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Some trends in sorption processes on thin phthalocyanine films

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The kinetic processes of adsorption of NO_2 on thin Cl_4PcCo films were studied, and their correlation with the film structure was established.

Thin films of metal phthalocyanines (PcM) have been suggested as possible sensitive layers of gas sensors, because they exhibit changes in conductivity and optical spectra upon the action of some toxic gases.[1–13] Since the processes studied are, in principle, physicochemical, they can be studied using the usual models and methods, *e.g.*, kinetic ones.[1–3] The quartz crystal microbalance (QCM) technique is widely used for studying adsorption phenomena[4–7] and, in addition, finds application in the study of chemical sensors.[6,7] Since in this case the procedure for the deposition of the sensitive PcM layer is the same as that required for electrophysical measurements (high-vacuum sublimation), we always[3,8–10] placed QCM substrates in a measuring cell along with the usual substrate for measuring the conductivity upon deposition and a gas inlet. This allowed us to obtain the important information presented in this work.

All procedures have been described previously.[3,8–10] A ChZ-38 (CIS) storage electronic-counter frequency meter was used for the QCM measurements. Cobalt(2+) 4,4′,4″,4‴-tetrachlorophthalocyanine was chosen as a scarcely studied material (partially described in refs. 3 and 8) with interesting properties. The kinetic curves (time dependencies of the number of sorbed gas molecules N at room temperature) are presented in Figure 1. They are related to three Cl_4PcCo films, which differ in thickness as measured by interferometry for the film already prepared and by the QCM method during deposition.[5] The data presented in Figure 1*a* were fitted to three well known equations, which are frequently used in the description of the dynamics of gas–solid interactions.[14] The first of them, $N(t) = \{N^*/(1 + b/P)\}[1 - \exp(at)]$, where a and b are coefficients with certain physical meanings and N is the total number of adsorbed centres, is a consequence of the Langmuir theory; the second equation $N(t) = (1/a)\ln\{abt + 1\}$ is the Elovich kinetic equation,[1] and the third, $N(t) = bt^a$, is an empirical formula, the so-called Banham's law.[14] Application of these formulae is restricted by either the degree of filling or the class of the systems described; however, all of them can be applied to the sorption of NO_2 on thin PcM films (see Figure 1*b*). The relative error (in %) of determination of the power coefficient a in these three equations was chosen as a convergence criterion, because it plays the most significant role.[14] The results are presented in Table 1, and the applicability of the models for a film 155 nm thick is illustrated in Figure 1*b*.

As seen in Table 1, the Banham formula describes most successfully the sorption kinetics of the objects studied, while the Elovich equation[1] recommended previously occupies an intermediate position. Banham's coefficient a increases as the thickness increases: under equivalent conditions, the sorption rate (the number of molecules bound per unit time) is higher for the thick film (Figure 1*a*), which is probably explained by its more friable, porous structure.[13] It should be noted that the value of the error for the Banham equation increases as the thickness increases. Conversely, the Langmuir equation, which is, generally speaking, poorly applicable to our systems, becomes more successful for thicker films (Table 1). Application of the Langmuir equation is based on the assumption that the energy of the adsorption surface is uniform.[14,16] Thus, the adsorption centre distribution over the thick film becomes more uniform.

The great significance of film thickness in the range studied has been mentioned by many authors.[1–3,5,12,13,15] For example, Hamann[15a] showed that sublimated polycrystalline PcCu layers thinner than 90 nm have the 'lying b-axes' type orientation, while layers thicker than 90 nm have the 'standing b-axes' orientation relative to a substrate. It has been established by X-ray diffraction analysis and slow electron diffraction[15b] that PcM films thinner than 30 nm obtained in a Knudsen chamber, have an ordered arrangement of molecular planes, and that disordering of the initial orientation occurs in

Table 1 Relative error (%) for determination of the coefficient a in various kinetic equations, $p(NO_2)$ = 18 Torr.

Film thickness/nm	Kinetic equation				Curve in Figure 1*a*
	Langmuir	Elovich	Banham	where a	
20	14	2.8	1.7	0.11	3
80	12	5.7	1.9	0.32	2
155	7	3.5	2.3	0.56	1

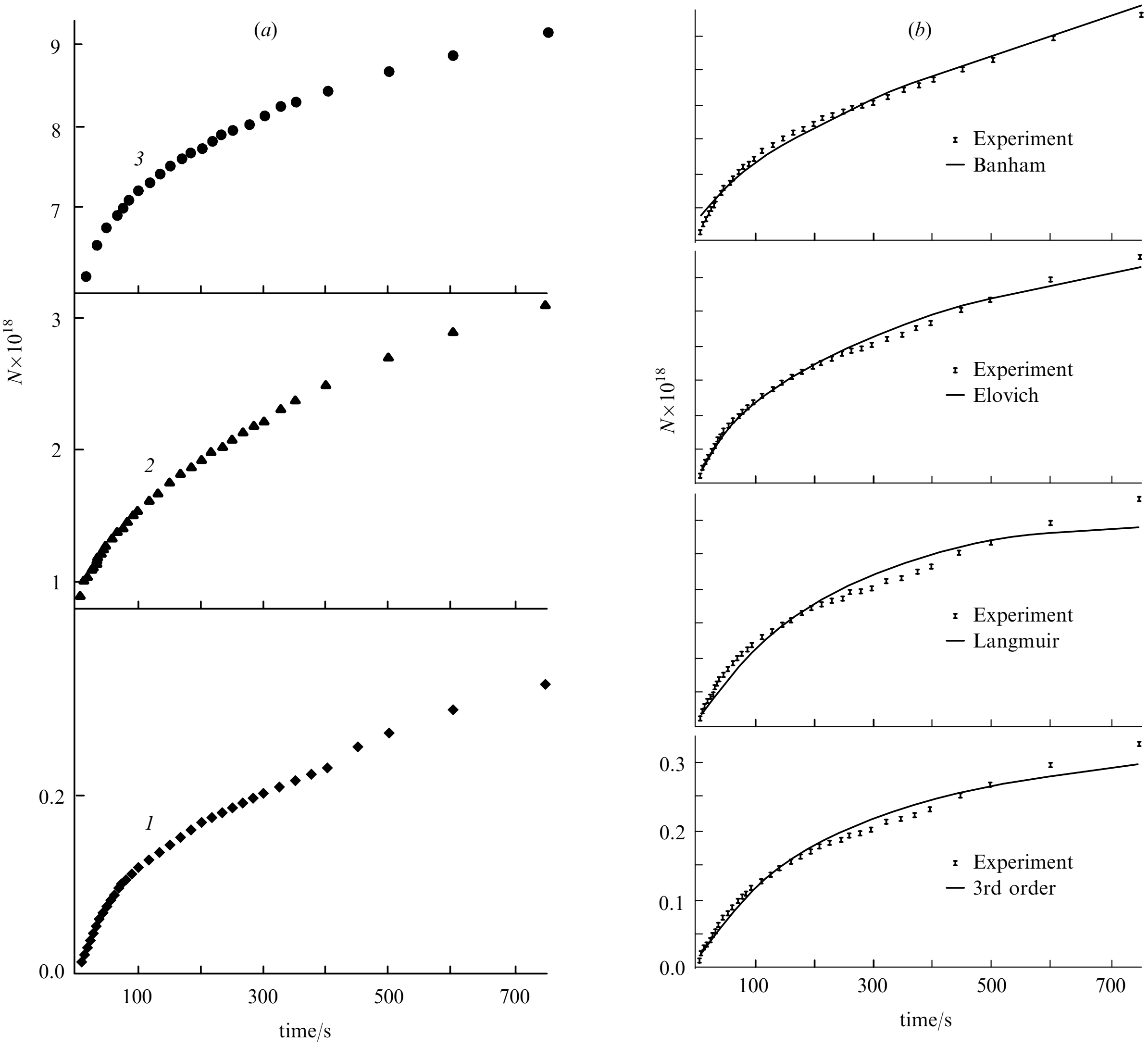

Figure 1 (*a*) Kinetic dependencies of the adsorption of NO_2 on thin Cl_4PcCo films (*1*) 155, (*2*) 80, and (*3*) 20 nm thick. (*b*) Application of various mathematical models to the experimental kinetic results shown in curve 1.

thicker films. It is evident that adsorption centres in the film are reorganized by this type of structural rearrangement: a quasi-amorphous thick film can be more uniform.

As follows from Figure 1*a*, the absolute value of N is higher for the thin film, *i.e.*, at some very short initial time it can provide more initial adsorption positions. At a later time, this ability decreases sharply. This phenomenon can be explained by the fact that the most favourable (low activation energy) adsorption centres are immediately filled, because the energy distribution of adsorption centres is evidently nonuniform. Further sorption occurs more slowly because of its higher activation energy, which is in the denominator of the formula of the reaction rate constant.[16] According to the rate distribution mentioned, all three dependencies in Figure 1*a* should intercept, if another mechanism is not realized at longer times; the abscissa of the interception point is about 2300 s.

Conversely, the '$PcM + NO_2$' type interaction can be considered as a chemical reaction,[2,4,5,12] whose energy effects have been well studied.[2] It is evident that trivial kinetic formulae of reactions of the *n*th order in their initial form cannot be applied to our system. Various cases were analysed, and only once for films 155 nm thick, at the initial region of the plot (Figure 1*b*), was a satisfactory correlation found, and that was with the equation $x = (k' \times t \times \text{const}^2)/(k' \times t \times \text{const} + 1)$, where x is the decrease in the reagent concentration, t is time and k is the rate constant. The equation formally corresponds to the homogeneous process of the '$A + B \longrightarrow$ *products*' type, when the initial concentrations of the reagents are equal.[16] This situation is not realized for our system, and the sole solution can be found in the following way; let N be equal to x, which is valid in general because N is the number of already sorbed (reacted) molecules. Only the equation of the '$2A + B \longrightarrow$ *products*' form can be simplified further, *i.e.*, it is formally the third-order reaction. Applying the Ostwald rule, at the initial reaction times (Figure 1*b*) [A] is still low, [B] can be accepted as considerably higher than [A] and, hence, its change can be neglected and approximated by a constant.[16] Then $dx/d(t) = k[A]^2[B]$ takes the form of $dx/d(t) \gg (A_0 - x)^2 \times k'$. This simple differential equation can be solved to give $k't = x(A_0 - x)$. Taking into account that in our case [B] is related to the Cl_4PcCo film (in fact, the ratio $N/N_{(Cl_4PcCo)}$ for the thick film at the initial reaction times is less than 10^{-2}) and [A] is related to gas molecules, we obtain the desired solution.

Thus, the presumable mechanism of the reaction in our system is the following: $2NO_2 + Cl_4PcCo \longrightarrow$ *products*. It has been suggested previously[4,5] that the interaction of nitrogen dioxide with PcM films results in the formation of mono-π-radical cations of the $[Pc^*M]^+$ type, and the NO_2^- acts as a counterion.[4] We also have previously observed the product $[Cl_4Pc^*Co]^+$ under similar conditions.[3,8] In this case, the determined stoichiometry of the reaction can mean the following: since the probability of oxidation of Cl_4PcCo is lower than that of nonsubstituted PcM due to electron-accepting substituents,[3,9,10] two oxidative molecules per phthalocyanine molecule are required to obtain the $[Cl_4Pc^*Co]^+$ product. The value of the conductivity response is proportional to the number of $[Pc^*M]^+$ formed, which is related to the p-type of gas-induced conductivity.[11] Perhaps this is the reason for the relatively low gas sensitivity found[3,10] for the films of substituted PcM in comparison with the initial complexes.

Of course, these are qualitative models (for example, such processes as $2NO_2 \rightleftharpoons N_2O_4$ were not taken into account[4]). However, we have tried to show that simple sorption measurements can serve as a useful additional method for studying and discussing regularities of the behaviour of gas sensors based on PcM. Similar results are relatively scarce in the literature. For example, one can conclude on the basis of this work that: (i) the kinetics of adsorption of NO_2 on sublimated Cl_4PcCo films obeys Banham's law (which is also valid for the majority of other PcMs[†]), and this fact can be used for the subsequent mathematical description of the dependencies $\sigma = f(N)$, which play an important role in the behaviour of gas sensors; (ii) variation of the film thickness results in considerable changes in the kinetics of the adsorption process: for example, a thicker film possesses a higher sorption activity, but, by contrast, the total number of sorbed gas molecules is lower; and (iii) a possible mechanism of interaction between the PcM film and gas molecules can be suggested on the basis of the kinetic data obtained.

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[†] A detailed comprehensive article on this subject is to be published: G. L. Pakhomov, V. V. Podol'sky, S. A. Anisimov and L. G. Pakhomov, 'Sorption processes on the thin films of some metal phthalocyanines', submitted to *Izv. Akad. Nauk* (*Russ. Chem. Bull.*).

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