INVESTIGAÇÃO DA ADSORÇÃO DE UM COPOLÍMERO AMFIPOLAR NA SUPERFÍCIE
HIDROFÓBICA DE NANOPARTICULAS DE FTALOCIANINA DE COBRE

INVESTIGATION OF AN AMPHIPOLAR COPOLYMER ADSORPTION ON THE
HYDROPHOBIC SURFACE OF COPPER PHTHALOCYANINE NANOPARTICLES

ИССЛЕДОВАНИЕ АДсорбции амфиполярного сополимера на
гидрофобной поверхности медных наночастиц фталоцианина

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RESUMO

Foram apresentados os dados sobre as espessuras da camada de polímero adsorvido, as quais foram obtidas para as dispersões de pigmentos de ftalocianina de cobre (CuPc) sob condições de processamento ultrassônico. As camadas mais espessas de adsorção, observadas nos sistemas de ultra-som, confirmam o fato de que a ativação da superfície do pigmento ocorre sob a ação da energia ultrassônica. O curso e a eficiência de adsorção do polímero na superfície do pigmento foram quantificados por medidas eletrocinéticas da amplitude do som (EIAZ). Tornou-se possível obter uma visão mais detalhada das interações pigmento-polímero e do mecanismo de adsorção do copolímero com base nos dados da mobilidade dinâmica, obtidos como resultado de medidas eletrocinéticas da amplitude do som. Para as dispersões aquosas de CuPc, estabilizadas com copolímero de poli(ácido acrílico)-poli(acrilato de isobornila) (PiBA-PAA), foram estabelecidas as concentrações de saturação do surfactante polimérico. Assim, o tratamento ultra-sônico permite obter suspensões pigmentares estáveis e altamente dispersas com uma superfície de pigmento modificada, o que abre novas perspectivas para uma mudança mais efetiva na superfície do pigmento.

Palavras-chave: *adsorção, ultra-som, pigmentos, polímeros.*

ABSTRACT

It was presented the data on the thicknesses of the adsorbed polymer layer, which were obtained for copper phthalocyanine (CuPc) pigment dispersions under ultrasonic processing conditions. The thicker adsorption layers, which are observed in ultrasound systems, confirm the fact that the activation of the surface of the pigment occurs under the action of ultrasonic energy. The course and efficiency of adsorption of the polymer onto the pigment surface were quantified by electrokinetic measurements of the amplitude of sound (EIAZ). It became possible to obtain a more detailed picture of the pigment-polymer interactions and the adsorption mechanism of the copolymer based on the data on the dynamic mobility, obtained as a result of electrokinetic measurements of the amplitude of the sound. For aqueous dispersions of CuPc, stabilized with a copolymer of poly (acrylic acid) -poly (isobornyl acrylate) (PiBA-PAA), it was established the saturation concentrations of polymeric surfactant. Thus, the ultrasonic treatment allows to obtain stable, highly dispersed pigment suspensions with a modified pigment surface, which opens up new prospects for a more effective change in the surface of the pigment.

Keywords: *adsorption, ultrasound, pigments, polymers.*

АННОТАЦИЯ

Приведены данные о толщинах адсорбированного полимерного слоя, которые были полученные для дисперсий пигментов фталоцианина меди (CuPc) в условиях ультразвуковой обработки. Более толстые адсорбционные слои, которые наблюдаются в ультразвуковых системах, подтверждают тот факт, что активация поверхности пигмента происходит под действием ультразвуковой энергии. Ход и эффективность адсорбции полимера на поверхность пигмента были количественно определены электрокинетическими измерениями амплитуды звука (ЭИАЗ). На основе данных о динамической подвижности, полученных в результате электрокинетических измерений амплитуды звука, удалось получить более подробное представление о пигментно-полимерных взаимодействиях и адсорбционном механизме сополимера. Для водных дисперсий CuPc, стабилизированных сополимером поли (акриловая кислота) -поли (изоборнилакрилат) (PiBA-PAA) были установлены концентрации насыщения полимерных поверхностно-активных веществ. Таким образом, ультразвуковая обработка позволяет получать устойчивые высокодисперсные пигментные суспензии с модифицированной поверхностью пигмента, что открывает новые перспективы для более эффективного изменения поверхности пигмента.

Ключевые слова: адсорбция, ультразвук, пигменты, полимеры.

1. INTRODUCTION

In recent years, aqueous colloidal dispersions of pigments have been of increasing interest from both scientific and practical points of view. Aqueous colloidal dispersions of pigments are important, ecologically friendly colloidal systems widely used in polygraphic and paint industries. The pigment particles are usually of 20 – 200 nm diameter and may be quite hydrophobic. In order to achieve a good stabilization in aqueous pigment dispersions, many formulations were proposed (Netz and Andelman, 2003; Bulychev *et al.*, 2004, 2008, 2018f; Zubov *et al.*, 2004; Kirilina *et al.*, 2009; Ioni *et al.*, 2011; Rudnev *et al.*, 2013; Burkhanov *et al.*, 2014; Ivanov *et al.*, 2017). Earlier it was reported on the role of mechanical, e.g., ultrasonic treatment for obtaining highly stable dispersions (Bulychev *et al.*, 2008; Ivanov *et al.*, 2017). It was shown, that using polymer surfactants in combination with mechanical action can significantly improve the quality of dispersed systems. However, specific aspects of the pigment-polymer interaction and structure formation of adsorption layers, especially under mechanical, i.e., ultrasonic action have not yet been studied in detail (Andreev and Gridina, 2016; Andreev and Gridina, 2017).

Electrokinetic sonic amplitude (ESA) measurements have been demonstrated to be a powerful method that could provide the desired information about the process of polymer adsorption (Bulychev *et al.*, 2008) and were employed in this work. Specially synthesized tailor-made PiBA-PAA block copolymers were used as stabilizers of aqueous dispersions of hydrophobic pigment CuPc. The polymer layers created on the particle surfaces in the absence and presence of mechanical (ultrasonic) action

were investigated (Gridina and Andreev, 2018).

2. MATERIALS AND METHODS

As a pigment, β -copper phthalocyanine (β -CuPc, BASF AG, Ludwigshafen) with primary particle size 0.1 μm and breadth of the particle size distribution of 15 nm, was employed as received.

The PiBA-PAA block copolymers of various well-defined structures, molecular weights, and narrow polydispersities, were synthesized by controlled radical polymerization as described (Bulychev *et al.*, 2004). This method enables to synthesize amphiphilic copolymers with a desirable length of hydrophilic and hydrophobic blocks. The copolymers were characterized by size exclusion chromatography.

For the preparation of aqueous pigment dispersions, the pigment was added to distilled water type IV alone or together with the polymer dissolved in THF and dispersing of the pigment was first achieved by means of a laboratory stirrer (700 rpm for 10 min). When ultrasonification was applied, the system was subsequently treated with ultrasound for 2 min with an ultrasonic generator Branson Sonifier B-12 with the actual power of 1.5 W/cm².

The colloidal stabilization of the aqueous dispersions was monitored by sedimentation measurements of 1 % dispersions of CuPc. The pigment-polymer interaction and the polymer adsorption layer formation were investigated by electrokinetic sonic amplitude (ESA) measurements as described elsewhere (Bulychev *et al.*, 2008). The particle size was measured by ESA (Bulychev *et al.*, 2008). ESA

technique has been proven to be a powerful method to obtain insights into adsorption/desorption phenomena (Bulychev *et al.*, 2008; Ivanov *et al.*, 2017). Such information can be derived from the dynamic mobility μD of the dispersed particle as shortly addressed below.

When an alternating electric field is applied to a colloid system, it exerts an electric force on the particles which causes them to move back and forth. It is this backward and forward motion that generates the ESA signal, which in turn provides information about the particle motion and thus on characteristics of the particles itself. In practice, the applied field is measured directly, and the acoustic impedance of the suspension can be determined by measuring the reflection coefficient of a sound wave at the electrode-colloid boundary.

The advantage of reporting electroacoustic data in terms of dynamic mobility μD , i.e., electrophoretic mobility of a particle in an alternating electric field rather than reporting the raw ESA measurement data, is that the dynamic mobility is a property of the suspension: so unlike the ESA it does not depend on the device geometry, on the acoustic properties of the device or on the strength of the applied electric field. With the Accoustosizer 2 instrument (Colloidal Dynamics, Australia), which is applied in the present study, dynamic mobility μD can be determined with an accuracy of $\pm 1\%$.

Standard optical equipment was used for refractive index measurements.

3. RESULTS AND DISCUSSION:

Data reported in the literature (Nikiforov *et al.*, 2016; Asratyan *et al.*, 2018; Averyushkin *et al.*, 2018a, 2018b; Dyakov *et al.*, 2018; Bulychev *et al.*, 2018a, 2018b, 2018c, 2018d, 2018e, 2018f; Kirichenko *et al.*, 2018a, 2018b, 2018c; Krasovskii *et al.*, 2018), showed that mechanical, in particular, ultrasonic treatment of aqueous dispersions of pigments in the presence of polymeric stabilizers leads to a significant enhancement of the stability of these dispersions as compared to dispersions prepared without ultrasonic treatment. It was proven by IR-analysis that the thickness and stability of the polymer adsorption layers were increased and improved by the ultrasonification. Parameters of polymer adsorption layers affected by the ultrasonic treatment were investigated (Bulychev *et al.*, 2008). However, the effect of the ultrasonic

treatment on the pigment-polymer interaction and polymer adsorption, especially for novel tailor-made amphipolar copolymers is still obscure and needs further investigation for the better elucidation of the phenomena observed.

First, sedimentation measurements for CuPc aqueous dispersions stabilized by a series of tailor-made amphipolar copolymers containing PiBA and PAA segments in the presence and absence of ultrasonic treatment have been carried out. These data are presented in Table 1.

First, as one can see from Table 1, all employed copolymers allow obtaining pigment dispersions even in the absence of ultrasonic action while recent data on the application of PMVE containing block copolymers showed the impossibility to obtain dispersions without mechanical treatment (Bulychev *et al.*, 2004). It could be ascribed to that fact that THF used as a polymer solvent in the present study is known to create micelles with water and so provide the transport of a polymer to the pigment surface. Second, it is evident that irrespective of the constitution of the copolymer, the ultrasonification substantially improves the dispersion stability as reflected from the comparison of the sedimentation half times of the non-treated and treated systems. The data also infer that there is an optimal copolymer structure with regard to the block length ratio; this is in accordance with previously discussed constitutional effects (Bulychev *et al.*, 2004). Third, there is a distinct effect of the pigment surface nature on the polymer structure acting as the best stabilizer: for hydrophobic CuPc, PiBA₅₃ – PAA₂₆ with the ratio PiBA/PAA ~ 2 revealed the best result.

ESA measurements of aqueous dispersions of CuPc, stabilized by block copolymers of PiBA-PAA, give quantitative information about the process of adsorption of polymers as reflected first from the dependence of the dynamic mobility μ on the relative polymer concentration (Bulychev *et al.*, 2008) as shown in Figures 1 and 2, and second from the comparison of this dependency for systems without and with ultrasonic treatment.

Comparing the values of saturation concentration without and after ultrasonic treatment, one can infer that the amount of polymer adsorbed on the particle surface significantly increases when ultrasonification is applied. In this context, it has to be considered that the ultrasonic treatment leads to a finer dispersion by decreasing the particle size, and, consequently leading to an increase of the

surface area prone to polymer deposition. Thus both the increase in the total surface area of the dispersed particles and a possible ultrasonically induced activation of the particle surface must be considered as being responsible for the observed effects (Gridina et al., 2019; Kovshov et al., 2019).

In these calculations a spherical shape of the pigment particle was assumed, and that the maximum polymer adsorption is indicated by the saturation concentration SC; this saturation concentration is reached when the dynamic mobility vs. relative polymer concentration curve (Fig. 1 – 2) becomes more or less parallel to the abscissa and doesn't change much for increasing polymer concentration (Bulychev et al., 2008).

First, the total surface area S_{tot} of the particles with surface area S_{part} is obtained from the measured average particle diameter part and the particle number in the dispersion. Since the saturation concentration, SC, as obtained by ESA measurements, corresponds to the total mass of amphiphilic polymer that is adsorbed on the dispersed particles, the increased particle diameter (due to the adsorbed polymer) and thus the thickness of the polymer adsorption layer can be calculated as well. For the background and the equations on which the calculations of the data compiled in Table 2 are based, it is referred to the literature (Bulychev et al., 2008).

Whereas the particle surface area S_{tot} increases upon ultrasonic treatment by about a factor of 2 (minimum) and up to a factor of about 2,7 (see column 4 of Table 2), the saturation concentrations SC as derived from the experimental curves Fig. 1 – 2 is 5 to 6 times higher for the ultrasonically treated systems as compared to the non-treated systems (see column 5 of Table 2); in other words, the SC ratio is about three times larger than the S_{tot} ratio (compare columns 4 and 5 in Table 2). This indicates that the amount of polymer adsorbed per unit of the particle surface after ultrasonic treatment is higher as compared to non-treated samples. Thicknesses d of the adsorption layer of the amphipolar copolymer on TiO₂ and CuPc was presented in Table 3.

4. CONCLUSIONS:

The ultrasonic treatment increases the pigment surface by creating a more fine dispersion, and also activates the pigment surface leading to ultimately higher polymer adsorption in comparison to the non-treated samples. The thicker adsorption layers observed

for the ultrasonically treated systems confirm that activation of the pigment surface occurs by the action of ultrasonic power. This enables to create more stable and fine dispersions in various particle-medium combinations for a wide range of practical applications.

In order to get some quantitative information about the polymer adsorption as revealed from the ESA data, and to correlate the amount of polymer adsorbed with the dispersing conditions, calculations of the surface area of the pristine pigment particle and of the polymer coated particle were done for both the systems without and with ultrasonic treatment and related to the amount of adsorbed polymer.

5. ACKNOWLEDGMENTS:

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Table 1. Sedimentation stability of CuPc aqueous dispersions stabilized by PiBA-PAA block copolymers

Polymer	Suspension stability (half-time of the sedimentation, days)	
	Without mechanical treatment	After ultrasonic treatment
PiBA ₇₂	3	10
PAA ₂₈	0.3	2
PiBA ₅₃ – PAA ₄₉	4	20
PiBA ₅₃ – PAA ₂₆	5	45
PiBA ₁₇ – PAA ₉₇	0.2	5
PAA ₁₇ – PiBA ₇₂ – PAA ₁₇	3	14

Table 2. Effect of ultrasonic treatment on the particle diameter d_{part} , and effect of ultrasonic treatment on the increase of the particle surface area (S_{tot}) as well as on the saturation concentration (SC) of added amphipolar copolymer as expressed by the corresponding S_{tot} and SC ratio; the indexes 1 and 2 refer to the non-treated (1) and ultrasonically treated (2) sample.

System	Averaged particle diameter d_{part} in μm .		Ratio between particle surface area with and without ultrasonic treatment $\frac{S_{tot\ 2}}{S_{tot\ 1}}$	Ratio between saturation concentration with and without ultrasonic treatment SC_2/SC_1
	Without ultrasonic treatment	After ultrasonic treatment		
CuPc + PiBA ₅₃ – PAA ₂₆	0.8	0.3	2.7	6

Table 3. Thicknesses d of the adsorption layer of the amphipolar copolymer on TiO₂ and CuPc surface for ultrasonically treated and non-treated dispersions as calculated on the basis of the saturation concentration SC obtained from the ESA measurements

System	Thickness d of the adsorption layer without ultrasonic treatment, nm.	Thickness d of the adsorption layer after ultrasonic treatment, nm.	Ratio between the thicknesses of treated and non-treated samples
CuPc + PiBA ₅₃ – PAA ₂₆	1	2.3	2.3

Figure 1. Dependence of the dynamic mobility on the relative concentration of $PiBA_{53} - PAA_{26}$ for 1 wt.-% CuPc aqueous dispersion without ultrasonic treatment

Figure 2. Dependence of the dynamic mobility on the relative concentration of $PiBA_{53} - PAA_{26}$ for 1 wt.-% CuPc aqueous dispersion after ultrasonic treatment