**ANÁLISE DAS CARACTERÍSTICAS GEOMÉTRICAS DO SISTEMA DE SOLVENTE
POLIMÉRICO DE DUAS FASES DURANTE A SEPARAÇÃO DE SOLUÇÕES DE
ACORDO COM A INTENSIDADE DA IMAGEM DE MICROGRAFIAS**

**ANALYSIS OF GEOMETRIC CHARACTERISTICS OF TWO-PHASE POLYMER-SOLVENT
SYSTEMS DURING THE SEPARATION OF SOLUTIONS ACCORDING TO THE
INTENSITY OF THE IMAGE OF MICROGRAPHS**

**АНАЛИЗ ГЕОМЕТРИЧЕСКИХ ХАРАКТЕРИСТИК ДВУХФАЗНЫХ СИСТЕМ ПОЛИМЕР-
РАСТВОРИТЕЛЬ ПРИ РАЗДЕЛЕНИИ РАСТВОРОВ ПО ИНТЕНСИВНОСТИ
ИЗОБРАЖЕНИЯ МИКРОФОТОГРАФИЙ**

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RESUMO

Este artigo discute o estudo das formas e tamanhos de gotículas de polímero formadas durante a separação de fases de suas soluções com o aumento da temperatura, bem como os parâmetros das camadas de transição de polímero condensado na superfície de gotículas formadas durante este processo. Para o estudo, optou-se por um copolímero de óxido de polietileno e óxido de polipropileno, cujo comportamento em soluções aquosas e a mudança no balanço hidrofílico-hidrofóbico dependem da temperatura. Foi estabelecido que a aplicação do método de processamento digital de imagens permite a introdução do critério quantitativo - intensidade de imagem de uma foto. Para um estudo mais detalhado do comportamento das moléculas do polímero no limite da fase, dependendo da temperatura, foram realizados estudos do comportamento dependente da temperatura de vários polímeros de diferentes composições e estruturas. O uso do método de processamento digital de imagens para gotículas de polímeros possibilita determinar os parâmetros de gotas e suas camadas de transição, determinar a dinâmica de nucleação e crescimento de gotículas e mudanças de densidade na camada de transição pelo parâmetro de intensidade de imagem. O artigo descobriu que os embriões de plurônico estão distribuídos de forma desigual em volume de solução com a presença de zonas com um número máximo de moléculas e uma zona com um mínimo de montagem de moléculas. O valor prático do trabalho está no fato de que os resultados do estudo podem ser usados para avaliar a dinâmica da separação de soluções de polímero sem envolver os métodos instrumentais de análise física e química que consomem tempo e são caros.

Palavras-chave: *soluções de polímeros, separação de fases de soluções, fotografia (quadro de vídeo), intensidade da imagem, densidade do material.*

ABSTRACT

This paper discusses the study of the shapes and sizes of polymer droplets formed during the phase separation of their solutions with increasing temperature, as well as the parameters of the transitional layers of

polymer condensing on the droplet surface formed during this process. For the study, a copolymer of polyethylene oxide and polypropylene oxide was chosen, whose behavior in aqueous solutions and the change in hydrophilic-hydrophobic balance depends on temperature. It has been established that the application of the method of digital image processing allows the introduction of the quantitative criterion – image intensity of a photo. For a more detailed study of the behavior of polymer molecules at the phase boundary, depending on the temperature, the studies of the temperature-dependent behavior of a number of polymers of different composition and structure have been carried out. The use of the digital image processing method for polymer droplets makes it possible to determine the parameters of droplets and their transition layers, to determine the dynamics of nucleation and droplet growth and density changes in the transition layer by the image intensity parameter. The paper has found out that embryos of pluronic are unevenly distributed by volume of solution with the presence of zones with a maximum number of molecules and a zone with a minimum of assembly of molecules. The practical value of the work is in the fact that the results of the study can be used to assess the dynamics of the separation of polymer solutions without involving the time-consuming and expensive instrumental methods of physical and chemical analysis.

Keywords: *polymer solutions, phase separation of solutions, photography (video frame), image intensity, material density.*

АННОТАЦИЯ

В данной работе рассматриваются вопросы исследования форм и размеров капель полимеров, образующихся при фазовом разделении их растворов при повышении температуры, а также параметры образующихся при этом переходных слоев конденсирующегося полимера на поверхности капель. Для более детального изучения поведения полимерных молекул на границе раздела фаз в зависимости от температуры были проведены исследования температурно-зависимого поведения ряда полимеров различного состава и структуры. Для исследования выбран сополимер полиэтиленоксида и полипропиленоксида, поведение которого в водных растворах и изменение гидрофильно-гидрофобного баланса зависит от температуры. Установлено, что применение метода цифровой обработки изображений позволяет ввести количественный критерий – интенсивность изображения фотографии. Применение метода цифровой обработки изображений капель полимеров позволяет определить параметры капель и их переходных слоев, установить по параметру интенсивности изображения динамику зародышеобразования и роста капель и изменения плотности в переходном слое. В работе было установлено, что зародыши п्लуроника неравномерно распределяются по объему раствора, с наличием зон с максимальным количеством молекул и зоны с минимальным их скоплением. Практическая ценность работы состоит в том, что результаты исследования могут быть использованы для оценки динамики разделения растворов полимеров без привлечения трудоемких и дорогостоящих инструментальных методов физико-химического анализа.

Ключевые слова: растворы полимеров, фазовое разделение растворов, фотография (видеокадр), интенсивность изображения, плотность материала.

1. INTRODUCTION

The results presented in the previous studies demonstrate the influence of the composition and structure of polymers, as well as the intense mechanical effect on the physical and chemical patterns of the behavior of polymer molecules at the phase boundary and reveal the conditions for the formation of active adsorption centers with the formation of nanostructured polymer layers with controlled structure and parameters (Ioni *et al.*, 2011; Burkhanov *et al.* 2014; Rudnev *et al.*, 2013; Kirilina *et al.*, 2009; Ivanov *et al.* 2017; Bulychiev *et al.*, 2018b; Bulychiev *et al.*, 2018e; Nikiforov *et al.*, 2016; Bulychiev *et al.*, 2018d; Bulychiev *et al.*, 2018c;

Bulychiev *et al.*, 2018d).

However, in this case, the possibility for creating the surface polymer layers is limited by the thermodynamics of the adsorption and desorption equilibrium and obtainment of the adsorption layers of a given thickness is difficult due to the achievement of the saturation concentration after which the polymer is not adsorbed, and the surface layer is not formed (Mykhalevskiy *et al.*, 2017; Sartabanov, 2017).

The surface activation through the intensive mechanical action expands the possibilities of modification changing the rate of polymer interaction with the surface and the nano-organization of the adsorption layers

obtained in this case; however, in this case, the amount of adsorbed polymer is limited by the number of active adsorption centers occurring on the surface, the affinity of polymer molecules to the surface and the ability of polymer molecules to self-aggregation.

Surface modification in the disperse systems can be carried out not only through the conventional (or activated under mechanical stress) polymer adsorption on the surface of particles of the dispersed phase, but also using the directional temperature-controlled polymer deposition process the physical and chemical properties of which, in particular, the hydrophilic-hydrophobic balance and solubility in the aqueous medium can change significantly with a slight increase in the temperature.

For a more detailed study of this phenomenon and the behavior of polymer molecules at the phase boundary, depending on the temperature and identifying the possibility of its usage to increase the efficiency of modification and directional changes in the properties of the phase interface, the studies of temperature-dependent behavior and temperature-controlled sorption of a number of polymers of different composition and structures have been performed.

For the selected polymers, the phase transition temperatures were found in a wide range of concentrations, and the phase diagrams for mixing the polymers with water were constructed.

2. MATERIALS AND METHODS

A copolymer of polyethylene oxide and polypropylene oxide (pluronic) was chosen as the polymer which exhibits the temperature-dependent behavior in the aqueous solutions and the change in the hydrophilic-hydrophobic balance depending on the temperature. The condition for the formation of such a solution is the fulfillment of known inequality Equation 1:

$$DG_{sm} = DH - TDS < 0, \quad (\text{Eq. 1})$$

where DG_{cm} is the Gibbs free energy of mixing, DH is the heat of mixing, DS is the entropy of mixing, T is the temperature.

According to the equation presented, the strength of mixing is determined by the signs and values of DH and DS . When mixing the liquids and hydrophilic polymers, the entropy in most cases increases, which contribute to their solubility. The dissolution occurs due to the penetration of macromolecular segments into the

solvent volume. As a result of diffusion, a transition layer which is a solution of polymer segments in a solvent appears on the phase boundary. The thickness (r) of the transition layer amounts to the tens (Nm) and depends on the difference between the cohesive energies and the surface tension of polymer solutions: the smaller it is, the greater the thickness of the layer will be.

During the phase separation of polymer solutions, the reverse is true: on the surface of growing particle of a new phase, there is a transition layer consisting of the segments of macromolecules surrounded by the solvent molecules.

For a more detailed study of the phase separation mechanisms of two-component polymer-water systems using the optical microscopy, a comparative study of the initial stages of the phase separation process of pluronic EO₇-PO₂₀-EO₇ has been conducted. The phase separation of two-component polymer-water systems was investigated based on the digital processing of micrographs of samples of EO₇-PO₂₀-EO₇ pluronic solutions with a consistent increase of temperature at the beginning of the phase separation (at the temperature equal to the low critical solution temperature (LCST)) and after 2 hours at a temperature above the LCST – that is, with full phase separation. Figure 1 shows the micrographs of the phase separation process of pluronic EO₇-PO₂₀-EO₇.

3. RESULTS AND DISCUSSION:

The use of optical microscopy with the obtainment of micrographs allows us to see the stages of the phase separation process. But this method is qualitative, which does not characterize this process in terms of quantity. The use of the method of digital image processing allows us to enter a quantitative criterion – the intensity of the image of the photo. This parameter is some indirect criterion of the physical process of interaction of the polymer and the solvent; it has a wide practical application in the analysis of complex processes in various fields: in gas dynamics (Abashev *et al.*, 2018; Bodryshev *et al.* 2016; Tarasenko *et al.*, 2017), when assessing the density and porosity of materials with determining the percentage of mineral phases (Remeyens and Swennen 2008; Van Geet *et al.*, 2001), when analyzing the structure of material (Bodryshev 2017; Li *et al.*, 2003; Marushchak and Konovalenko 2010;

Solodushkin *et al.*, 2011), when analyzing the structure of adsorption layers of polymers on the surface of metal oxide microparticles (Bulychev *et al.*, 2018a). Thus, the task is with the use of the criterion of the intensity of the image of photographs to analyze the process of phase separation of polymers taking into account its temperature-time nature and scale effect.

The function $L_i=f(x_i, y_i)$ of the image intensities in the given micrograph cell is a quantitative characteristic — a white level. The micrograph itself is reduced to a gradation of a gray color. In this case, the micrograph is represented by the $M \times N$ matrix with non-negative integers (reduced to 0-255 gradation range), where $M=[kx]+1$, $N=[ky]+1$, $k=\Delta_{uz}/\Delta_p$ is the sampling rate, and Δ_{from} , Δ_p is the fraction of the size of elements in the digital image and its value in reality, respectively. The value of L_i is specified in the size of a pixel according to the coordinates of the corner or its center. Due to this, the matrix $M \times N$ is reduced significantly.

The processing of the intensity matrix was performed using the graphics application of the *Image Processing Toolbox (IPT)* package of *MATLAB* system. Figures 2 and 3 demonstrate the graphs of function $L_i=f(x_i, y_i)$ for the micrograph sections in Figure 1 and the corresponding bar charts.

Based on the bar chart (Figure 3a), it can be seen that at the first moment of phase separation – the emergence of new phase embryos – the image intensity in the image cells has the almost normal distribution law. For the case of complete separation in the region of $L \approx 255$, a second vertex arises which characterizes the presence of a nucleus in the drops of pluronic separated from the aqueous solution.

All this is confirmed by the three-dimensional graphs of the intensity of the image of Pluronic drops in the process of phase separation (Figure 4).

Figure 5 shows the diagrams $L_i=f(x_i, y_i)$ in section 1 (Figure 4). It is clearly seen that in the version with embryo the image intensity is much higher which also characterizes their condensation in the solution medium, while at the same time when the droplets of Pluronic are completely separated, they differ from the aqueous solution.

Thus, after 2 hours of phase separation, there are clear zones of Pluronic drops and the zones of “water solution”. Based on the above,

we can conclude that Pluronic embryos are unevenly distributed throughout the solution, with zones with the maximum number of molecules (density of aggregation) and zones with minimal accumulation (zones in the form of circular image intensity data shown in Figure 3a). Apparently, their accumulation occurs around the zones with the maximum density (Figure 6a), and their complete separation is carried out. The drop of Pluronic is clearly visible as a function of $L=f(x, y)$ in Figure 6a. It is characterized by the annular form consisting of transition layer where the process of diffusion of polymer segments into the solution at the phase boundary with the subsequent appearance of the amorphous nucleus is observed. All this takes place in the surrounding water solution with a small amount of Pluronic.

Let us turn to numerical analysis using the statistical data of function $L=f(x, y)$ passing through the center of droplets of different sizes. Figure 7 shows the measurement data of L_{min} , L_{max} , ΔL_i in the drops of different diameters.

It is seen that for the droplets with diameter less than $d_k = 0.9$ microns, L_{max} increases to a value of 255. Further, it remains constant. Herewith, with an increase in d_k , the core site with a given value increases, which indicates an increase in the area of adhesion of Pluronic molecules into one amorphous medium. Up to $d_k = 0.9$ microns, the values of L_{min} , ΔL_i change slightly. From the moment of $d_k \geq 0.9$ microns, an increase in ΔL_i occurs with a corresponding decrease in L_{min} . In the region of $d_k = 1.3$ microns, the depth of change in the intensity of the image L_{min} reaches the bottom.

4. CONCLUSIONS:

The parameter (image intensity) is a quantitative parameter that determines the dynamics of the process of separation of the pluronic solution according to the geometric characteristics. For the full phase separation option (Figure 3b) there are two peaks: 1 peak corresponds to the intensity around 90 and the second peak – around 255. At the first moment of phase separation, the emergence of embryos of a new phase, the presence of cavities affects the dynamics of the intensity changes, its value has a bright wave character with a significant range of ΔL_i scatter.

It can be assumed that the appearance of the transition layer is associated with the

formation of ordered areas of the liquid-state nature in the separation process at the phase boundary. As a result of research on the method of digital image processing, the mechanism of phase separation of solutions of Pluronic in the form of nucleation and growth has been confirmed.

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Figure 1. Micrograph of the phase separation process of pluronic EO₇-PO₂₀-EO₇. a is the first moment of phase separation – the emergence of new phase embryos, b is its enlarged image, c is the complete separation after two hours.

Figure 2. A three-dimensional image of function $L_i=f(x_i,y_i)$ of the phase separation process of pluronic EO₇-PO₂₀-EO₇. a is the first moment of phase separation – the emergence of new phase embryos, b is the complete separation after two hours.

Figure 3. Bar graphs of the distribution of cells with a given image intensity: a is the first moment of phase separation – the emergence of new phase embryos, b is the complete separation after two hours.

Figure 4. The cropped area of Pluronic EO₇-PO₂₀-EO₇ at the time of the phase emergence of embryos of new phase (a), complete separation after two hours (b).

Figure 5. Diagrams of intensity changes in longitudinal section 1.

a)

b)

Figure 6. The charts for change of function $L=f(x,y)$ of the cropped areas of Pluronic EO₇-PO₂₀-EO₇ (Figure 4) at the time of the phase emergence of embryos of a new phase (a), complete separation after two hours (b).

Figure 7. Diagrams of intensity change in the drop of Pluronic EO₇-PO₂₀-EO₇, depending on its size