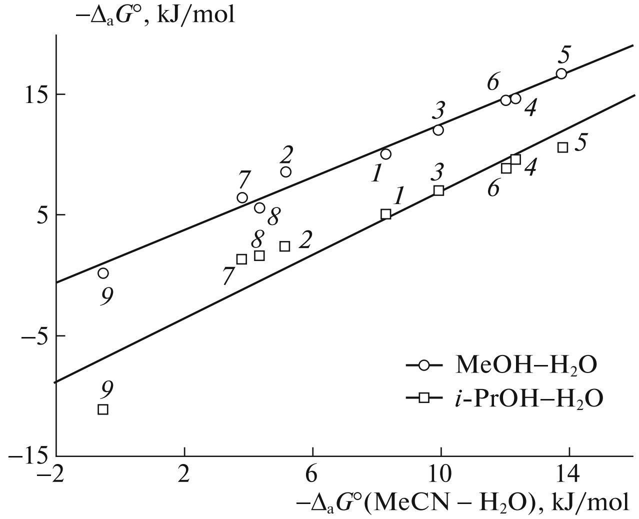


Fig. 4. Dependences of standard differential molar changes of the Gibbs energy upon adsorption of the investigated dipyridyls from water–alcohol solutions on the corresponding values measured upon adsorption from a solution of MeCN–H_2O ($\Phi_{i\text{-PrOH}} = \Phi_{MeOH} = \Phi_{MeCN} = 0.70$).

solvation of 2,2'-dipyridyl-*N*-oxide molecules with water on sites containing semi-polar bonds, so retention grows somewhat (see Table 2).

While the monotonically falling dependences of $-\Delta_aG°$ on Φ_{MeCN} are characteristic of most of the investigated dipyridyls, the medium–property dependences for the absolute magnitudes of standard differential molar changes in enthalpy $\Delta_aH°$ and entropy $T\Delta_aS°$ for all the investigated compounds are of a nontrivial growing character. Depending on the nature of adsorbates, these dependences are characterized by either extrema or inflections, or turn out to be monotonous (see Table 3 and Fig. 2). In the case of 2,2'-dipyridyl and 4,4'-dipyridyl, the dependences of the enthalpic and entropic constituents of the Gibbs energy of adsorption on the composition of the MeCN–H_2O medium are characterized by an extremum in the vicinity of $\Phi_{MeCN} = 0.60$ (Fig. 2a). With 6-methyl-2,2'-dipyridyl, the dependences of the absolute magnitudes of $\Delta_aH°$ and $T\Delta_aS°$ on the composition are monotonous, but also exhibit nontrivial growth (Fig. 2b). With di(2-pyridyl)ketone, inflections in the medium–property dependences for enthalpic and entropic constituents of the Gibbs energy of adsorption are observed near $\Phi_{MeCN} = 0.6$–0.7 (Fig. 2c). The growing character of the medium–property dependences for enthalpy and entropy is likely to result from changes in the dependences of the composition of adsorbed solution as the content of water in the bulk solution is reduced. As a result, π–π interactions begin to predominate upon adsorption from solutions with large volume fractions of acetonitrile, and the impact from hydrophobic interactions is naturally reduced. The presence of extrema or inflections in the medium–property dependences is probably due to oversolvation of the adsorbate molecules by acetonitrile as the content of water in the bulk solution is reduced.

For each of the investigated adsorbates, there is compensation between the values of $\Delta_aH°$ and $\Delta_aS°$ measured upon the adsorption of one substance from MeCN–H_2O media of different composition. Figure 3 presents one such compensation diagram that is characteristic of 6-methyl-2,2'-dipyridyl. At the same time, the regions of mobile phase compositions in which extrema or regions of inflection are observed for the medium–property dependences of the TCAs of the investigated dipyridyls are the same for the enthalpic and entropic constituents of the Gibbs energy of adsorption (Fig. 2). Since the values of $\Delta_aH°$ and $\Delta_aS°$ are parts of the Gibbs–Helmholtz equation, simultaneous variation of these values results in the disappearance of the extrema and inflections on the curves of $\Delta_aG°(\Phi_{MeCN})$ (Fig. 2) [25].

Variations in the composition of the MeCN–H_2O medium and the nature of the mobile phase upon moving to MeOH–H_2O and *i*-PrOH–H_2O media did not alter the adsorption selectivity of the investigated systems, or the order of the elution of adsorbates from the column with PGC, as is apparent from the linear correlations between the values of $\Delta_aG°$ in the series of studied dipyridyls. Figure 4 shows these correlations between the values of $\Delta_aG°$ measured upon the adsorption of dipyridyls from liquid media of different natures.

The data obtained in this work enabled us to predict the adsorption behavior of the investigated dipyridyls, their derivatives (including isomers), and their analogs upon the separation of liquid phases in PGC.

ACKNOWLEDGMENTS

This work was performed on equipment at the shared resource center of the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences.

FUNDING

This work was performed as part of State Task for the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences.

B.R. Saifutdinov thanks the Russian Foundation for Basic Research, project no. 17-03-01308-a; the Council on Grants of the President of the Russian Federation for State Support for Young Russian Scientists and for State Support for Leading Scientific Schools of the Russian Federation, project no. MK-5757.2018.3; and the Ministry of Science and Higher Education of the Russian Federation, project no. 4.7150.2017/8.9, for partial financial support of the research.

REFERENCES

1. E. Duffy, X. He, E. P. Nesterenko, et al., RSC Adv. **5**, 22906 (2015).
2. A. Gomis-Berenguer, L. F. Velasco, I. Velo-Gala, and C. O. Ania, J. Colloid Interface Sci. **490**, 879 (2017).
3. S. Mukdasai, U. Crowley, M. Pravda, et al., Sens. Actuators, B **218**, 280 (2018).
4. H. Mansouri, R. J. Carmona, A. Gomis-Berenguer, et al., J. Colloid Interface Sci. **449**, 252 (2015).
5. S. N. Lanin, S. A. Rychkova, A. E. Vinogradov, et al., Diamond Relat. Mater. **64**, 49 (2016).
6. A. Peristyy, B. Paull, and P. N. Nesterenko, J. Chromatogr., A **1391**, 49 (2015).
7. N. Apel, E. Ulianchenko, S. Moyses, et al., J. Chromatogr., A **1488**, 77 (2017).
8. T. P. Weber, P. T. Jackson, and P. W. Carr, Anal. Chem. **67**, 3042 (1995).
9. C. West, C. Elfakir, and M. Lafosse, J. Chromatogr., A **1217**, 3201 (2010).
10. P. G. Stevenson and G. Guiochon, J. Chromatogr., A **1247**, 57 (2012).
11. M. Melmer, T. Stangler, A. Premstaller, and W. Lindner, J. Chromatogr., A **1217**, 6092 (2010).
12. C. D. Iverson and C. A. Lucy, J. Chromatogr., A **1373**, 17 (2014).
13. D. B. Lunn, Y. J. Yun, and J. W. Jorgenson, J. Chromatogr., A **1530**, 112 (2017).
14. Q. H. Wan, P. N. Shaw, M. C. Davies, and D. A. Barrett, J. Chromatogr., A **697**, 219 (1995).
15. B. R. Saifutdinov, A. A. Pimerzin, N. S. Emel'yanova, and S. V. Kurbatova, Russ. J. Phys. Chem. A **86**, 289 (2012).
16. B. R. Saifutdinov, N. S. Emel'yanova, S. V. Kurbatova, and A. A. Pimerzin, Russ. J. Phys. Chem. A **86**, 1152 (2012).
17. B. R. Saifutdinov, N. S. Emel'yanova, S. V. Kurbatova, and A. A. Pimerzin, Russ. Chem. Bull. **61**, 1643 (2012).
18. B. R. Saifutdinov, N. S. Emel'yanova, and A. A. Pimerzin, Prot. Met. Phys. Chem. Surf. **50**, 317 (2014).
19. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 09, Rev. A.02* (Gaussian Inc., Wallingford, CT, 2009).
20. L. L. Merritt and E. D. Schroeder, Acta Crystallogr. **9**, 801 (1956).
21. A. Göller and U.-W. Grummt, Chem. Phys. Lett. **321**, 399 (2000).
22. O. Bastiansen, H. M. Seip, and J. E. Boggs, in *Perspectives in Structural Chemistry,* Ed. by J. D. Dunitz and J. A. Ibers (Wiley, New York, 1971), Vol. 4, p. 60.
23. Y. Zeng, L. Prasetyo, V. T. Nguyen, et al., Carbon **81**, 447 (2015).
24. N. Klomkliang, R. Kaewmanee, S. Saimoey, et al., Carbon **99**, 361 (2016).
25. B. R. Saifutdinov, Russ. Chem. Bull. **63**, 2609 (2014).

Translated by E. Khozina