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STUDY OF THE ADSORPTION LAYER OF NEMATIC MESOGEN WITH BRANCHED END FRAGMENTS AT THE CARBON ADSORBENT SURFACE

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Vapor adsorption of organic compounds of different polarity on graphite-like adsorbent Carbopack Y modified by a monomolecular layer of a «double swallowtail type» liquid crystal was studied using gas chromatography. Adsorption thermodynamic characteristics (differential molar heats of adsorption and the entropy change during adsorption) were determined through the temperature dependencies of the Henry constant. Adsorption thermodynamic characteristics of the original carbon adsorbent and the adsorbent covered with the liquid crystal monomolecular layer were compared. The theoretical model of delocalized adsorption (model of an ideal two-dimensional gas) is used to analyze the change in entropy values. It is shown that the modification as a whole leads to the increase of the adsorption localization. Analysis of values of the thermodynamic characteristics revealed that they are influenced by possible monomolecular layer structure of liquid crystal. Possible structure of a monolayer of the «double swallowtail type» liquid crystal on a flat uniform carbon surface of Carbopack Y is proposed. The nature of the adsorption entropy change leads to the conclusion that the liquid crystal molecules are self-organized in the monolayer as a regular structure with little linear size intervals not permitting the interaction of the substrate with the adsorbate molecules.

***Key words**: adsorption, gas-adsorption chromatography, modified carbon adsorbents, monolayers, liquid crystals, adsorbate-adsorbent interactions.*

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ИССЛЕДОВАНИЕ АДСОРБЦИОННОГО СЛОЯ НЕМАТИЧЕСКОГО МЕЗОГЕНА С РАЗВЕТВЛЕННЫМИ КОНЦЕВЫМИ ФРАГМЕНТАМИ НА ПОВЕРХНОСТИ УГЛЕРОДНОГО АДСОРБЕНТА

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С использованием метода газовой хроматографии проведено исследование адсорбции паров органических соединений различной полярности на углеродном графитоподобном адсорбенте Carbopack Y, модифицированном мономолекулярным слоем жидкого кристалла типа «двойной ласточкин хвост». Из температурных зависимостей констант Генри адсорбции определены термодинамические характеристики адсорбции (дифференциальные молярные теплоты адсорбции и величины изменения энтропии при адсорбции). Проведено сопоставление полученных термодинамических характеристик адсорбции на исходном углеродном адсорбенте и адсорбенте с монослоем жидкого кристалла. Для анализа изменения величин энтропии привлечена теоретическая модель делокализованной адсорбции (модель идеального двумерного газа). Показано, что модифицирование в целом приводит к усилению локализации адсорбции. На основе анализа термодинамических величин выявлена связь между характером их изменения и возможным строением мономолекулярного слоя жидкого кристалла. Предложено возможное строение монослоя жидкого кристалла типа «двойной ласточкин хвост» на плоской однородной углеродной

поверхности твердого носителя. Указано, что характер изменения величин энтропии адсорбции позволяет говорить о том, что молекулы жидкого кристалла в монослое самоорганизуются в виде регулярной структуры, имеющей промежутки малых линейных размеров, практически не допускающих взаимодействия подложки с молекулами адсорбатов.

***Ключевые слова**: адсорбция, газо-адсорбционная хроматография, модифицированные углеродные адсорбенты, монослои, жидкие кристаллы, взаимодействия «адсорбат – адсорбент».*

Introduction

One of the methods of obtaining supramolecular, mono- or multilayer systems on the phase boundary is adsorption or chemical modification of solid surfaces which allows their chromatographic study. The nature of the solid carrier bares great importance in such modification is very important, since its surface structure has great impact on the structure and the degree of ordering of the formed modifier layer. In this regard, the study of the monomolecular layers of mesogenic and nonmesogenic compounds with anisometric molecules is very interesting, because their spatial structure of molecules contributes to a spontaneous self-ordering on the substrate surface [1, 2].

At present there are sufficiently many studies of gas phase organic compound adsorption on mono- and polylayers of various mesogens (liquid crystals (LC)), as well as their structures [3–7]. Mesogen compounds with branched end fragments belong to a special group. In accordance with the adopted in the literature terminology, such liquid crystals are called «swallowtail» or «double swallowtail» mesogens [8]. They form a class of compounds allowing a variation of the molecular structure in a fairly wide range that leads to a diversity of possible mesophases.

The purpose of this work was the gas chromatographic study of vapor adsorption of organic compounds of various polarity at the Carbopack Y (CpY) carbon adsorbent modified by the monomolecular layer of a nematic liquid crystal of the «double swallowtail» type – *bis*[2,2’-di-(*n*-hexyloxycarbonyl)ethynyl]phenyl ether of 4,4’-biphenyldicarboxylic acid (BAHPh).

Experiment

Carbopack Y (*Supelco Inc.)*, non-porous carbon adsorbent-carrier, characterized by the geometric and chemical homogeneity of the surface (specific surface area 33,6 m^2/g) was selected as a solid substrate for LC monolayer formation.

The BAHPh modifier* (fig. 1) was applied from a chloroform solution in the amount required for obtaining dense monomolecular layer. To determine the needed quantity of the modifier the landing site of the LC molecule was calculated as to 485 Å^2. The mass of the modified adsorbent in the column (1 m x 2 mm) was 1,2726 g (CpY – 1,2708 g, BAHPh – 11,7 mg).

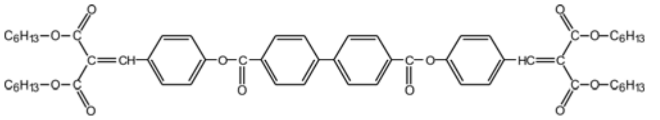

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Fig. 1. Structure and phase transition temperatures of BAHPh

The experiment was conducted using the inverse gas chromatography method on Tsvet-100 chromatograph with a flame ionization detector. Based on the experimental data Henry adsorption constants were calculated according to the formula:

$$K_{1,c} = V_S^T = \frac{(t_R - t_M)\cdot F_{P_a,T_c}\cdot j_3^2}{W_S \cdot s_{sp}} = \frac{(t_R - t_M)\cdot F_{\bar{P},T_c}}{W_S \cdot s_{sp}}, \quad (1)$$

where t_R – the retention time of the studied substance; t_M – the retention time of the nonsorbent; W_s – the adsorbent mass; s_{sp} – absorbent specific surface area CpY (assuming the specific surface area of the adsorbent does not change after the modifier application); F_{P_a,T_c} – rate of volume flow of the carrier gas at the column outlet at the column temperature; j_3^2 – James-Martin coefficient; $F_{\bar{p},T_c}$ – rate of volume flow of the carrier gas reduced to the column temperature and the pressure averaged over the length of the column determined via the «cold» calibration method [9].

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*Synthesized in the Martin Luther University (Halle, Germany) and kindly provided for research by the Doctor of Chemical Sciences, Professor of Saint Petersburg University Sokolova E.P.

Differential molar heat of adsorption ($\bar{q}_{dif,1}$) as well as the entropy change during adsorption ($\Delta\bar{S}^0_{1,c}$) were determined through the temperature dependencies of the Henry constant according to the known ratio [10]:

$$\ln K_{1,c} = \frac{B}{T} + A = \frac{\bar{q}_{dif,1}}{RT} + \frac{\Delta\bar{S}^0_{1,c}}{R} + 1, \qquad (2)$$

where $\bar{q}_{dif,1} = -\Delta \mathrm{U}_1$ – differential molar heat of adsorption; $\Delta\bar{S}^0_{1,c} = \bar{S}^{S^o}_1 - \tilde{S}^o_{g,c}$, $\bar{S}^{S^o}_1$ – standard ($\Gamma = 1$ mcmol/m^2) differential entropy of the adsorbed substance, $\tilde{S}^o_{g,C}$ – standard adsorbate entropy in the gas phase with concentration $C = 1$ mcmol/cm^3.

Considering that the coefficients A and B in the first approximation do not depend on the temperature and determining the coefficients from linear dependencies $\ln K_{1,c} = f(1/T)$, the experimental values of the adsorption thermodynamic characteristics of the studied substance were determined.

Results and Discussion

Fig. 2 shows temperature dependencies of the Henry constants of *n*-hexane, cyclohexane, benzene and butanol-1 adsorption on the original (CpY) and modified (CpY/BAHPh) adsorbents. After modification Henry constants' reduction has been observed for all researched substances. That is specific for modifications of graphite thermal soots by molecules forming dense monolayers capable of shielding the carbon substrate surface [6, 10].

The analysis of the Henry constants of adsorption indicates that *n*-alkanes are adsorbed slightly better on the modified adsorbent than arenes with the same number of carbon atoms in the molecule (*n*-hexane comparing to benzene, fig. 2). Moreover, it should be noted that the CpY modification in case of cyclohexane and butanol-1 leads to a much smaller reduction of Henry constants comparing to the original CpY than for the arenes and alkanes of the normal structure.

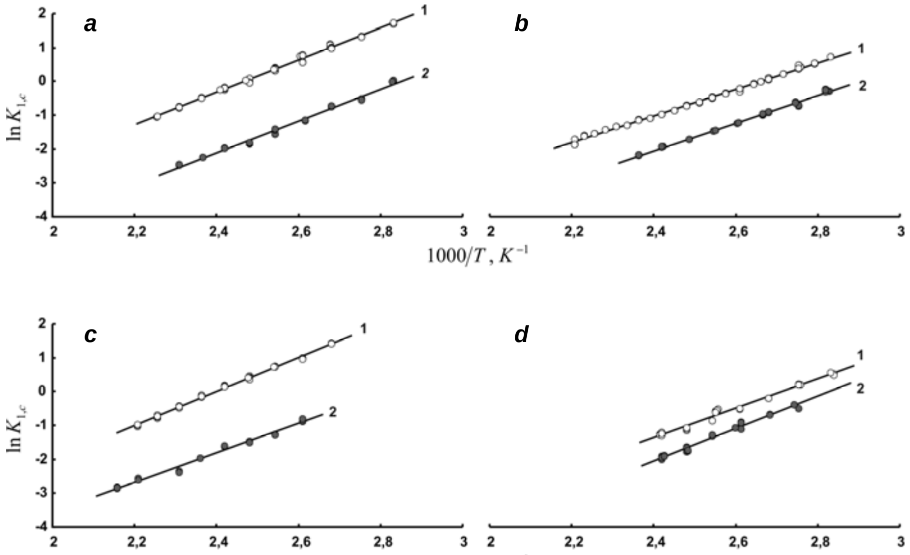

Fig. 2. Temperature dependencies of the Henry constants of adsorption on the examined adsorbents; benzene (*a*), cyclohexane (*b*), *n*-hexane (*c*) and butanol-1 (*d*); CpY (1), CpY/BAHPh (2)

Table represents the numerical values of the thermodynamic characteristics of adsorption, calculated from the temperature dependencies of the Henry constants in comparison with the data for the non-modified adsorbent.

The data shows that in *n*-alkanes modification leads to a reduction of the heat of adsorption and to an increase of the absolute value of the entropy change. The *n*-hexane is an exception. Its $-\Delta\bar{S}^o_{1,c}$ value almost does not change.

For the heat of adsorption values a similar trend is evident for aromatic hydrocarbons. However, arenes' entropy change except for benzene is almost identical on the original and modified adsorbents ($|\Delta\Delta\bar{S}^{o}_{1,c}|$~2–5 J/(mol·K)). A similar situation is evident for pyridine. Presence of a monolayer polar to BAHPh leads to an increase of the thermodynamic characteristics of adsorption for studied spirits. Carbon tetrachloride, cyclohexanone and tetrahydrofuran behave similar to spirits. Thus, when BAHPh is applied as a polar modifier the nature of the change of the adsorption thermodynamic characteristics is determined by the adsorbate molecule polarity.

Table. **Thermodynamic characteristics of adsorption of the researched substances on CpY and CpY/BAHPh adsorbents**

№	Adsorbates	α, Å^3	$\bar{q}_{dif,1}$, kJ/mol		$-\Delta\bar{S}^{o}_{1,c}$, J/(mol·K)	
			CpY	CpY/BAHPh	CpY	CpY/BAHPh
1	*n*-Hexane	11,78	41,9±0,9	36,0±1,8	108,7±2,1	109,8±4,4
2	*n*-Heptane	13,62	48,6±2,0	45,2±1,7	114,9±4,6	123,7±4,1
3	*n*-Octane	15,45	54,3±1,3	50,1±1,2	118,9±2,8	126,8±2,8
4	*n*-Nonane	17,29	59,6±1,0	55,7±1,5	120,9±2,2	132,4±3,4
5	*n*-Decane	19,10	–	59,1±1,3	–	132,4±2,9
6	*n*-Undecane	20,96	–	64,8±6,9	–	137,5±15,0
7	*n*-Dodecane	22,79	–	68,6±4,2	–	138,7±8,8
8	Cyclohexane	11,01	32,7±0,4	33,9±0,5	95,4±1,1	106,8±1,4
9	Benzene	10,43	40,0±0,8	38,7±1,6	107,2±2,1	118,9±4,2
10	Toluene	12,27	47,2±2,8	41,0±1,5	112,2±6,3	114,1±3,6
11	Chlorobenzene	12,40	47,5±0,9	43,9±1,1	110,1±2,1	116,6±2,7
12	Ethylbenzene	14,10	51,5±1,0	44,7±1,4	116,1±2,3	115,8±3,2
13	*o*-Xylene		55,3±1,4	49,4±1,1	118,2±3,0	123,1±2,7
14	*m*-Xylene		54,4±2,6	47,4±1,8	117,2±5,8	119,4±4,3
15	*p*-Xylene		56,2±0,8	46,9±1,9	120,3±1,8	117,2±4,4
16	Butanol-1	8,75	35,8±1,9	39,6±1,9	105,6±4,9	120,6±5,0
17	2-Methylpropanol-1		34,3±1,3	36,8±5,6	104,6±3,4	116,2±15,2
18	2-Methylpropanol-2		32,0±2,2	36,1±5,0	103,4±5,7	118,9±13,5
19	Pentanol-1	10,60	–	47,8±1,3	–	131,7±3,3
20	3-Methylbutanol-1		–	44,9±2,2	–	125,7±5,7
21	Hexanol-1	12,42	–	52,2±1,6	–	134,2±4,0
22	Cyclohexanol	11,65	40,5±0,3	42,5±0,9	105,0±0,7	115,4±2,2
23	Cyclohexanone	11,10	39,8±0,3	42,4±1,0	104,0±0,7	115,4±2,5
24	1,3-Dioxane	8,61	35,0±0,3	35,8±0,4	104,3±0,8	110,3±1,0
25	1,4-Dioxane		34,8±0,3	35,1±0,4	104,2±0,8	109,2±1,1
26	Pyridine	9,73	46,9±0,7	40,8±1,3	123,3±1,7	119,1±3,4
27	Tetrahydrofuran	7,98	33,6±1,0	36,8±2,0	107,0±2,5	121,5±5,3
28	Cyclohexene	10,70	36,8±0,2	39,7±1,4	103,3±0,6	121,4±3,6
29	Carbon tetrachloride	10,30	30,2±0,7	32,9±1,3	94,6±1,7	107,8±3,4

Non-polar and low-polar compounds with cyclic molecular structure constitute a special group of compounds. For example, the heat of adsorption on both adsorbents are nearly the same for cyclohexane, cyclohexene, and isomeric dioxanes. Entropy changes after modification are greater on average by 5–18 J/(mol·K).

In general, the heat of adsorption values on CpY and CpY/BAHPh adsorbents increase with polarizability (size) growth of the adsorbate molecules (fig. 3, table). For spirits in case of the modified adsorbent the heat of adsorption is higher than for hydrocarbons approximately by 9–15 J/(mol·K) (e.g., cyclohexanol and cyclohexane, hexanol-1 and *n*-hexane). That corresponds well to the typical energy values of the hydrogen intermolecular bond. It is common for both adsorbents that increase in the degree of branching of a hydrocarbon radical in a spirit molecule leads to some decrease of the heat of adsorption. In case of the original adsorbent that comes from the weakening of intermolecular bonds of the spirit molecules with the flat surface, thus, with the decrease of energy of the dispersion interaction. While in case of the CpY/BAHPh adsorbent it comes from steric hindrances in hydrogen bond formation. Toluene – chlorobenzene combination, whose molecules have virtually the same molecular volumes, is also characterized by the same $\bar{q}_{dif,1}$ values on the CpY adsorbent. Because in this case, the energy of interaction is determined only by dispersion interactions. Modification leads to a weakening of the dispersion interactions for both compounds, but provides a contribution to the dipole-dipole interactions in the overall energy of adsorption for chlorobenzene leading to an increase of its heat of adsorption.

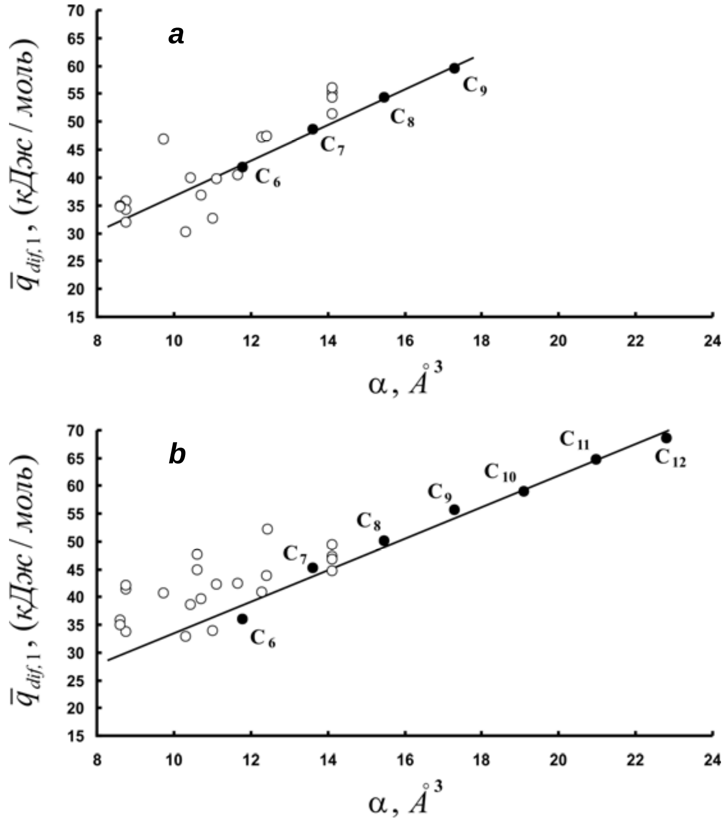

Fig. 3. Relation between the differential molar heat of adsorption and the polarizability of the adsorbates on the examined adsorbents; CpY (*a*), CpY/BAHPh (*b*); lines are drawn through the *n*-alkane points

Entropy dependence analysis demonstrates that in general adsorption on the surface of the original adsorbent is delocalized in nature (fig. 4, *a*) and in the first approximation is described by the following equation [11, 12]:

$$-\Delta\bar{S}^{o}_{1,c\,(deloc)} = 65.27 + 4.157\,\ln(MT), \qquad (3)$$

where M – adsorbate molar mass (g/mol), T – temperature (K).

It can be noted that in case of the modified adsorbent the experimental values of the absolute entropy change for all compounds are slightly higher than it is predicted by the model of an ideal two-dimensional gas (fig. 4, *b*). This demonstrates the lesser mobility of the adsorbed molecules on the modified surface comparing to a flat homogeneous surface along which adsorbate molecules can move freely.

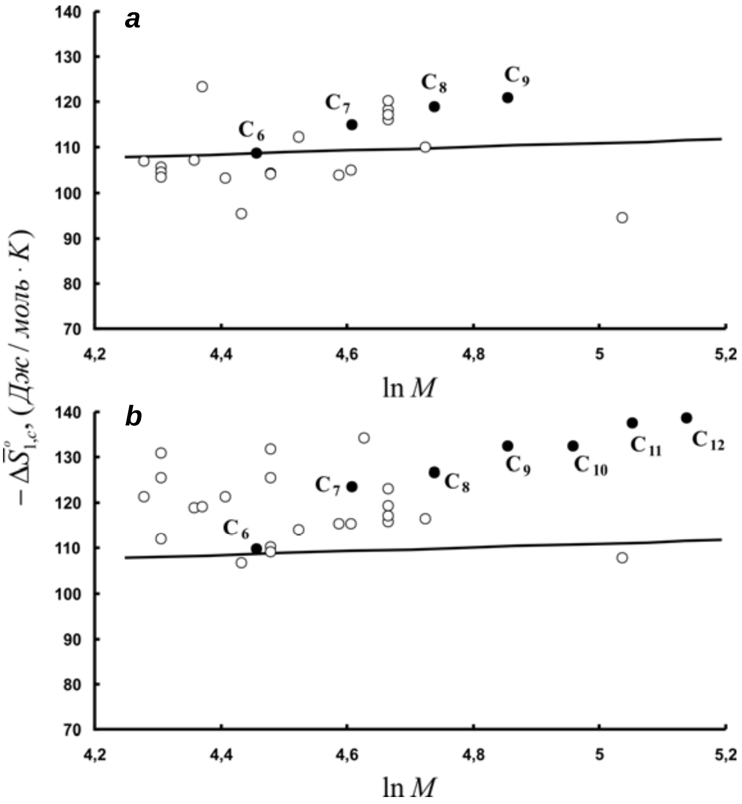

Fig. 4. Relation between the differential molar entropy change during adsorption and the molar mass of the adsorbates for examined adsorbents; CpY (*a*), CpY/BAHPh (*b*); lines are drawn based on the equation (3); for all adsorbates the temperature T = 403,15 K

Such nature of the entropy dependence for CpY/BAHPh reveals the heterogeneity of the BAHPh's monolayer surface and suggests that the movement of the adsorbed molecules along the surface overall ceases to be free. This effect may also be observed in a case where modifier molecules are loosely adjacent to each other in the monolayer leaving part of the substrate open. Thereby the adsorption capacity of the modified surface varies periodically along the way. Those parts of the surface which correspond to the potential minima are the centers of the partial localization of the adsorbed molecules. In our case the effect of the adsorption localization on the surface of the modified adsorbent is weak. That comes from the fact that observed entropy changes (no more than ~140 J/mol·K) do not reach in absolute value the expected levels for the full localization of molecules, i.e. complete loss of all three degrees of freedom of translational motion.

Based on the collected data it can be assumed that in the monolayer on a carbon substrate surface the BAHPh molecules are located in such a way that between their hard central fragments, as well as between the branched end groups, intervals may arise (fig. 5).

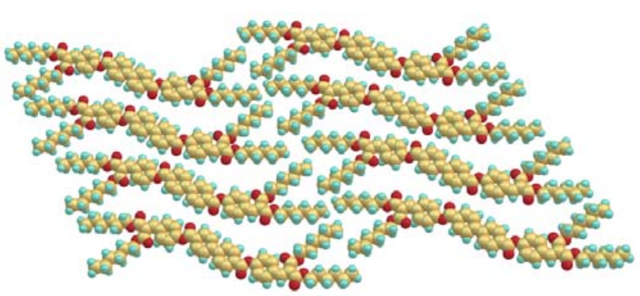

Fig. 5. Supposed BAHPh monolayer structure on the CpY flat surface

Presence of available substrate surface between BAHPh molecules should have lead to a growth of the thermodynamic characteristics of adsorption, as this would have increased the energy of the «adsorbent-modifier-adsorbate» disperse interaction by increasing the number of intermolecular contacts between the carbon substrate, LC and adsorbate molecules. Similar results were observed researching another liquid crystal [13]. However, in case of the BAHPh monolayer the width of the formed intervals is not enough even for small adsorbate molecules to penetrate them embedding in the monolayer structure.

Conclusions

Modification of the carbon adsorbent surface by an LC monolayer of the «double swallowtail» type shields the surface. That is expressed in the Henry constants reduction for all researched compounds compared to the original CpY adsorbent. It has been revealed that the decrease in the heat of adsorption resulting from the decline in the adsorption capacity of the firm substrate after modification is poorly offset by the specific interactions in addition to the disperse interactions. The nature of the adsorption entropy change leads to the conclusion that the BAHPh molecules are self-organized in the monolayer as a regular structure with little linear size intervals not permitting the interaction of the substrate with the adsorbate molecules.

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