


Dispersive surface free energy of adsorbents modified by supramolecular structures of heterocyclic compounds

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Abstract

In the present work, the dispersive surface free energy was calculated by Dorris-Gray method for 30 samples of adsorbents modified with chiral supramolecular structures of uracil, 6-methyluracil, 5-hydroxy-6-methyluracil, 5-fluorouracil, thymine, melamine, cyanuric and barbituric acids, and perylene-3,4,9,10-tetracarboxylic dianhydride. It was shown that the homologous series of n-alkanes is better suited for measuring dispersive surface free energy than the homologous series of alcohols. It was established that the classical Dorris-Gray method does not allow obtaining well interpretable data for the objects studied. This is due to a noticeable effect that inductive interactions of a polar surface as an inductor with nonpolar alkane molecules have on the calculated values. We suggested to modify the Dorris-Gray method, making it possible to obtain data on the dispersive component of the free energy of adsorption. It was shown that the changes in dispersive surface free energy as a result of the modification correlate well with data on the structure and properties of supramolecular ensembles of the modifiers used. The results obtained can be used to predict the enantioselectivity of chiral adsorbents.

Keywords

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Dorris-Gray method
linear free energy relationship
supramolecular structure
chiral 2D surfaces

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Key findings

- The classical Dorris-Gray method for dispersive surface free energy estimation cannot give reliable results.
- To calculate the dispersive component for adsorption materials, one should take inductive interactions into account.
- The dispersive component can be used to predict the properties of supramolecular layers.

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1. Introduction

Inverse gas chromatography (IGC) is the leading method in the studies on the adsorption properties of various materials. Throughout the development of IGC, there was a challenge to suggest a single surface property that would allow one to characterize the adsorbent in full. The dispersive surface free energy (γ_s^d , mJ/m²) is among the most successful characteristics of this kind. Approaches to the calculation of this parameter were suggested by Dorris and Gray (DG) [1] and Schultz [2]. The first approach involves the determination of the contribution of one methylene group to the Helmholtz energy of adsorption (ΔF_{CH_2} , kJ/mol) [1, 3]. This value can be calculated as the slope of the dependence of adsorption free energy on the number of carbon atoms in

a homologous series (usually n-alkanes); it can also be determined by calculations using formula [4]:

$$\Delta F_{CH_2} = -RT \ln \left(\frac{V_g^{n+1}}{V_g^n} \right), \quad (1)$$

where V_g is the specific retention volume, ml/g. The value of γ_s^d can be calculated from:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}} \left(\frac{-\Delta F_{CH_2}}{N \cdot a_{CH_2}} \right)^2, \quad (2)$$

where γ_{CH_2} is the surface dispersive free energy of a material only consisting of methylene groups, N is Avogadro's number, and a_{CH_2} is the cross-sectional area of an adsorbed methylene group.

The Schultz method is based on the suggestion that for *n*-alkanes the dispersive component of the free energy of adsorption actually coincides with the total energy of adsorption, and, therefore, for the dispersive component [5, 6]

$$-\Delta F^{\text{disp}} = NaW_a. \quad (3)$$

Then the dispersive components can be calculated as:

$$RT \cdot \ln V_g^n = 2N \cdot a \cdot (\gamma_l^d)^{0.5} \cdot (\gamma_s^d)^{0.5} + C, \quad (4)$$

where γ_l^d is the surface dispersive free energy of the liquid alkane. By plotting $RT \cdot \ln V_g^n$ vs. $a \cdot (\gamma_l^d)^{0.5}$ for a series of liquid *n*-alkanes, a line can be obtained. Then, the dispersive free energy can be calculated from the slope of that line [5].

These methods were successfully applied to a wide range of systems [4, 6–14]. However, despite the apparent versatility, the application of both methods faces certain challenges. Thus, it was shown [5] that the traditional surface free energy parameters of *n*-alkanes listed in the papers using the Schultz method are not accurate enough. It was shown [3] that the values of methylene middle parameter calculated by classic methods differ slightly from the true ones. Therefore, further improvement of methods for determining dispersive surface free energy remains relevant.

In the present work, the DG method was used to measure γ_s^d in a series of adsorbents modified with various heterocyclic compounds, such as uracil and its derivatives, melamine, thymine, cyanuric and barbituric acids, thymine, and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). All these compounds applied from solutions on the surface of various solids can form chiral supramolecular structures with various forms and dimensions. In fact, depending on the concentration, uracil forms either 1D-rows or 2D-net structures, either with cavities measuring about 7 Å or without them [15–20]. According to X-ray diffraction analysis, 6-methyluracil is also capable of producing either 1D or 2D structures with a cavity size of about 9 Å. At the same time, 5-fluorouracil forms only 2D structures [21]. In this case, cavities of about 7 Å in size are formed, with four fluorine atoms inside. Cyanuric acid applied to various surfaces forms chiral 2D structures with the cavity dimensions of 10–11.5 Å [22, 23], while barbituric acid and thymine form only 1D-rows [24, 25]. Melamine has a chiral 2D structure without cavities [23]. PTCDA forms many 1D and 2D structures, while the supra-structure form depend on the experimental conditions [26–28]. Differences in the structure of supramolecular ensembles should also affect the ability of the surface covered by a layer of such a structure to participate in disperse interactions. Previously we established a relationship between the structure of supramolecular ensembles and the variation in the heat and entropy of adsorption [29–32]. It was shown that the size of the cavity of the supramolecular structure directly affects the thermodynamic characteristics of adsorption, while the polarity of

the cavity determines the polarity of the resulting adsorbent surface. However, it remains unclear how applying a layer of a supramolecular structure to a sorbent surface affects its ability to be involved in dispersion interactions. Therefore, it was of interest to determine the γ_s^d values for such novel adsorbents and to study the possible correlations between γ_s^d and the supramolecular ensemble structure.

2. Materials and Methods

2.1. Adsorbent samples

Porous polymers Dowex L-285 (Dow Chemical, Midland, USA), Polisorb-1 (Vecton, St. Petersburg, Russia), Porapak N (Waters, Milford, USA), and Sepabeads SP-207 (Sigma-Aldrich, Milwaukee, USA) were chosen as the initial adsorbents for modification. Their specific surface areas are given in Table 1. The particle size fraction of 0.25–0.5 mm of the initial adsorbents was used.

Uracil (Vecton, St. Petersburg, Russia, 98%, CAS 66-22-8), 6-methyluracil (Vecton, St. Petersburg, Russia, 99%, CAS 626-48-2), 5-fluorouracil (Sigma-Aldrich, USA, 99%, CAS 51-21-8), 5-hydroxy-6-methyluracil (Ufa Institute of Chemistry of the RAS, Ufa, Russia, 99%, 7417-28-9), melamine (Vecton, St. Petersburg, Russia, 97%, CAS 108-78-1), thymine (Vecton, St. Petersburg, Russia, 96%, CAS 65-71-4), cyanuric acid (Vecton, St. Petersburg, Russia, 98%, CAS 108-80-5), barbituric acid (Sigma-Aldrich, USA, ReagentPlus, 99%, CAS 67-52-7), as well as PTCDA (Sigma-Aldrich, USA, 97%, CAS 128-69-8) were used as the surface modifiers. A modifier (except for PTCDA) in the range from 10⁻⁴% to 10% mass was impregnated into the adsorbents' surfaces by evaporation of aqueous solutions at 60 °C. The temperature choice was necessary to uniformly impregnate the modifier on the surface. PTCDA is insoluble in water and in other solvents, so it was impregnated on the adsorbent surface from its solution in NaOH (pH 13) by slow neutralization with 1M hydrochloric acid followed by adsorbent filtration. Then the resulting sample was washed with high purity water to pH 7.

2.2. Gas chromatography

The sorbents studied were packed into stainless steel columns measuring 500x3 mm. A Chrom 5 (Czech Republic) and a Chromos GH-1000 (Chromos, Russia) gas chromatographs equipped with a flame ionization detector were used. The amount of the sorbent sample packed into the column was varied from 0.8 to 1.2 g. The column temperature was 200 °C. To measure the column overpressure, the chromatographs were equipped with manometers at the column inlet. The inlet pressure was 1.3–1.5±0.001 bar. The flow rate of nitrogen carrier gas (>99%) was 20–60 ml/min. At this flow rate, the peak desorption branches superimposed, and the specific retention volumes were independent of the flow rate. All the samples were conditioned overnight at 200 °C.

Table 1 Dispersive surface free energy of the adsorbents studied.

Initial adsorbent (specific surface area S , m^2/g)	Modifier	The amount of modifier ω , %	γ^d , mJ m^{-2}				r		
			n -Alkanes		n -Alcohols		n -Alkanes	n -Alcohols	LFER
			DG	DG-LFER	DG	DG-LFER	DG		
Dowex L-285 (800)	No		290	250	360	200	0.9999	0.9999	0.9600
	Uracil	10	220	250	250	160	0.9972	0.9989	0.9887
	6-Methyluracil	1	300	210	380	200	0.9996	0.9997	0.9876
		5	310	240	-	-	0.9941	0.9946	0.9940
	5-Fluorouracil	10	310	270	460	140	0.9908	0.9989	0.9345
		1	410	260	350	160	0.9992	0.9987	0.9844
		5	280	240	270	180	0.9976	0.9976	0.9877
	5-Hydroxy-6-methyluracil	10	450	210	300	180	0.9999	0.9979	0.9935
		1	380	250	420	110	0.9926	0.9999	0.9994
	Melamine	1	290	220	380	190	0.9999	0.9956	0.9827
		10	410	260	470	210	0.9809	0.9999	0.9775
	Cyanuric acid	1	320	290	290	250	0.9992	0.9995	0.9894
	Barbituric acid	3	340	-	510	-	0.9997	0.9369	0.9841
	Thymine	1	210	200	240	170	0.9900	0.9891	0.9714
	PTCDA	1	190	190	210	240	0.9981	0.9715	0.9807
Sepabeads SP-207 (650)	No		340	220	430	170	0.9993	0.9995	0.8351
	5-Hydroxy-6-methyluracil	1	320	190	210	130	0.9992	0.9988	0.9589
	Melamine	1	470	170	540	140	0.9995	0.9973	0.9807
		10	350	200	410	90	0.9990	0.9995	0.9708
	Uracil	10	130	70	110	80	0.9988	0.9996	0.9966
Polysorb-1 (250)	6-Methyluracil	10	80	50	60	30	0.9961	0.9957	0.9900
	5-Hydroxy-6-methyluracil	1	90	50	110	30	0.9886	0.9868	0.9962
	Melamine	10	210	120	100	20	0.9841	0.9990	0.9734
Porapack N (350)	5-Hydroxy-6-methyluracil	10	170	130	280	80	0.9990	0.9990	0.9902

n -Hexane, n -heptane, n -octane, benzene, toluene, ethanol, n -propanol, n -butanol, i -propanol, i -butanol and ethyl acetate (all of “chemically pure” grade, Chimreaktivsnab, Russia) were used as the probes. The probes were injected as vapours in the minimum possible amount (the amount of the probe was close to the minimum detectable quantity, i.e., 10^{-9} moles), which allowed us to consider adsorption processes in the column as ideal linear chromatography, making it possible to equate V_g with the adsorption-desorption equilibrium constants.

2.3. Calculation

The specific retention volumes were calculated by the well-known formula [33–35]. The calculation of dispersive surface free energy was carried out in two ways. In the first case, the classical DG method was used according to (2). In the second case, instead of the total free adsorption energy of the substance, the dispersive component of the free energy of adsorption (ΔF^{disp} , mJ/m^2) calculated by the linear free energy relationship (LFER) method was used for the Dorris-Gray calculation (DG-LFER). The LFER method assumes that the free energy of adsorption is the

sum of the energies of dispersion, induction, orientation and donor-acceptor interactions:

$$-\Delta F = \Delta F^{disp} + \Delta F^{spec} + \Delta F^{da}, \quad (5)$$

where ΔF^{spec} and ΔF^{da} are free energies of orientation+induction and of the donor-acceptor interactions, respectively. Equation 5 is more simple for some probes from Section 2.2. For example, alkanes are only capable of dispersion and induction interactions (if a polar surface induces a dipole in an alkane); therefore, for alkanes Equation 5 can be written as follows:

$$-\Delta F = \Delta F^{disp} + \Delta F^{ind} \quad (6)$$

where ΔF^{ind} is the energy of induction interaction between a polar surface and an alkane molecule. Any interaction energy can be considered as the product of the adsorbent coefficient and the molecule descriptor. In this work, the Larionov equation was used [36]:

$$-\Delta F = K_1 \alpha_B + K_2 \left(\frac{2\mu_B^2}{3kT} + \alpha_B \right) + K_3 W_B^a + K_4 W_B^d + K_5, \quad (7)$$

where

$$-\Delta F^{\text{disp}} = K_1\alpha_B + K_5, \quad (8)$$

$$-\Delta F^{\text{spec}} = K_2 \left(\frac{2\mu_B^2}{3kT} + \alpha_B \right), \quad (9)$$

$$-\Delta F^{\text{da}} = K_3W_B^a + K_4W_B^d, \quad (10)$$

and K_1 – K_5 are the coefficients characterizing the sorbent surface properties: dispersive, induction and orientation, electron-donor and electron-acceptor ones, respectively. The K_5 coefficient also characterizes dispersive interactions [37]. α_B , μ_B , W_B^a and W_B^d are the polarizability, dipole moment, and electron-acceptor and electron-donor constants of the adsorbate, respectively; k is the Boltzmann constant, and T is temperature, K. Equation 7 was composed for each probe listed in Section 2.2. In each equation, K_1 – K_5 were unknown, whereas the molecular descriptors were well known from various literature sources; the ΔF value was known from the chromatographic experiment. So, we have a set of 11 equations, each of which has 5 unknowns. Such set of equations was successfully used for LFER calculations previously [31, 38]. It was fitted by multiple linear regression analysis. The analysis results contain the K_1 – K_5 coefficients. After that, the coefficients were substituted into Equation 7 to obtain the ΔF^{disp} values.

3. Results and Discussion

Table 1 shows the values of dispersive surface free energy calculated by the DG and DG-LFER methods using a homologous series of *n*-alkanes and alcohols along with the regression coefficients for the alkane line using the DG method and for the LFER calculations. As it can be seen from the data obtained, the results of the DG-LFER calculation differ markedly from the values obtained by the classical method. Table 1 shows that nearly in all the cases, the γ_s^d value calculated by the DG method is higher than that calculated by the DG-LFER method. Moreover, all data obtained show relatively high γ_s^d values. This was explained by the adsorption in the cavities of the 2D supramolecular network. Similar high γ_s^d values were reported before [11]. In the vast majority of works where the DG method was applied, non-porous samples with low specific surface areas and accordingly low γ_s^d values were studied [14, 39–41].

Comparison of the data obtained using different homologous series shows that, according to the results of the DG-calculation, the γ_s^d values obtained with alcohols are higher than those obtained with *n*-alkanes in 15 cases, whereas the opposite is observed in 8 cases. According to the DG-LFER method, the γ_s^d with *n*-alkanes are higher in 20 cases and slightly lower in only two cases. Therefore, regularity is attained only if the DG-LFER method is used.

From the theoretical point of view, no differences in γ_s^d with the same mechanism of adsorption measured using different homologous series should be observed. If

the adsorption mechanism differ, the differences are possible, but even in this case it is difficult to imagine a situation in which the dispersive surface free energy for linear *n*-alkanes would be lower than that for alcohols. However, the opposite is possible if the mechanism of adsorption of alcohols prevents all parts of the hydrocarbon chain from contacting the surface. In the case of the samples under study, the interaction of alcohols with the surface is predominantly due to the hydroxyl group forming H-bonds with the modifiers. So, the contact between the hydrocarbon chain of the alcohol and the adsorbent surface can be difficult. This should lead to lower values of dispersive surface free energy for a homologous series of alcohols.

Thus, the data obtained by the DG-LFER method were found to be more consistent with the theoretical concepts than the data of the classical DG method. The results obtained using a homologous series of *n*-alkanes are more appropriate for further analysis. Therefore, further data will be subjected to this analysis by default.

From the data obtained, it can be seen that when the surface of Dowex L-285 is modified with 6-methyluracil, an insignificant increase in γ_s^d occurs according to DG, while, according to DG-LFER data, from the initial adsorbent to the modified 1% 6-methyluracil, a decrease in γ_s^d by 40 mJ/m² occurs, while a further increase in the amount of the modifier applied leads to an increase in γ_s^d . In the case of 5-fluorouracil application, the DG data show a discontinuous change in the dispersive surface free energy: after modification with 1% of 5-fluorouracil γ_s^d increased to 120 mJ/m²; after increasing the amount of the modifier from 1 to 5%, γ_s^d decreased to 130 mJ/m², virtually to the values of the initial adsorbent. Then, an increase to 450 mJ/m² for the sample with 10% 5-fluorouracil was observed.

More regular changes are observed in the analysis of DG-LFER data: with increasing amount of applied 5-fluorouracil, γ_s^d decreases to 210 mJ/m². For melamine, both Dowex L-285 and Sepabeads SP-207 modified adsorbents are characterized by an increase in γ_s^d , calculated by the DG-LFER method, with an increase in the melamine amount. At the same time, the classical DG approach shows that, with an increase in the amount of melamine from 1 to 10%, a noticeable increase in dispersive surface free energy occurs if Dowex L-285 is used as the initial adsorbent, whereas with Sepabeads SP-207, which has similar surface characteristics, a similar noticeable decrease occurs.

It can be concluded that the results obtained by the DG-LFER method are more reliable than the data of the classical DG. Perhaps, this is due to the high polarity of the samples studied. The polar surface is capable of inducing a dipole moment in a nonpolar molecule, which leads to induction interactions. Therefore, even for *n*-alkanes in this case, the total free energy of adsorption used in the classical DG method does not coincide with the dispersive component of the free energy of adsorption:

$$\Delta F = \Delta F^{\text{disp}} + \Delta F^{\text{ind}}, \Delta F^{\text{ind}} \neq 0. \quad (11)$$

This leads to the fact that, for strongly polar surfaces, the value of γ_s^d calculated by the classical DG method differs from the true one, resulting in hard-to-interpret data.

Using the LFER method according to Equations 6–10, it is possible to isolate the free energy value corresponding to the dispersive interactions only and then use it for a more accurate calculation with the Dorris-Gray method. Therefore, the further comparison of γ_s^d values will be performed only using the DG-LFER method and the homologous series of *n*-alkanes.

The general regularity of the data obtained is that the dispersive surface free energy of any modified samples increases with the specific surface area of the initial adsorbent. This is due to the ability of supramolecular structures to cover any surface with a uniform layer during adsorption instead of forming microcrystals (as is typical of other solid bodies applied from solutions on the surfaces of other solids).

From the theoretical point of view, when any modifiers are applied to porous adsorbents, the dispersive interactions should be weakened since the modifier is adsorbed on the most active centers of the surface, thereby blocking them [42] (we will call this the first factor). However, in the case of the formation of a 2D-supramolecular network with cavities, the latter give an additional contribution to the dispersive surface free energy [29, 32] (we will call this the second factor). Therefore, the data of Table 1 show a multidirectional change in γ_s^d , depending on the prevalence of one of these factors. Thus, when 1% 6-methyluracil is applied to the Dowex L-285 surface, the decrease in γ_s^d observed is due to the action of the first factor, since at low concentrations, 6-methyluracil forms 1D structures that do not have cavities [43]. However, when the amount of 6-methyluracil is increased, mainly 2D structures with cavities begin to form, which leads to an increase in γ_s^d . For uracil and 5-hydroxy-6-methyluracil, the decrease in dispersive surface free energy due to the coverage of active surface centers is compensated by the growth of γ_s^d due to the contribution of the cavities of the supramolecular structure. For cyanuric acid, a growth of the dispersive surface free energy is observed, since the cyanuric acid supramolecular structure forms are stabilized by 6 H-bonds cavities even at low concentrations. For thymine and PTCDA, a de-

crease in γ_s^d is observed because their superstructures have no cavities, so only the first factor is operative.

After modification of Dowex L-285 with 1% melamine, the decrease in γ_s^d is explained by the absence of cavities in the supramolecular structure of melamine. However, under the influence of a high temperature, splitting of some melamine molecules from its superstructure with formation of a cavity measuring 5 Å can occur [23]. It is possible that with a large amount of melamine, several layers of the modifier can be formed on the surface, and the molecules of the upper layer would be more weakly bound to the surface. Most likely, this would lead to cleavage of a number of melamine molecules and, hence, to the formation of cavities and an increase in γ_s^d .

Unlike in 6-methyluracil, cavities in 5-fluorouracil are formed even if 1% of the modifier is applied [29]. However, when a greater amount of 5-fluorouracil is applied to the surface of Dowex L-285, a decrease in the dispersive surface free energy was observed. This is caused by the transition of the porous 2D-supramolecular structure to a dense 2D structure without cavities, followed by an increase in the concentration of the modifier, which leads to a weakening of the second factor.

To confirm the hypothesis about the competing effect of the two above factors on the dispersive surface free energy, a study was made of the effect of the concentration of uracil, melamine and cyanuric acid on the γ_s^d of the Dowex L-285 adsorbent. The data obtained are given in Table 2.

As it can be seen from the table, the constancy of the γ_s^d values is observed only for cyanuric acid. This is probably due to the high stability of the structures formed and the fact that cyanuric acid always forms only one type of supramolecular structure [22, 23]. Therefore, with an increase in the amount of cyanuric acid, the number of blocked adsorption centers increased, but the number of cavities in the supramolecular structure also increased, which led to mutual balancing of the two factors with some predominance of the second one. Unlike 5-fluorouracil, which also gives a 2D supramolecular structure at low concentrations of the modifier, there is no decrease in γ_s^d when 10% cyanuric acid is applied. This is due to the fact that in the case of cyanuric acid, the cavities are located not parallel but perpendicularly to the initial adsorbent surface [23].

Table 2 Dispersive surface free energy of the Dowex L-285 adsorbent modified by various quantities of uracil, melamine and cyanuric acid, according to DG-LFER method with *n*-alkanes as the probes.

The amount of modifier ω , %	γ_s^d , mJ m ⁻²			<i>r</i>					
	Uracil	Melamine	Cyanuric acid	Uracil		Melamine		Cyanuric acid	
				DG	LFER	DG	LFER	DG	LFER
10 ⁻⁴	140	230	280	0.9826	0.9877	0.9979	0.9849	0.9994	0.9902
10 ⁻³	280	330	290	0.9984	0.9813	0.9820	0.9626	0.9691	0.9748
10 ⁻²	370	380	280	0.9999	0.9819	0.9876	0.9848	0.9999	0.9929
0.1	210	330	280	0.9959	0.9828	0.9926	0.9854	0.9992	0.9849
1	240	220	290	0.9926	0.9848	0.9995	0.9843	0.9992	0.9875
10	250	260	280	0.9972	0.9864	0.9990	0.9876	0.9998	0.9901

For melamine and uracil, the values of γ_s^d vary noticeably. When the concentration of the modifier increases from 10^{-4} to $10^{-2}\%$, the growth of γ_s^d is observed, after which a sharp decrease occurs at 0.1%. This is probably due to a change in the structure of the superstructure: thus, for uracil at low concentrations, a more porous structure is more typical, while as the concentration is increased to a monolayer, a dense 2D structure is formed [15]. The transition from a structure containing cavities to that without cavities reduces the effect of the second factor and leads to a decrease in γ_s^d .

4. Conclusions

It was shown that in the case of adsorbents modified with high-polarity modifiers, the use of a homologous series of *n*-alkanes is preferable to the use of alcohols. In the latter case, incomplete contact between the hydrocarbon chain and the adsorbent surface is possible. It was found that the high polarity of heterocyclic compounds used as modifiers causes a noticeable effect of inductive interactions between the surface of the adsorbent and *n*-alkanes. This leads to a distortion of the results of the classical DG method. An addition to the DG method based on the preliminary separation of the dispersive component of the free energy of adsorption by the LFER method was suggested and successfully tested. It was shown that the data obtained by the DG-LFER method are more relevant.

The change in the dispersive surface free energy after the modification is most likely due to the opposite effect of two factors: a decrease in γ_s^d due to the blocking of the active sites of the adsorbent by the modifier (first factor) and the growth of γ_s^d due to the additional contribution of adsorption in the cavities of the supramolecular structure (second factor). Analysis of the data obtained in this work shows a direct correlation between the structure of supramolecular ensembles and the change in γ_s^d . All observed variations of the second factor agree with the literature data on the properties of chiral supramolecular structures. Thus, we demonstrated that the value of γ_s^d is sensitive to the impregnation of chiral supramolecular structures on the surface of porous adsorbents. The results obtained can be used to analyze the relationships between supramolecular structure properties and the enantioselectivity of chiral adsorbents.

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

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