



Vapour pressure of tetra-*tert*-butyl substituted phthalocyanines

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ABSTRACT

In this work, the results of mass spectrometric studies of the composition of gaseous phase under solid compounds of tetra-*tert*-butyl substituted phthalocyanines $\text{MPC}(\text{t-Bu})_4$, with $\text{M} = \text{Cu}(\text{II}), \text{VO}$ are presented. The vapour pressure of this phthalocyanine is determined as a function of temperature by the Knudsen effusion method, in which the rate of effusion of the equilibrium vapour through a small orifice is measured. It is shown that these tetra-*tert*-butyl-phthalocyanines exhibit higher volatility than their unsubstituted analogues. Such data are needed in order to improve the operating conditions of the growth of thin films by OMBD. The investigation of structural features of $\text{MPC}(\text{t-Bu})_4$ films was carried out using UV–vis spectral and XRD data.

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1. Introduction

Phthalocyanines are among the most important fine chemicals in industry and are utilized in many technological applications such as sensors, organic semiconductors, pigments, optoelectronic devices, solar cells, catalysis, nonlinear optics and nanomaterials [1,2]. In order to optimise their potential utility for optical or electronic device applications, it is necessary to obtain uniform films of these compounds with easily controllable architecture and ordering. The choice of film deposition method depends on the phthalocyanine properties, and thin films of unsubstituted phthalocyanines are usually obtained by vacuum thermal evaporation or organic molecular beam deposition (OMBD) technique [3].

The introduction of peripheral substituents in the metallophthalocyanine molecule, i.e. *tert*-butyl analogues, provides better solubility and extends the potential applications of these macromolecules. The *tert*-butyl substituted phthalocyanines are characterized by both, high solubility in organic solvents and good volatility in vacuum, and they were shown to be good candidates for preparation of thin films not only by “wet” procedures [4–9] but also by vacuum thermal evaporation.

There are some examples of deposition of tetra-*tert*-butyl metal phthalocyanine films by thermal evaporation in literature. The deposition of tetra-*tert*-butyl copper phthalocyanine films was carried out at base pressure of 3×10^{-5} Torr onto substrates

kept at room temperature [10], and the effects of heat treatment on films' characteristics and their gas sensing properties were studied. Using scanning tunneling microscopy/spectroscopy (STM/STS) the room temperature growth under ultra-high-vacuum conditions and the ordering of copper(II)2,9,16,23-tetra-*tert*-butyl-phthalocyanine surface have also been investigated [11]. In Ref. [12], copper tetra-*tert*-butyl-phthalocyanine was vacuum deposited onto substrates of hydrophilic glass, hydrophobic silanized-glass, and onto glass slides pre-coated with one layer of $\text{CuPc}(\text{t-Bu})_4$ Langmuir–Blodgett film. The effects of the substrate surface treatment on the growth behavior and characteristics of $\text{CuPc}(\text{t-Bu})_4$ films were studied by atomic force microscopy as well as XRD and dynamic contact angle analyzer.

In order to develop the regimes of thermal evaporation correctly it is found necessary to measure the vapour pressure of these phthalocyanines as a function of a temperature by the Knudsen effusion method. On the basis of these data the intensities of molecular beam and the rate of film growth are calculated, and the conditions of deposition of polycrystalline phthalocyanine films are optimised.

The investigation of CuPc and chlorinated CuPc in the gaseous phase by mass spectrometry has been carried out in Refs. [13–15]. Mass spectra for $\text{PcM}^{\text{III}}\text{X}$ ($\text{M} = \text{Al}, \text{In}, \text{Y}$; $\text{X} = \text{Cl}, \text{Br}$) and $\text{PcM}^{\text{V}}\text{X}_3$ ($\text{M} = \text{Ta}, \text{Nb}$; $\text{X} = \text{Cl}, \text{Br}$) have been reported in Ref. [16]. The authors of Ref. [17] used mass spectra for the identification of aluminum phthalocyanines. Using the effusion method, the vapour pressure of copper phthalocyanine in the temperature range from 384 to 449 °C was found 30 years ago by Curry and Shaw [18]. Vapour pressures of cobalt and tin phthalocyanines and some substituted free phthalocyanines have been measured by the effusion technique [19], and

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heats and entropies of sublimation were obtained. The evaporation rate and saturated vapour pressure for series of metal phthalocyanines such as CuPc, NiPc, PbPc and TiOPc have been evaluated by thermogravimetry in vacuum by Yase et al. [20].

While the saturated vapor pressure of some unsubstituted phthalocyanines have been studied, the data on investigation of the behavior of substituted phthalocyanines in the gas phase are practically absent in the literature. The vapour pressure of two halogen-substituted phthalocyanines, hexadecachloro- and hexadecabromo-phthalocyanines (H_2PcCl_{16} and H_2PcBr_{16}) were studied [19]. Mass spectrometric studies of the composition of the gaseous phase and the measurements of temperature dependence of the saturated vapour pressure of hexadecafluorinated phthalocyanines of copper, zink and vanadyl were performed by the authors of Ref. [21].

In this work, the results of mass spectrometric studies of the composition of gaseous phase under solid compounds of tetra-*tert*-butyl substituted phthalocyanines $MPc(t-Bu)_4$, with $M=Cu(II)$, or VO are presented. The vapour pressure of these phthalocyanines is determined as a function of temperature by the Knudsen effusion method, in which the rate of effusion of the equilibrium vapour through a small orifice is measured. Such data are needed in order to improve the operating conditions of the growth of thin films by OMBD.

2. Experimental details

The 2,9,16,23-tetra-*tert*-butyl-phthalocyanine $CuPc(t-Bu)_4$ was purchased from Aldrich Chemical Co. (ID number 423165, purity >97%), and was purified by sublimation in vacuum gradient heater at residual pressure of 5×10^{-5} Torr.

$VOPc(t-Bu)_4$ was synthesized by heating a 4:1 mixture of sublimed 4-*tert*-butyl-1,2-dinitrile (Aldrich) and V_2O_5 powder to 220 °C in a vacuum-sealed (10^{-4} Torr) glass tube. The tube was then opened and the product was purified by gradient sublimation at 400 °C under vacuum of about 5×10^{-5} Torr. The resulting purple powder was identified as vanadyl tetra-*tert*-butyl-phthalocyanine (Found: C, 71.69; N, 13.98; H, 5.87; Calc. C, 71.64; N, 13.93; H, 5.97). The yield of the product after sublimation was 15%. Four peripherally substituted isomers of $VOPc(t-Bu)_4$ molecules, which come from two possible substituting locations of each *tert*-Bu group were obtained during the synthesis. Separation of the isomers was not carried out.

The composition of phthalocyanines vapour was investigated by mass spectrometry technique in the temperature range up to 600 °C. Mass spectra were obtained by means of MKH-1310 mass spectrometers. The molecules effusing from the cell were ionized by means of electrons of 35 eV energy. The evaporation temperature was increased by a step of 20–30 °C. The entire spectrum to 1000 mass units was recorded at each temperature. Weight of investigated samples was about 2×10^{-3} g.

The vapour pressures of these phthalocyanines were determined as a function of temperature by the Knudsen effusion method by means of MI-1201 mass spectrometer [21–23]. The Knudsen cells of 0.70 cm inner diameter and depth were constructed from molybdenum and quartz. The diameters of the orifice were 0.020, 0.025, 0.030 cm and the channel length was 0.020 cm. The ratio of evaporation area to the area of the orifice was about

1000. The Clausing factor was considered for every Knudsen cell according to the cell's size parameters (0.3946, 0.4632, 0.6240 for 0.020, 0.025, 0.030 cm of orifice's diameter, respectively) [22]. Powder samples of 2 mg measured with accuracy $\pm 5 \times 10^{-5}$ g were set inside the cell. The temperature of the effusion cell was increased by a step of 5–10 °C and measured by a calibrated Pt/PtRh 10% thermocouple with absolute accuracy of ± 2 °C. The experimental error of pressure measurements was 10%.

Thin films of $CuPc(t-Bu)_4$ and $VOPc(t-Bu)_4$ were obtained by OMBD technique using the "VUP-5M" installation. The evaporation was carried out at a residual pressure of 10^{-5} Torr with the deposition rate of 0.6 nm s^{-1} . The evaporation temperature of phthalocyanines, chosen on the basis of temperature dependence of saturated vapour pressure, was 420 °C for $CuPc(t-Bu)_4$ and 400 °C for $VOPc(t-Bu)_4$. Silicon and quartz plates were used as substrates and were held at room temperature during film deposition.

UV-vis spectra of the solutions and films on quartz substrates were recorded with a UV-vis-NIR scanning spectrophotometer (UV-VIS-3101PC «Shimadzu») in the range from 400 to 900 nm.

X-ray diffraction (XRD) measurements of $VOPc(t-Bu)_4$ films were performed using of DRON-3M diffractometer with $Cu K\alpha$ irradiation.

3. Results

3.1. Mass spectrometric studies of phthalocyanines

The mass spectra confirm the molecular formulas of phthalocyanines, because ions with appropriate parent molecular weights are observed ($CuPc(t-Bu)_4^+$ ($m/e=800$), and $VOPc(t-Bu)_4^+$ ($m/e=804$)). These ions are accompanied by the corresponding doubly charged ions. The data of high thermal mass spectrometry show that tetra-*tert*-butyl substituted phthalocyanines sublime without thermal decomposition until 600 °C, as is also the case with other phthalocyanines [21,24].

The analysis of the mass spectra shows that the investigated $MPc(t-Bu)_4$ phthalocyanines sublime in the form of monomers. This points to monomolecular sublimation process and comparatively weak associative intermolecular interaction in the crystal phase. These data play important role in the interpretation of results of the measurement of temperature dependence of saturated vapour pressure.

3.2. Vapour pressure measurements

The vapour pressures of these phthalocyanines were determined as a function of temperature by the Knudsen effusion method. The principle of this technique was extensively described in the literature [23–27].

It is well known that the dependence of vapour pressure on temperature is expressed by the Clapeyron–Clausius equation as

$$\log P(\text{atm}) = -\frac{A}{T} + B, \quad (1)$$

where $A = \Delta H_T/R$ and $B = \Delta S^0_T/R$ [17–18] and ΔH_T is enthalpy, ΔS^0_T is entropy of vaporization at the mean temperatures T , and R is ideal gas constant. The results of vapour pressure measurement are plotted in Fig. 1. Values of the constants A and B correspond-

Table 1

Values of constants A and B corresponding to the equation $\log P(\text{atm}) = B - A/T$, the enthalpies and entropies of sublimation.

Compound	A	B	ΔH_T , kcal/mol	ΔS^0_T , cal/mol K	T , °C	Reference
CuPc	12111	12.47	55.4 ± 0.5	57.1 ± 0.7	345–440	[15]
$CuPc(t-Bu)_4$	9697	9.29	44.4 ± 1.5	42.5 ± 2.3	310–440	This work
VOPc	10164	7.80	46.5 ± 0.7	35.7 ± 1.2	305–400	[16]
$VOPc(t-Bu)_4$	9378	9.80	42.9 ± 1.8	44.8 ± 3.0	315–440	This work

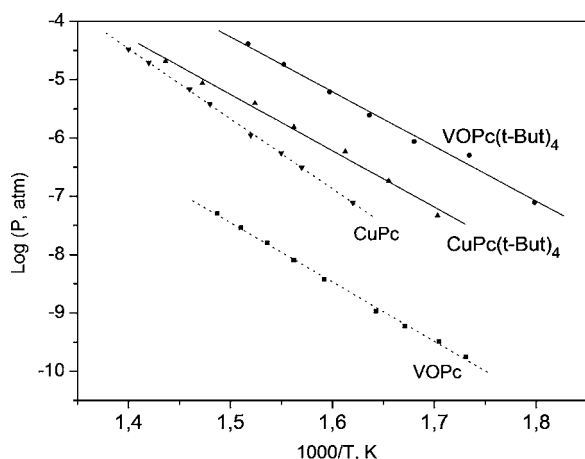


Fig. 1. Temperature dependence of the saturated vapour pressure of tetra-*tert*-butyl-phthalocyanines MPC(*t*-Bu)₄, M=Cu, VO and their unsubstituted analogues.

ing to Eq. (1) as obtained from the least square fitting of measured data in Fig. 1, together with the enthalpies and entropies of sublimation are presented in Table 1. The meanings of phthalocyanines' vapour pressure are presented in Table 2. The obtained data are entirely new, as references devoted to the investigation of thermal behaviour in the gaseous phase and vapour pressure data are available only for a limited number of phthalocyanines [18–21,24].

It is interesting to compare MPC(*t*-Bu)₄ vapour pressure with the analogous results obtained early for the unsubstituted β -CuPc and VOPc [21,24]. These data are included in Fig. 1 for comparison. It is clearly shown that MPC(*t*-Bu)₄ phthalocyanines exhibit higher volatility than its unsubstituted analogues. *Tert*-butyl substitutes are very bulky; they can prevent coplanar π - π -interaction between phthalocyanine molecules and have influence on crystalline polymorphic state of the metal phthalocyanine molecules. Analysis of X-ray data of ZnPc(*t*-Bu)₄ shows that four *tert*-butyl groups have influence on the distance between the phthalocyanine molecules within one stack and basic period [28]. This distance for the β -polymorph of ZnPc(*t*-Bu)₄ (5.27 Å) [28] is larger than that for the ZnPc (4.85 Å) [29].

The energy of intermolecular interaction is characterized by the enthalpy of sublimation. CuPc(*t*-Bu)₄ and VOPc(*t*-Bu)₄ phthalocyanines have lower values of the enthalpy of sublimation in comparison with their unsubstituted analogues (Table 1).

3.3. Investigation of the MPC(*t*-Bu)₄ films

Comparison of intermolecular interactions in the unit cell of solid phthalocyanines [30,31] can be made on the basis of analysis of the electron absorption spectra using exciton model described by Kasha et al. [32] for molecular crystals of aromatic compounds.

The films of CuPc(*t*-Bu)₄ and VOPc(*t*-Bu)₄ were both produced at deposition rate of 0.6 nm s⁻¹ onto the substrates kept at room

Table 2
Vapour pressure of copper(II)tetra-*tert*-butyl-phthalocyanine and of vanadyl(IV)tetra-*tert*-butyl-phthalocyanine by Knudsen effusion method.

	CuPc(<i>t</i> -Bu) ₄		VOPc(<i>t</i> -Bu) ₄	
	T, K	Log P, atm	T, K	Log P, atm
1	587	-7.33023	556	-7.10669
2	604	-6.73805	576	-6.29589
3	620	-6.23542	595	-6.06294
4	640	-5.81557	611	-5.60897
5	656	-5.40366	626	-5.20964
6	679	-5.06417	644	-4.73936
7	696	-4.68677	659	-4.3861

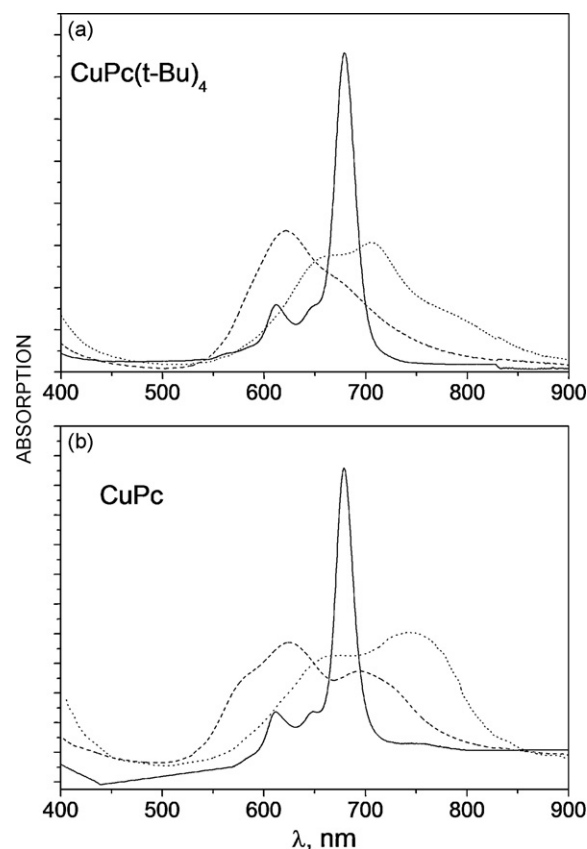


Fig. 2. Optical absorption spectra of copper(II)tetra-*tert*-butyl-phthalocyanine CuPc(*t*-Bu)₄ (a) and copper(II)phthalocyanine CuPc (b) solutions (solid lines), films on quartz substrate before (dashed lines) and films after annealing in vacuum at 220 °C for 5 h (dotted lines).

temperature. This regime is very close to the conditions reported in literature [33–35] for unsubstituted and fluorosubstituted copper and vanadyl phthalocyanines.

Absorption spectra of CuPc(*t*-Bu)₄ and VOPc(*t*-Bu)₄ film on quartz substrates are given in Figs. 2a and 3a, respectively. The spectra of unsubstituted CuPc and VOPc are also included for comparison (Figs. 2b and 3b). The spectrum of CuPc film before annealing (dashed line) corresponds to the α -modification of copper phthalocyanine [36] (Fig. 2b). It was shown earlier that different crystal structures were observed in CuPc films [36–38]. A transformation of the α -modification to the monoclinic structure (β -phase) takes place after annealing above 150 °C (Fig. 2).

The absorption spectrum of CuPc(*t*-Bu)₄ film deposited at the same conditions gives a unique single peak at 622 nm for the Q-band with a shoulder at 680 nm (Fig. 2a, dashed line) which coincides with the maximum of the Q-band in the solution spectrum (Fig. 2a, solid line). This spectrum appears to correspond to the film containing a mixture of crystalline and amorphous phases, which is also confirmed by the data of X-ray phase analysis.

It is necessary to mention that in our investigations of phthalocyanines vapour pressure we always use thermodynamically stable crystal modifications of phthalocyanines (β -CuPc and φ_{II} -VOPc) because the phase transition was shown in Refs. [37,39] to proceed during vapour pressure measurements. Stable crystal modifications may be obtained by sublimation of crude complexes in vacuum [24]. The CuPc(*t*-Bu)₄ and VOPc(*t*-Bu)₄ powders were sublimed at similar experimental conditions. The crystal structure the MPC(*t*-Bu)₄ powders is similar to that of their films after annealing because their XRD patterns and the absorption spectra are practically the same as in the case CuPcF₁₆ and VOPcF₁₆ films [21,33].

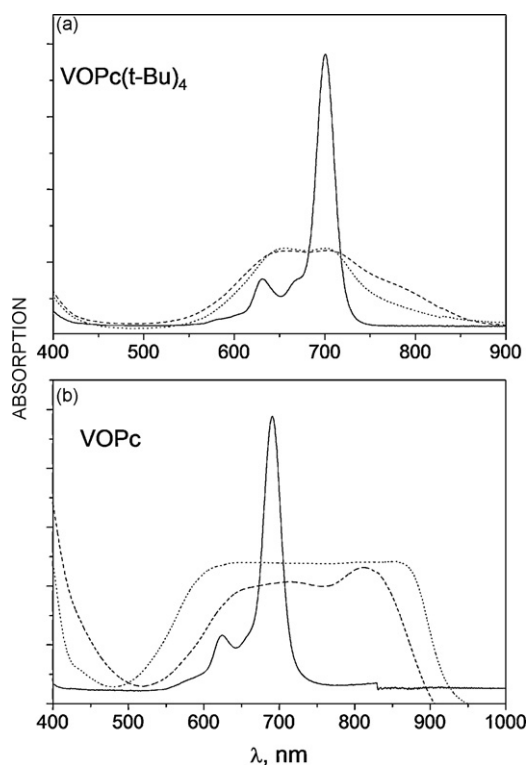


Fig. 3. Optical absorption spectra of vanadyl(IV)tetra-*tert*-butyl-phthalocyanine VOPc(*t*-Bu)₄ (a) and vanadyl(IV)phthalocyanine VOPc (b) solutions (solid lines), films on quartz substrate before (dashed lines) and films after annealing in vacuum at 220 °C for 5 h (dotted lines).

The absorption spectrum of the CuPc(*t*-Bu)₄ film annealed at 220 °C for 5 h in vacuum ($\sim 10^{-4}$ Torr) is presented in Fig. 2a (dotted line). The spectrum of annealed CuPc(*t*-Bu)₄ film exhibits characteristic splitting of Q-band on two separated peaks (Q_x and Q_y are at 657 and 707 nm, respectively) which is known as Davydov splitting [40]. Following the model of Kasha et al. [32] the larger splitting energy points towards a quite stronger interaction between adjacent molecules in the unit cell of the molecular crystal. In the film of β -modification of CuPc film we observe higher value of the Q-band splitting (659 and 745 nm). This fact allows us to suppose that β -CuPc have stronger interaction between adjacent molecules in the unit cell in comparison to tetra-*tert*-butyl copper phthalocyanine.

The absorption spectrum of VOPc(*t*-Bu)₄ film deposited on quartz substrate gives two peaks at 654 and 706 nm for the Q-band with a wide shoulder at about 780 nm (Fig. 3a, dashed line). After annealing of this film in vacuum ($\sim 10^{-4}$ Torr) at 220 °C for 5 h we observed some changing in spectrum view. The band in the absorption spectrum (Fig. 3a, dotted line) becomes narrower with Q_x and Q_y components at 658 and 702 nm, respectively, and the intensity of shoulder at 780 nm decreases significantly.

The value of splitting of the Q-band is much higher in the spectrum of the unsubstituted VOPc film after annealing at the same conditions (Q_x and Q_y components are at 664 and 813 nm, respectively), this fact is the evidence of weaker interactions between the molecules in the unit cell and of increasing volatility of tetra-*tert*-butyl vanadyl phthalocyanine in comparison to the unsubstituted vanadyl phthalocyanine.

4. Conclusions

The vapour pressure of tetra-*tert*-butyl-phthalocyanines MPc(*t*-Bu)₄, M = Cu, VO, was determined as a function of temperature

by the Knudsen effusion method. It was shown that these tetra-*tert*-butyl-phthalocyanines exhibit higher volatility than their unsubstituted analogues. A difference in MPc and MPc(*t*-Bu)₄ volatility appears to be explained by different intermolecular bonding in the solids. The bulky *tert*-butyl substituents prevent coplanar π - π -interaction between phthalocyanine molecules, leading to the weakening of intermolecular interaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.01.019.

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