# ENCAPSULATED DI-2-ethylhexylphosphoric Acid: SYNTHESIS, DISPERSITY AND EXTRACTION PROPERTIES

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**ABSTRACT**

Encapsulation of di-2-ethylhexylphosphoric acid was carried out by ionic complex of gelatine with cetyltrimonium bromide. Dispersity of obtained microcapsules at various extractant and oil phase contents was determined by optical microscopy and dynamic light scattering measurements. It was found that kinetic parameters and efficiency of iron removal from aqueous medium by encapsulated extractant is more attractive in comparison with the results of liquid or membrane extraction.

Keywords*:* Encapsulation, Iron extraction, Polymer-surfactant complex

## INTRODUCTION

Encapsulation of various bioactive substances is one of fast developing branches of nanotechnology [1-3]. In separation chemistry the application of extractant- containing nanoparticles covered by thin polymer film allows putting into practice some advantages of membrane extraction.

Physico-chemical methods of microencapsulation deal with phase separation and precipitation of a polymer onto a surface of a dispersed compound [1,2]. As a rule, such a polymer membrane has limited permeability. Thus, it would be desirable to find a method of changing permeability through a polymer film. It can be supposed that formation of

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any polymer film of insoluble complexes of a surfactant and polyelectrolyte allows controlling the permeability of an interfacial shell.

The purpose of this study is to develop a new extraction method with an encapsulated reagent and apply the obtained microcapsules for wastewater treatment.

## EXPERIMENTAL

The weighed quantity of di-(2-ethylhexyl)phosphoric acid (**EHPA**, Sigma Chemical Co, USA) was dissolved in a definite volume of paraffin oil (Hansen and Rosenthal KG, Germany, specific density $\rho^{15}$ = 860 kg/m$^3$, viscosity $\nu^{20}$= 70 mm$^2$/s). The emulsion of the obtained oily solution in aqueous medium was stabilized by gelatin (Reachem, Russia, "photographic" quality, MM 140 kD) and homogenized ("Ace", Japan, 5 min, 4000 rpm). In the presence of the cationic surfactant - cetytrimethylammonium bromide (CTMAB, $C_{16}H_{33}NBr(CH_3)_3$, "Fluka", Switzerland), solid polymer particles were precipitated onto the emulsion droplet surface. The obtained encapsulated extractant was kept in cool place for 20-24 hours and then isolated by filtration.

Gelatin - CTMAB complex formation was studied by photometric titration [4] at 470 nm using a colorimeter "Jenway 6051". The diffusion coefficient and hydrodynamic sizes of microcapsules were determined by light scattering measurements with a "Photocor SP" device. A photon-correlation spectrometer has 5 mW He-Ne laser as a light source. Obtained correlation function was treated by cumulant method [5]. Along with the microcapsule size, distribution was established by optical microscopy [6]. Iron concentration in the solution was determined according to the procedure, described earlier in [7].

### Liquid extraction.

Slightly acidic ([HCl] =0.1 M) solution with iron (III) of 0.02-0.5 mM concentration was added to 0.26 mM solution of EHPA in hexane medium and softly stirred up. Oil/water volume ratio was equal to 1:1. Kinetic study of iron concentration demonstrated, that extraction equilibrium is reached within 6-24 hour. Partition coefficients were calculated as a ratio of iron equilibrium concentration in organic ($c^o_e$) and aqueous ($c^w_e$) phases.

### Membrane extraction.

Experimental setup consists of the membrane module with a polypropylene hollow fibrous membrane, peristaltic pump (velocity 500-800 ml/hour), bottles, and circulating hydrodynamic contours for water and oil phases. An aqueous iron solution inside the membrane flows in the direction opposite to the organic phase outside of the membrane. The system operates under a quasi-stationary regime, i.e. there is no flux of liquid phases through a membrane. Reactant concentrations in the

membrane extraction are similar to those in the liquid extraction. The equilibrium state was reached within 20-24 hours. Partition coefficients were found using iron equilibrium concentration in the oil and aqueous phases.

### Iron extraction by encapsulated EHPA.

It was shown by a preliminary study, that "empty" microcapsules (without EHPA in the oil phase) do not influence iron concentration in the aqueous phase. Kinetic and thermodynamic studies of iron extraction were carried out with microcapsules containing 5-30 % vol. of EHPA in paraffin oil. Thus, extractant concentration was equal to 0.15-0.9 M in the microcapsule oil core or 0.3 – 7.2 mM in the media, containing 0.012 mM (0.7 mg/l) of iron (III). Extraction equilibrium was reached after 45-60 minutes. Equilibrium concentration $c^o_e$ was calculated as the difference of iron (III) initial and equilibrium concentration related to the volume of the microcapsule oil core.

### RESULTS AND DISCUSSION

In order to optimize polymer precipitation, it is necessary to get deeper insight into polymer-surfactant complex formation.

### Gelatin-CTMAB complex formation

The interaction of gelatin and cationic CTMAB leads to the formation of a water insoluble complex. As a result, an increase in the solution optical density (**D**) results from the quantity and sizes of newly formed solid substance particles. Complex formation essentially depend on reactants ratio $n = m_s/m_g$ (where $m_s$ and $m_g$ – surfactant and gelatin mass amounts, respectively, Fig.1).

$D(n)$ curves exhibit a maximum similar to the ones for mixtures of cationic and anionic polymers [8] and might be interpreted in terms of colloid stability of solid particles. If there is an excess of one of the polymers, then an insoluble polymer particles are charged and stabilized. Small particle sizes result in low optical density of the solution. At equivalent quantities of reactants (**n**), particles of the polyelectrolyte complex have no charge. Hence, a mixed polymer solution became turbid because of solid particles coagulation. It was found (Fig. 1.) that the larger polymer concentration, the smaller values of $n$. Apparently, a decrease in $n$ corresponds with a rise of particles flocculation at the increased polymer content.
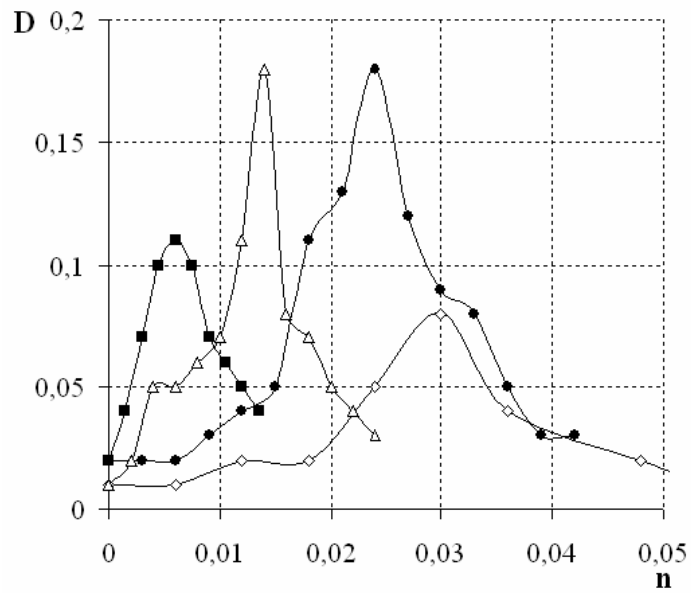
Fig. 1. Optical density of mixed surfactant-gelatin systems at various $n$ – values.
[Gelatin], g/l: –◇– 0.5;–•– 1.0; –△– 1.5; –■–2.0.
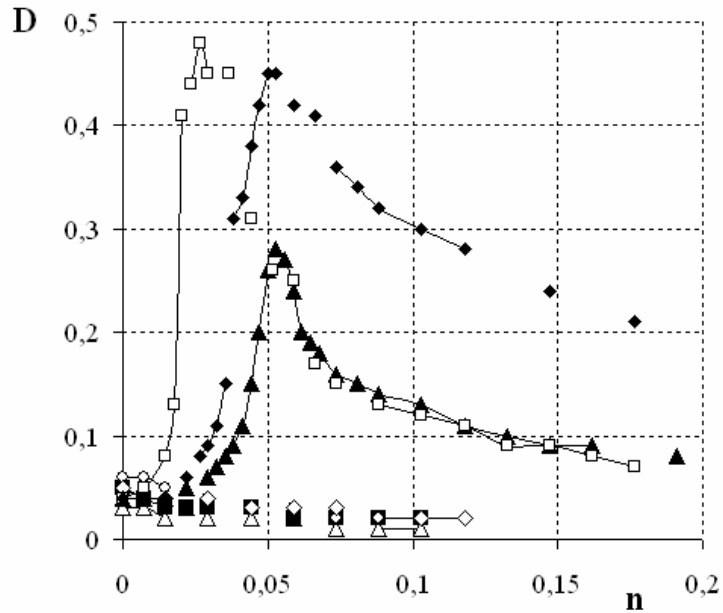


Fig. 2. $D(n)$ - curves at the different pH of the aqueous phase. pH: –△– 2.2;
–■– 2.3;–○– 3.0;–◇– 4.2; –▲– 6.3; –□– 8.2; –♦– 10.1.
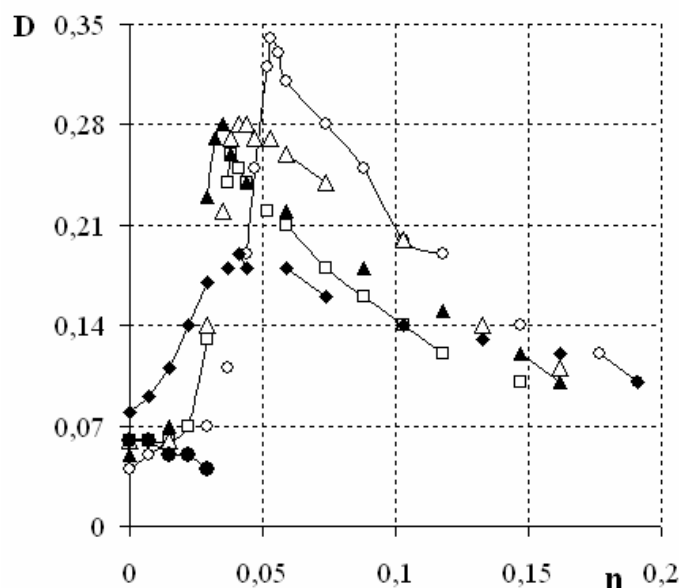
Fig.3. $D(n)$ - curves at the various ionic strength of the aqueous phase. [NaCl], % wt.: −○− 0; −□− 0.1; −△− 0.2; −▲− 0.4; −◆− 0.6; —●— 1.0.

Gelatin - CTMAB interaction is of electrostatic nature. Variation of pH or ionic strength of the solution should change the degree of polar groups dissociation and finally, influences the formation of polyelectrolyte complex [9]. It was established that pH of the solution significantly influences surfactant-polymer interactions (Fig.2). On the other hand, in the presence of sodium chloride, weakening of polymer-surfactant interaction shifts $D(n)$-curves to smaller $n$ (Fig. 3). Features of polymer-CTMAB interaction at different pH and composition allow defining the optimum regime of polymer complexes formation and their precipitation at the oil/water interface during the extractant encapsulation. In most cases, encapsulation of the extractant was carried out at $n \approx 1$ and pH = 4.2-6.3

### Fraction distribution of microcapsules

In order to obtain microcapsules, a surfactant solution was added to gelatin –stabilized emulsions containing 5-15 % vol. of oil phase. Volume fraction of the extractant (EHPA) in the oil phase was equal 5 – 30 % vol. Laser light scattering and optical microscopy measurements were applied to find the size distribution pattern of microcapsules at various quantities of gelatin, oil, and the extractant. It was found that the particle size distribution does not depend strongly on polymer concentrations (Fig. 4.). Increasing the encapsulated oil contents leads to the rise of microcapsules sizes.

The size distribution pattern at various volume fractions and compositions of oily phase at the constant gelatin quantity (2 g/l) shows a rise of an average particle size at an increased oil content. Simultaneously, at a smaller gelatin concentration (1 g/l) an increase in the oil content does not change strongly the particle size distribution. It means that, at low polymer concentration results mainly in change of particles concentration. It seems that, at a larger polymer concentration, a change in microcapsules size distribution takes place due to a rise in the intensity of flocculation processes [10].
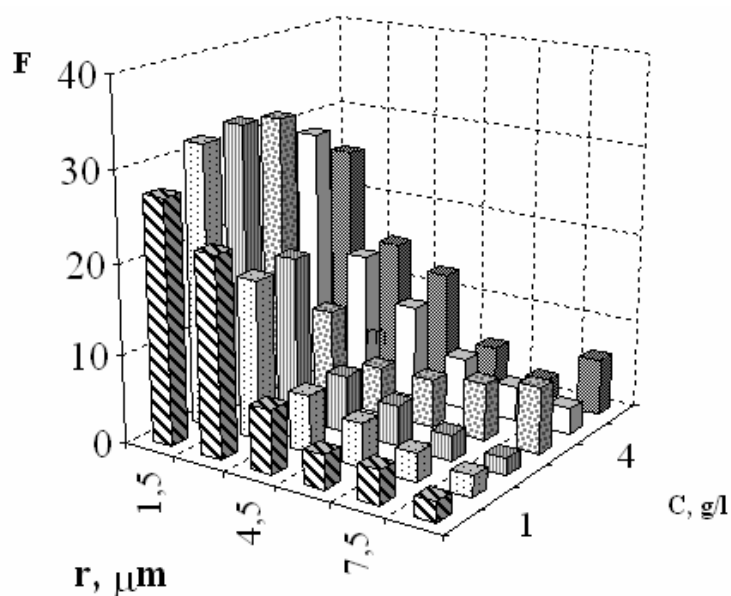


Fig. 4. Particles size distribution histogram. Oil contents 8 % vol. Gelatin concentration see in the legend box.

It was found that dispersity parameters for emulsions and the resulting microcapsules are similar, i.e. under the formation of the polymer shell, a distribution of particle sizes does not change noticeably. Taking into account the data concerning droplet sizes and polymer quantities (1-7 g/l) in emulsions (oil volume fraction 5-30 % vol., average radii ≈3-5 micron), it is possible to calculate thickness of the polymeric film at the oil/water interface. In dependence on the encapsulation conditions, the obtained values are equal to 10-110 nm. Kinetic and thermodynamic studies of iron

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extraction by microcapsules were carried out using particles obtained under the same condition: oil content - 10 % vol., polymer concentration - 2 g/l, EHPA concentration in the oil phase - 10-30 % vol., estimated shell thickness ≈20 nm. It was established that the obtained microcapsule systems have similar distribution of particle sizes.

The results of analysis of microcapsules sizes distribution allows defining the polymer concentration and oil content required to manufacture the particles of 100-5000 nm in size.

### Kinetic and thermodynamic features of iron extraction

The most essential parameters, which should influence on extraction efficiency by encapsulated extractant are microcapsule concentration, total interfacial surface, an EHPA concentration in the oil phase, and permeation properties of the polymer shell [11].

It might be supposed that a degree of iron extraction ($\alpha$) is related to the amount of an encapsulated extractant. The key parameter which allows considering extraction data at different contents of microcapsules is a mole ratio $n$ = [iron]/[extractant].
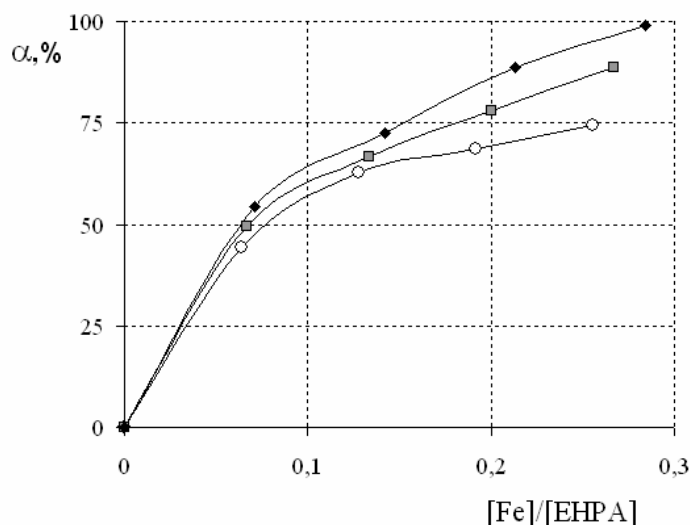


Fig. 5. Degree of iron extraction at different $[Fe^{+3}]$/[EHPA] ratio.
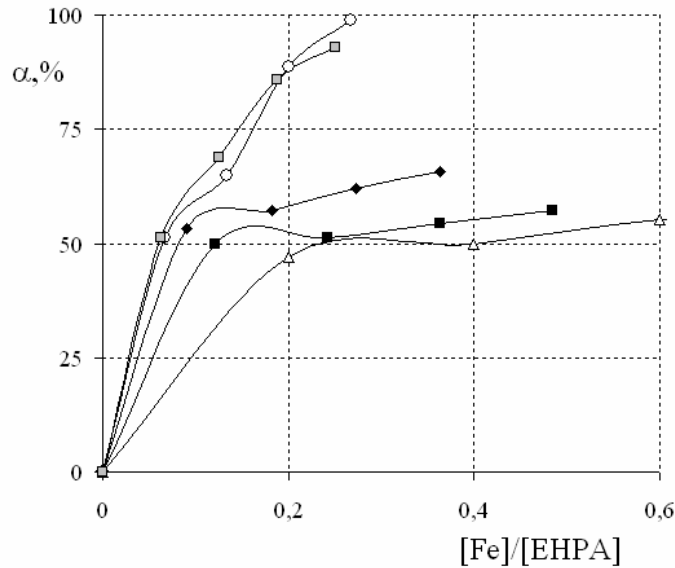Oil contents, % vol.: $-\circ-5.0$; $-\blacksquare-10.0$; $-\blacklozenge-15.0$

Fig. 6. Degree of iron extraction at different $[Fe^{+3}]/[EHPA]$ ratio. Contents of EHPA in the oil phase. % vol,: $-\triangle-$ 10.0; $-\blacksquare-$15.0; $-\blacklozenge-$ 20.0; $-\circ-$25.0; $-\blacksquare-$30.0.

It was found that extraction efficiency depends on the particle size (Fig. 5) and the extractant concentration in the oil phase (Fig. 6). The larger the particle interface (or EHPA concentration) the higher the degree of iron extraction. The obtained data suggest that the limiting stage of extraction is the extractant complex diffusion from interface to the volume of the oil phase.

In case of diffusion – controlled processes, kinetics of iron extraction by encapsulated extractant should obey the following equation [12]:

$$c = c_e \exp \{[\ln (c_i/c_e)] \exp (-\kappa \cdot \tau)\} ,$$

where $c_i$, $c_e$ *and* $c$ – are iron concentrations in the solution at the initial, infinite (equilibrium) and given time $\tau$, $\kappa$ - kinetic parameter. It was established that the results of kinetic studies of iron extraction are well described by this equation (fig. 7-8). The calculated kinetic parameter $\kappa$ changes proportionally to EHPA contents and the volume fraction (table 1) of microcapsules in the extraction system.
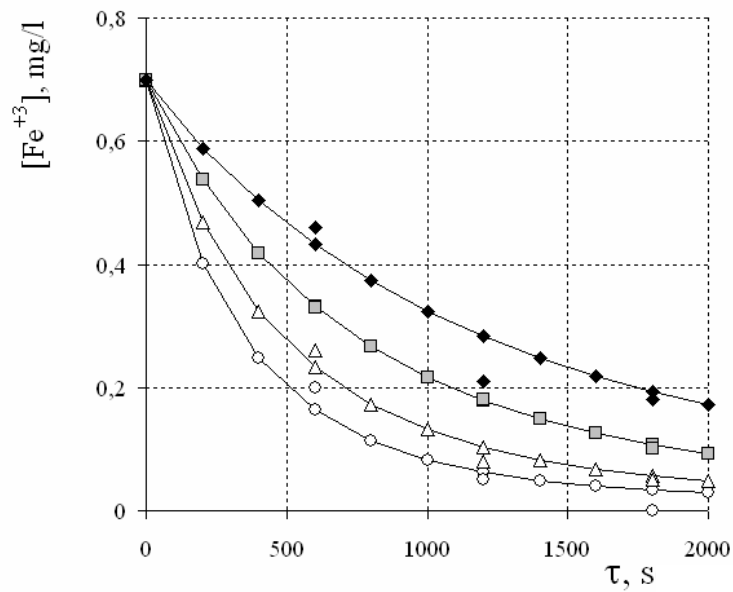
Fig.7. Kinetics of the iron extraction by encapsulated EHPA. Contents of EHPA in the oil phase is equal to 25 % vol. Microcapsule quantity in the extraction system, % vol.: −♦− 0.2; −■−0.4;−△− 0.6; −○− 0.8.
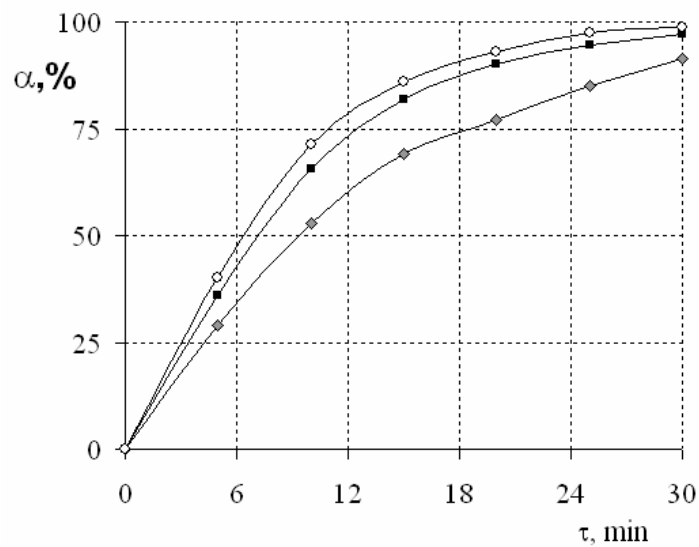


Fig. 8. Kinetics of iron extraction by encapsulated extractant. Microcapsule quantity is equal to 0.8 % vol. Contents of EHPA in the oil phase, % vol.: −♦− 15; −■−20; −○− 25.

Table 1 Kinetic parameters of iron extraction by encapsulated extractant

| Contents of EHPA in oil, % vol. | $\alpha \ 10^4$, s$^{-1}$ | | | |
|---|---|---|---|---|
| | Microcapsule amount in the extraction system, % vol. | | | |
| | 0.2 | 0.4 | 0.6 | 0.8 |
| 15 | 1.1 | 1.7 | 2.3 | 3.4 |
| 20 | 1.7 | 2.6 | 4.0 | 5.5 |
| 25 | 2.0 | 3.2 | 5.0 | 7.0 |

In order to clarify the features of the extraction by encapsulated EHPA, iron extraction by other extraction methods have been studied. It should be pointed out that, at the same degree of extraction ($\alpha$ = 97 %), partition coefficient ($D$) with encapsulated EHPA is much higher than in the case of common (liquid) or membrane extraction (Table 2). Moreover, application of an encapsulated extractant allows us to achieve the same level of iron removal in shorter time $\tau_e$ (Table 2).

Table 2. Extraction of Fe(III) by D2EHPA

| Parameter | Method | | |
|---|---|---|---|
| | Liquid extraction | Membrane extraction | Extraction by encapsulated extractant |
| $\alpha$ | 97 | 97 | 97 |
| $\tau_e$ | ≈20 hours | ≈20 hours | ≈1 hour |
| D | 40 | 40 | 4000 |

## CONCLUSION

In our opinion, exceptionally high extraction efficiency of the encapsulated extractant is results from a large interfacial surface (due to of micro- and nano- dimensions of particles), high permeability of the surfactant-polymer film, and finally, increase of hindrance of iron re-extraction.

Analyses of the obtained data indicate that encapsulated forms of extractants are very promising as nanosized chemical sensors and highly selective, efficient water purification reagents.

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