Interactions of copper tetra-*tert*-butylphthalocyanine with nitrogen- and sulfur-containing compounds in solutions

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Interactions of ammonia, aliphatic amines, hydrogen sulfide, and sulfur dioxide with copper tetra-*tert*-butylphthalocyanine (CuPc) in squalane were studied by spectrophotometry and gas liquid chromatography in the CuPc concentration range of $1 \cdot 10^{-3}$—$5 \cdot 10^{-2}$ mol L^{-1}. The sorption properties of the CuPc—squalane stationary liquid phases (SLPs) are governed by the physicochemical nature of the CuPc nanoaggregates in solution. The β-type nanoaggregates exhibit particularly high activity to hydrogen sulfide; the activities to primary and secondary amines are also high.

Key words: copper phthalocyanine, aliphatic amines, hydrogen sulfide, sorption.

Phthalocyanine films find application as sensitive layers of chemical sensors.[1] A topical task is to prepare films that selectively sorb hydrocarbons,[2,3] ammonia,[4,5] aliphatic amines,[6,7] and hydrogen sulfide.[8] It is known[2] that the response value of microgravimetric sensors with metal (MPc, M = Cu, Co, Fe) tetra-*tert*-butylphthalocyanine films to hydrocarbon and alcohol vapors varies in parallel with the boiling points of the sorbates. This indicates that the films of coordinatively unsaturated phthalocyanines sorb molecules of organic bases only due to nonspecific interactions. A similar situation is found for cobalt and manganese tetraphenylporphins.[9]

Sensors based on some MPc possess low sensitivity.[2,4] It is known that a high sorption activity is typical of the crystalline β-form of phthalocyanines,[10,11] whereas MPc films are composed of nanoaggregates in the χ-form.[12,13] The possibility of changing the sorption properties of phthalocyanine films by controlling their supramolecular structure was demonstrated in relation to the *tert*-butyl-substituted binuclear copper phthalocyanine.[3] The development of selective sorbents based on phthalocyanines of a number of metals was confirmed by the data[14,15] derived from a gas-chromatographic study of the MPc—squalane stationary liquid phases (SLPs) (M = Cu or Co). The reduced partition coefficient (K_R) of organic sorbates between the gas phase and the SLP show a maximum for MPc concentrations of 10^{-3}—10^{-1} mol L^{-1}; the height of the maximum may be appreciably different for sorbates with similar chemical nature.[15] The constants K_R can be used to identify active supramolecular forms present in concentrated solutions of MPc.

This study deals with sorption of nitrogen- and sulfur-containing electron-donating molecules by the SLPs composed of CuPc and squalane. Copper phthalocyanine (CuPc) is readily soluble in organic media and enters mainly into noncovalent interactions, which should be favorable for reversible sorption of strong organic bases at low temperatures.

Experimental

Reagent grade alkylamines purified by fractional distillation were used in the study; H_2S and SO_2 were prepared by treatment of the sodium salts of the corresponding acids with H_3PO_4.

The Langmuir—Blodgett (LB) film of CuPc on a quartz plate was prepared using the Schaefer method on a NT-MDT trough (Molecular Devices and Tools for Nano-Technology, Zelenograd, Russia).[16] The conditions for the monolayer formation on the aqueous surface were as follows: benzene solution ([CuPc] = $3.0 \cdot 10^{-4}$ mol L^{-1}), initial surface concentration of CuPc $3.0 \cdot 10^{-7}$ mol m^{-2}, transfer pressure 20 mN m^{-1}.

The UV-Vis spectra of CuPc were measured on a Specord M400 instrument (Carl Zeiss, Jena, Germany).

The retention times of the sorbates were measured on a Chrom-5 gas chromatograph (Czechia) with a FID. The procedures for the chromatographic experiment and processing of the primary data were described previously.[14] The packings were prepared (Table 1) using squalane (Merck, Darmstadt, Germany) and Chromaton N-AW (0.40—0.63 mm, Chemapol, Czechia) as a solid support. The packing were placed in 1000×3 mm steel

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1441—1444, July, 2003.

Table 1. Composition of packings

$[CuPc] \cdot 10^2$ (25 °C)/mol L^{-1}	Weights of the components packing/g		
	Support	Squalane	CuPc
0	3.9762	0.9903	0
0.11	4.8530	0.9695	0.0012
1.17	4.9675	0.9818	0.0117
3.47	4.9299	0.9524	0.0338
4.96	4.4438	0.8458	0.0433

columns. The measurements were carried out under isothermal conditions at five temperatures in the 75—140 °C range. Sorbates were injected with 1 and 500 μL syringes (Hamilton, Switzerland). The primary chromatographic data are given in Table 2 as temperature dependences of the constants K_R.

To study the interaction of sorbates with the SLPs, the reduced partition coefficients ($K_R/K_R{}^0 - 1$) were calculated, where K_R and $K_R{}^0$ are the partition coefficients measured on the column with CuPc and on the column with pure squalane, respectively. This constant is determined only by the interaction of sorbates with CuPc. When CuPc is missing and pure squalane is used as the SLP, this value is equal to zero.

Table 2. Coefficients of the equation $\ln K_R = a + bt^{-1} + ct^{-2} + dt^{-3}$, describing the temperature dependence of the partition coefficients of sorbates between the gas phase and the CuPc—squalane stationary liquid phase at T = 75—140 °C

a	$b \cdot 10^{-4}$	$c \cdot 10^{-6}$	$d \cdot 10^{-10}$
	tert-Butylamine		
28.576	−2.6808	6.72976	0
22.174	−2.2437	6.03007	0
18.098	−1.9264	5.40052	0
61.891	−5.2416	11.7663	0
714.276	−82.2364	313.815	−3.94135
	Dimethylamine		
9.175	−1.2362	4.15350	0
8.949	−1.1492	3.87632	0
−508.631	57.2187	−215.089	2.73304
64.972	−5.4729	12.2610	0
1913.801	−220.5270	844.165	−10.7056
	Trimethylamine		
−31.564	2.2822	−3.68293	0
−7.237	0.3363	0.217818	0
−6.662	0.3230	0.207919	0
−9.151	0.4917	−0.05675	0
2.798	−0.4419	1.73207	0
	Ammonia		
−616.201	71.6457	−278.640	3.64058
1608.568	180.8590	−679.086	8.53059
2.849	−0.5716	2.24597	0
−22.230	1.4188	−1.79610	0
	Sulfur dioxide		
−7.211	0.4773	−0.184269	0
1.966	−0.2077	1.107810	0
−6.115	0.3994	−0.049364	0
−6.319	0.4085	−0.049029	0

Results and Discussion

Figure 1 shows the UV-Vis spectra of the chromatographic packings, which reflect the state of CuPc in the SLP. In the concentration range of [CuPc] ≤ $1.2 \cdot 10^{-2}$ mol L^{-1}, these spectra, like the spectra of CuPc-doped polystyrene films,[17] exhibit bands with absorption maxima at *ca.* 680 and 620—630 nm, which correspond to single molecules and to χ-type nanoaggregates. The UV-Vis spectrum of the packing with [CuPc] = $3.5 \cdot 10^{-2}$ mol L^{-1} (see Fig. 1, curve *1*) indicates that an increase in the concentration leads to a more intricate state of CuPc, because the spectrum contains a band with a maximum at *ca.* 730 nm, typical of the β-form.[13] When [CuPc] is increased to $5 \cdot 10^{-2}$ mol L^{-1}, the band for the β-form becomes weaker and merges with the broad band related to the χ-form (see Fig. 1, curve *2*). The spectrum of the LB film does not exhibit the band corresponding to the β-form (see Fig. 1, curve *3*).

The results of a gas-chromatographic study are presented as relationships between the reduced partition coefficients ($K_R/K_R{}^0 - 1$) and the CuPc concentration in squalane (Fig. 2).

The weakest interaction was found between CuPc and sulfur dioxide (see Fig. 2, *e*), where the ($K_R/K_R{}^0 - 1$) values are close to zero over a broad range of CuPc concentrations and temperatures. In the case of ammonia and *tert*-butylamine (see Fig. 2, *d* and *c*), the ($K_R/K_R{}^0 - 1$) constant grows jumpwise in the region of [CuPc] ≈ $3 \cdot 10^{-2}$ mol L^{-1}. The patterns of dependences typical of sorption of hydrocarbons or pyridine[14] are observed only for trimethylamine (see Fig. 2, *a*). In the case of dimethyl-

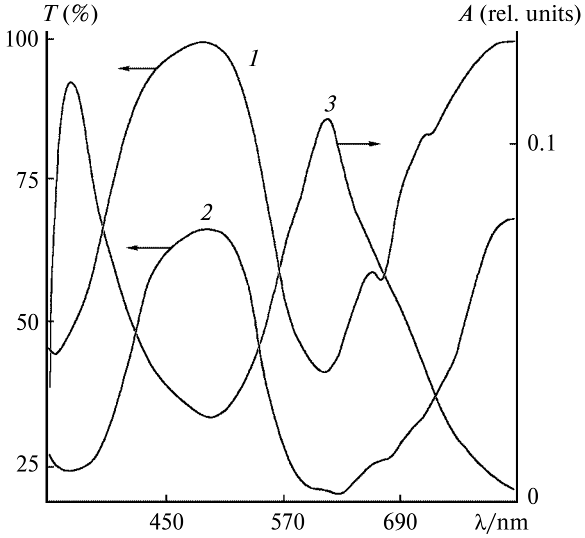

Fig. 1. UV-Vis spectra of diffuse reflection of the liquid-phase CuPc—squalane sorbent at [CuPc] = $3.5 \cdot 10^{-2}$ (*1*) and $5.0 \cdot 10^{-2}$ mol L^{-1} (*2*) and UV-Vis spectrum of the CuPc LB film (*3*). (*T* is transmission, *A* is optical density.)

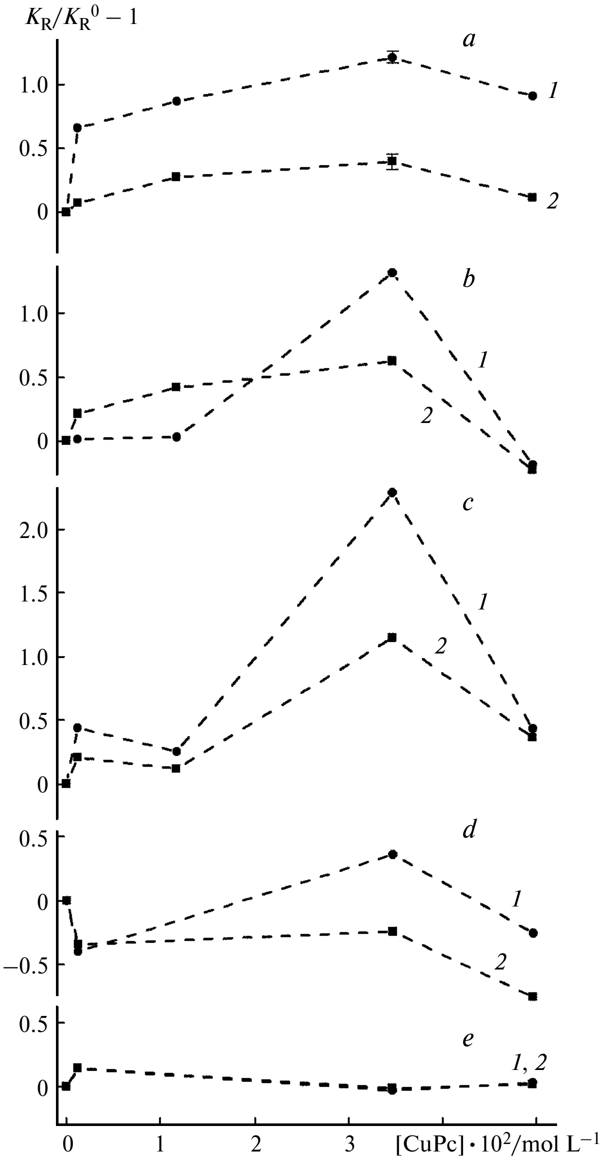

Fig. 2. Reduced partition coefficients of Me_3N (*a*), Me_2NH (*b*), Bu^tNH_2 (*c*), NH_3 (*d*) and SO_2 (*e*) *vs.* CuPc concentration in squalane at 80 (*1*) and 120 °C (*2*).

amine (see Fig. 2, *b*), the dependence of $(K_R/K_R^0 - 1)$ on [CuPc] at 80 °C is described by a curve with a maximum whose height decreases at high temperatures. The K_R values decrease in the sequence: *tert*-butylamine > dimethylamine > trimethylamine > ammonia.

The results obtained by chromatography can be interpreted in the following way. The Lewis acidity of the CuPc molecule is insignificant; therefore, CuPc does not coordinate amines. Hence, the interaction between CuPc molecules and organic bases can be either a dipole type interaction involving the Cu atom or a hydrophobic interaction with the phthalocyanine macrocycle. In the [CuPc] ≤ $1 \cdot 10^{-3}$ mol L^{-1} region, the molecular form predominates for CuPc and sorption is associated predominantly with dipole forces. This is indicated by the value $(K_R/K_R^0 - 1) > 0$ for highly polar SO_2.

When [CuPc] increases to $1 \cdot 10^{-2}$ mol L^{-1}, small χ-type nanoaggregates are formed in the SLP; they have low polarity and are capable of hydrophobic interactions. Therefore, in the case of nitrogen bases not liable to hydrophobic interactions (ammonia, *tert*-butylamine), the $(K_R/K_R^0 - 1)$ value somewhat decreases with an increase in the CuPc concentration from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ mol L^{-1}. In the case of relatively low-polar trimethylamine, the variation of the $(K_R/K_R^0 - 1)$ value following the increase in the CuPc concentration is described by smooth curves. The mechanism of the interaction between dimethylamine and χ-type nanoaggregates (see Fig. 2, *b*) depends on the temperature.

As [CuPc] increases to $3 \cdot 10^{-2}$ mol L^{-1}, active β-type nanoaggregates appear in the SLP. This sharply enhances sorption of nitrogen bases, first of all, *tert*-butylamine. At high concentrations of CuPc, large χ-type nanoaggregates, inert with respect to sorbates of any chemical nature, apparently predominate in solution.

The sorption of hydrogen sulfide is not fully reversible even at the highest temperatures of the chromatographic experiment: the chromatogram exhibits peaks with a strongly extended rear corresponding to short retention times; an increase in the column temperature after emergence of the chromatographic peak is accompanied by emission of hydrogen sulfide. Hence, the first portions of hydrogen sulfide injected into the column modify the packing, and the peaks observed at the outlet characterize sorption on the passivated SLP. This proves chemisorption of hydrogen sulfide on the active sites of the CuPc—squalane liquid-phase system, whose number is limited.

After absorption of hydrogen sulfide, the color of the packing turns from light-blue to gray-green along the whole length of the column. As this takes place, the band with a maximum at 730 nm disappears from the UV-Vis spectrum of the packing (Fig. 3, curve *1*), being replaced by structureless absorption in the region of 400—500 nm. This resembles the spectroscopic consequences following the formation of the Lewis axial complexes of phthalocyanines, namely, the appearance of a weak band at 450—500 nm caused by charge transfer from the macrocycle to the metal.[18] Sorption of hydrogen sulfide induces irreversible changes in the CuPc—squalane system. After the packing has been kept in the open air for many days, the absorption at *ca.* 400—500 nm does not vanish completely (*cf.* Fig. 1, curve *1* and Fig. 3, curve *2*). This is also accompanied by a change in the ratio of intensities of the peaks of supramolecular forms, indicative of the structural rearrangement of CuPc nanoaggregates along the χ → β route.

This situation differs, in principle, from that observed upon sorption of nitrogen dioxide, which reacts with

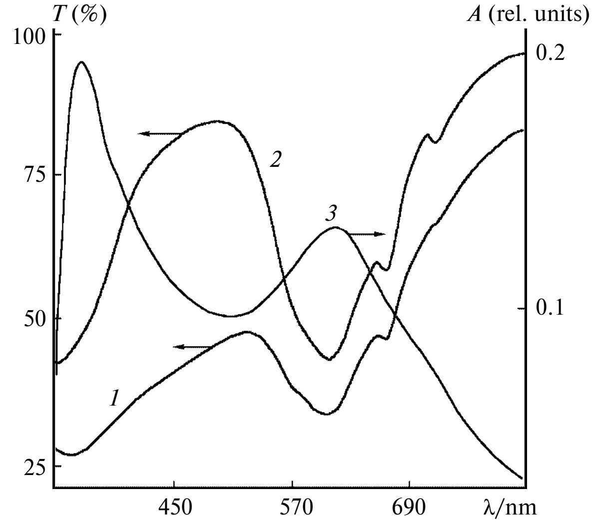

Fig. 3. UV-Vis spectra of diffuse reflection of the liquid-phase CuPc—squalane sorbent at [CuPc] = $3.5 \cdot 10^{-2}$ mol L^{-1} under hydrogen sulfide atmosphere (*1*) and after sorbent regeneration for 7 days (*2*) and UV-Vis spectrum of the CuPc LB film under hydrogen sulfide atmosphere (*3*). (*T* is transmission, *A* is optical density.)

phthalocyanines to form radical ion species.[19,20] Nitrogen dioxide cannot be detected at the outlet of the column, as it is bound entirely by CuPc. In this case, the packing is clearly separated into two zones, crimson- and blue-colored ones. Nevertheless, the packing saturated with nitrogen dioxide is fully recovered on keeping in the open air for 48 h.

No charge transfer interaction between CuPc and hydrogen sulfide can be detected in either highly dilute solutions or in the crystalline state of phthalocyanine. The saturation with hydrogen sulfide of a hexane solution containing 10^{-6}—10^{-5} mol L^{-1} of CuPc entails slight spectral changes similar to those brought about by aggregation of phthalocyanines in solution.[21,22] Treatment of the LB film of CuPc with hydrogen sulfide results in a change in the intensity ratio of the long-wavelength band and the Soret band (see Fig. 3, curve *3*), which may be indicative of enhanced interaction between the nanoaggregates not acompanied by a change in their structures. In addition, as shown by microgravimetry,[4] MPc films sorb hydrogen sulfide less efficiently than they sorb ammonia.

Thus, the specific interaction of CuPc with hydrogen sulfide proceeds exclusively at the supramolecular level with participation of β-type CuPc nanoaggregates. Since the values of both Drago—Wayland parameters are lower for thioethers than for alkylamines,[23] this interaction does not resemble the axial coordination of bases by the phthalocyanine Cu atom. Most likely, the hydrogen sulfide molecule interacts simultaneously with two nanoaggregates, giving rise to a stable intercalate.

Copper phthalocyanine films with the β-type structure can be recommended as sorbents for selective binding of primary and secondary amines in the presence of tertiary amines. Usually, these adsorbents are employed only to determine either the total amount of dimethyl- and trimethylamines[6] or only trimethylamine[7] in air, the reversibility of the sensor effect being relatively low.[7] The results of this study confirm the conclusion[5] that copper phthalocyanine films are of little value for determining the content of ammonia in air.

Copper phthalocyanine films are of interest as selective sorbents for hydrogen sulfide. The ability of β-type nanoaggregates to bind hydrogen sulfide more efficiently than strong organic bases can be utilized in the design of galvanic hydrogen sulfide sensors operating in aqueous media of a complex composition[8] and instruments for determining the quality of fish food.[9]

This work was financially supported by the Commission of the Russian Academy of Sciences for Young Scientists and by the Russian Federation Ministry of Education (Scientific Program 015 "Universities of Russia", Project No. UR.01.01.010, 2002).

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Received May 23, 2002;
in revised form December 15, 2002