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## NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

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# Electrokinetic Properties of Metal Phthalocyanite Nanoparticles

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**Abstract**—The effect of the nature of the metal in metal phthalocyanites on the electrokinetic potential and pH of the isoelectric point (pH(I)) in suspensions of these substances in NaCl solution (0.1 mol/L) is elucidated. The pH(I) values of unmodified MPC increases in a sequence MnPc < CoPc < CuPc ≈ ZnPc on account of the decreasing effective charge of the coordinated metal ion that corresponds to the Irving–Williams series. The impact of the functional group upon heterogeneous modification of MPC nanoparticles is studied, as well. It is established that the modifying group (the oxygenic properties) exerts a stronger influence on (pH(I)) than the metal nature.

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## INTRODUCTION

The efficiency of photodynamic therapy with metal phthalocyanines (MPC) serving as photosensibilizers depends on its electrostatic binding with cell membranes [1–3]. This is, in turn, defined by the charges of the active centers of molecules and/or colloidal particles.

Some reports have been made on the production of metal-composite coatings (CCs) with water-insoluble cobalt (copper) phthalocyanine [4] via electrochemical or chemical methods, as well as applying water-soluble phthalocyanine derivatives, to improve the functional properties of coatings [5, 6]. One model describing the synthesis of CCs [7] is based on the charge,  $\zeta$ -potential, and adsorption ability of dispersed-phase particles.

In [8], the  $\zeta$ -potential values reported for 4-sulphthalocyanine copper in NaNO<sub>3</sub> aqueous solution at pH 6.9 are from –42 to –32 mV, depending on the concentration. Colloidal solutions, such as crown ruthenium phthalocyanine, are found to be unstable, exhibiting self-consistent aggregation upon their storage [9]. The electrochemical properties of metal phthalocyanines in anhydrous media have been investigated in [10].

Reviewing the source literature reveals only a few studies aimed at determining the  $\zeta$ -potential and pH values of the isoelectric point (pH(I)) and zero charges of various phthalocyanine derivatives.

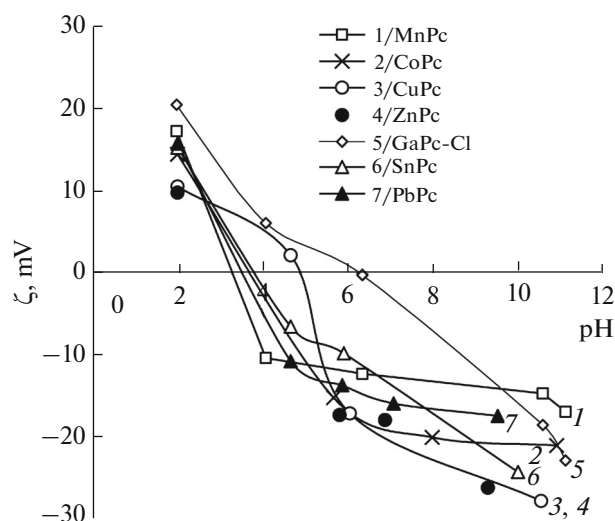
As there are no reported data on the influence of pH medium, nature of phthalocyanine-coordinated metal, and modifying functional groups on the elec-

trokinetic properties of metal phthalocyanines, this work is motivated by the desire to better understand the above effects.

## EXPERIMENTAL

Unsubstantiated phthalocyanines (Pc) of d- and p-elements—Co(II), Zn(II) and Sn(II), Pb(II), respectively—were synthesized according to known techniques [11–13]. The cupreous phthalocyanine complex was presented by a commercial product (Pigment PJSC, Russia) in the form of blue phthalocyanine pigment ( $\beta$ -modification, the average aggregate size is 0.5–1  $\mu$ m). Manganese (II) phthalocyanine and gallium phthalocyanine chloride were produced by Sigma-Aldrich Corp. All MPC were purified with acetone and ethanol extractions in a Soxhlet's apparatus and then dried in vacuum or in air. The CuPc nanoparticle surface was modified by acylation following the Gomberg–Bachman reaction using sulfanyl and 4-aminobenzoic acids and OH-containing modifying agents synthesized on the base of 4-nitrobenzoic acid [14]. These modifying agents enabled us to achieve the surface properties provided by –C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, –C<sub>6</sub>H<sub>4</sub>COOH and –C<sub>6</sub>H<sub>4</sub>CON(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> groups.

The  $\zeta$ -potential was measured via electrophoresis at 25°C on a Malvern Zetasizer Nano Series(ZS) setup (United Kingdom) equipped with the 21CFR part 11 software allowing the analysis of the particle mobility and evaluation of the  $\zeta$ -potential. The particle mobility was determined from scattering of a laser beam at wavelength  $\lambda$  of 633 nm directed to the sample at angle  $\theta = 173^\circ$ . Each sample was subjected to five measure-



**Fig. 1.** The  $\zeta$ -potential of 0.1 wt % suspension of unmodified phthalocyaninates of (1) Mn, (2) Co, (3) Cu, (4) Zn, (5) Ga, (6) Sn, and (7) Pb as a function of pH of NaCl solution (0.1 mol/L).

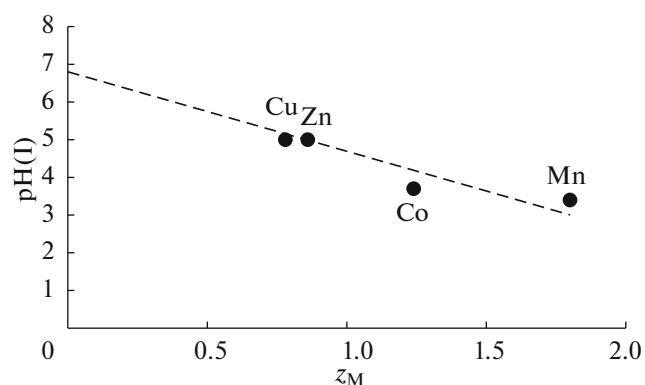
ments of 12–100 primary measurement cycles, and the measurement error was, thus, no worse than  $\pm 1$  mV.

The electrokinetic properties of water-insoluble metal phthalocyaninates were established in 0.1 and 0.005 wt % suspensions in NaCl solution (0.1 mol/L). The prepared suspensions were treated with ultrasound (the ultrasound amplitude was 10 dB, the power was  $\approx 26$  W, and the specific power was  $\approx 375$  W/L).

## RESULTS AND DISCUSSION

As is shown by an example of unmodified metal phthalocyaninates, the  $\zeta$ -pH dependences in NaCl solution (0.1 mol/L) (Fig. 1) intersect the abscissa at pH of 3.4–6.5 (isoelectric point, pH(I)) at the increasing pH.

The studies involving various metal phthalocyaninates (Fig. 1) reveal that there is no clear dependence of the  $\zeta$ -potential on the coordinated metal ion nature in acidic solutions. The coordinated metal ion affects the  $\zeta$ -potential value mainly in the alkaline pH range (Fig. 1). At pH values below 3, the  $\zeta$ -potentials of MPc particles with different natures of coordinated metal ions are as close to each other as possible, enriching  $+15 \pm 5$  mV at pH of 2, which indicates a positively charged internal plane of the double electric layer of particles and adsorption of hydrogen and/or sodium cations onto their surface. The pH(I) values for manganese, tin, lead and cobalt phthalocyaninates were 3.4–4.0; for copper and zinc phthalocyaninates, it was 5.0; and for gallium phthalocyaninate chloride it attained 6.4. At higher pH, the particle surface is recharged and the polarity changes from positive to negative. At pH of 8, the  $\zeta$ -potential is stabilized at a level of from  $-15$  to  $-25$  mV, which is insufficient to



**Fig. 2.** The correlation dependence between pH of the isoelectric point of metal phthalocyaninates in 0.1 wt % suspensions in NaCl solution (0.1 mol/L) and the effective charge of the metal atom in metal phthalocyaninates.

ensure colloidal-system stability on account of the electrostatic forces.

A key characteristic in understanding the physico-chemical properties of compounds, as well as in establishing and interpreting the relation between structure and property is the charge state of atoms in a molecule. The calculated charge states of atoms of *d*-elements in MPc are reported in [15, 16]. It appears that the charge of a central metal atom varies from  $0.78|e|$  to  $1.8|e|$  and decreases in the sequence  $\text{MnPc} > \text{CoPc} > \text{CuPc} \approx \text{ZnPc}$ , coinciding with the Irving–Williams order [17], which is frequently used in the analysis of the properties of coordination compounds [18]. The pH(I) value increases in the series  $\text{MnPc} < \text{CoPc} < \text{CuPc} \approx \text{ZnPc}$ . A comparison of two sequences allows us to affirm that, the lower the effective charge at the coordinated metal atom, the higher the pH(I) values, tending to 7 at  $z_M \rightarrow 0$ , i.e., at the missing charged-molecule centers (Fig. 2).

This effect can be experimentally observed for phthalocyaninates of *p*-elements, such as gallium phthalocyaninate chloride and tin and lead phthalocyaninates. The extracoordinated chlorine ions are expected to decrease the effective gallium charge to quasi-zero values, which results in the experimentally observed pH(I) value of 6.4 (Fig. 1, curve 5). If there are no extracoordinated ligands in MPc (M–Sn, Pb, as representatives of *p*-elements), pH(I) shifts back to the acidic range, attaining values of 3.6–3.8.

The above situation is also typical of metal phthalocyaninates modified with carboxyl groups. In these suspensions (0.005 wt %) the pH(I) values were found to be as follows: for tin PCs, 3.8; for lead PCs, 3.4; for cobalt PCs, 3.2; for zinc PCs, 3.0; and for copper PCs, 2.9. At pH 6, the  $\zeta$ -potential gained in suspensions based on carboxylized copper phthalocyaninate particles is  $-30$  mV, whereas at pH 7 it stabilizes at a level of  $-45$  mV, ensuring suspension stability on account of the electrostatic forces. In alkaline solutions (pH > 8)

the  $\zeta$ -potential shifts to the negative values, while passing from coordinated ions of *p*-elements (Sn, Pb) to *d*-elements (Co, Cu, Zn). For example, at pH 8 for carboxylized copper and tin phthalocyaninates, the  $\zeta$ -potential is, consequently,  $-45$  and  $-21$  mV. Attention is drawn to a quite narrow pH(I) value range with the changing coordinated metal ion nature. Apparently, in this case, the particle surface charge and the pH(I) values have nothing in common with predominant absorption at the active molecule centers, but are favored by partial dissociation of the surface carboxyl groups.

The pH(I) parameter evaluated from the  $\zeta = f(\text{pH})$  dependences in 0.1 wt % suspensions (the dispersion medium was aqueous NaCl solution (0.1 mol/L)) of copper phthalocyaninates modified with various functional groups was found to noticeably depend on the modifying functional group. In a series of the pristine CuPc sample and CuPc modified with  $-\text{C}_6\text{H}_4\text{CON}(\text{C}_2\text{H}_4\text{OH})_2$ ,  $-\text{C}_6\text{H}_4\text{COOH}$ , and  $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$  groups, the pH(I) value naturally shifts toward the acidic range in the sequence of 5, 2.8, 0. This change is sympathetic to a decrease in  $\text{pK}_a$  of such molecules, as ethanol (10 [19]) > benzoic acid (4.2) > benzene sulfonic acid (2.55 [20]), considered as models of the modifying functional fragments at the MPc particles.

The most negative  $\zeta$ -potential value of  $-40$  mV at pH above 6 is established for copper phthalocyaninate, wherein the nanoparticles are modified with carboxyl or sulfo-groups, which provides durable stability of suspensions (more than a month).

## CONCLUSIONS

The pH value of the isoelectric point in unmodified MPc was shown to increase in the sequence  $\text{MnPc} < \text{CoPc} < \text{CuPc} \approx \text{ZnPc}$  on account of the reducing effective charge of coordinated metal ion that coincided with the Irving–Williams order.

A decrease in the effective metal charge to zero is expected to result in pH(I) values close to 7, which has been experimentally grounded by the example of gallium phthalocyaninate chloride possessing pH(I) of 6.4.

In heterogeneously modified MPc nanoparticles, the metal nature plays an important role as well, whereas the acidic properties of the modifying functional group exert a strong influence on pH(I).

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