

Influence of Polymer Matrix Based on Mixtures of Cellulose Diacetate and Polyvinyl Formal on Kinetics of Complex Formation of Zn^{II} with Tetraphenylporphine

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Influence of polymer matrix based on mixtures of cellulose diacetate and polyvinyl formal on kinetics of Zn tetraphenylporphine complex formation was studied. Basic kinetic and diffusion characteristics of the process were measured. Decisive influence of polymer matrix rigidity on porphyrin reactivity was found.

Keywords: Porphyrin, complex formation, membranes, cellulose diacetate, polyvinyl formal.

Introduction

Reactivity of both natural and synthetic porphyrins depends on nature of solvation interactions in solutions and polymer matrices. Presence of various reaction centers in macroheterocycle molecules provides the possibility of porphyrin-solvent specific interactions, which determine different reactivity of porphyrin in various media.^[1]

Previously in work,^[2] reactivity of tetraphenylporphine (H₂TPP) incorporated in cellulose diacetate (CDA) membrane was determined by hindrance of rigid-chain polymer matrix on macroheterocycles deformation, and that did not depend on diffusion rate of aqueous solutions of zinc and cadmium acetates. Increasing of swelling degree of CDA in water-ethanol mixtures in the range 10-40% is accompanied by acceleration of metalloporphyrin formation by five orders of magnitude.

This fact is consistent with scheme of metalloporphyrin formation,^[3] in which deformation of macrocycle plays a crucial role. Thus, changing conditions of solvation at the transition from low-molecular solvent to polymer matrix and then to polymer matrix based on a mixture of two polymers with different hydrophilic properties, it is possible to identify the factors that strongly influence on the kinetics of complex formation.

Experimental

Diffusion membranes based on regular hydrophilic polymer – CDA (secondary cellulose acetate, the manufacturer – company «Phöne-poulenc») and polyvinyl formal (PVF, obtained from polyvinyl alcohol; molar content of vinyl formal units 68.7%, vinyl alcohol units 27.2%, vinyl acetate units 4.1%) obtained by dry spinning.^[4] Content of PVF varied from 100% to 60% (by weight of polymer). A lower content of PVF, up to 20%, does not allow to obtain homogeneous film. The thickness of obtained membrane was measured using a thickness meter with an accuracy of 0.5 microns.

Spectral analysis in the UV and visible regions indicates the molecular-dispersed state of H₂TPP, as evidenced by

implementation of Lambert-Beer law. Electronic absorption spectra were recorded on a Perkin - Elmer "UV/VIS Lambda 20" scanning spectrophotometer with a setting accuracy of wavelength ± 0.1 nm. Thermostatic attachment "Peltier" was used for measurements at different temperatures with an accuracy of 0.15 °C. All measurements were performed in 0.2 cm and 1 cm standard quartz cuvettes. Computer program developed by Ocheretovy A.S.^[5] was used to calculate rate constants of reaction. This program based on the using of absorbance measurements in the maximum possible number of points of spectra series, obtained by means of spectrophotometer which provides automatic digital recording. The error in determining of reaction rate constants did not exceed 7%.

Swelling (sorption) of polymer films was studied in water vapor atmosphere (at 100% humidity and T = 298 K) by gravimetric method using an analytical balance VLR-200. Previously films were dried in an exsiccator over phosphorus pentoxide at rt until constant weight. Quantitative characteristic of the swelling was swelling (sorption) degree (α, %), calculated by Equation (1):

$$\alpha = (m - m_0) / m_0 \cdot 100\% \quad (1)$$

The permeability coefficient of membranes was measured by electrical conductivity. Platinum electrode in addition to immittance meter LCR-817 was used to measure the resistance of zinc acetate solutions. The relative error of concentration did not exceed 5%. Amount of passing through membrane substance was determined by calibration dependence of test solutions resistance on their concentration.

Before kinetics and diffusion studies the polymeric membranes were kept in distilled water for five hours at a temperature of 298 K, because time necessary to reach equilibrium swelling degree is approximately 5 hours for both modified and unmodified polymeric membranes. Further, by means measuring the resistance of studied solutions, amount of salt passed through membrane for a certain period of time was determined.

Value of dQ/dt was calculated from the straight-line part (stationary process) of dependences Q = f(t), then permeability coefficient P was determined according to Fick's equation:^[6]

$$P = Q \cdot \delta / (t \cdot S \cdot C) \quad (2),$$

where Q – the amount of salt passing through the membrane, mole; P – permeability coefficient, m^2/s ; δ – thickness of films, m ; S – film area, m^2 ; C – salt concentration, mol/l , t – time, s .

Half-time diffusion was calculated based on amount of salt passed through membrane during the time t according to Equation 3:

$$t_{1/2}^D = t \cdot \delta \cdot \rho \cdot S / (4 \cdot Q \cdot M_{M(OAc)_2}) \quad (3),$$

where t – time, s ; δ – thickness of film, cm ; ρ – density of the solution, g/cm^3 ; S – film area, cm^2 ; Q – amount of moles of salt passed through membrane at time t , mol ; M – molecular weight of salt.

The error in determining the permeability coefficient does not exceed 5%.

Results and Discussion

Complex formation kinetics of zinc acetate ($Zn(OAc)_2$) with H_2TPP incorporated in polymer matrix based on polymer mixtures PVF – CDA was investigated. Electronic absorption spectra for the modified polymer membranes in contact with $Zn(OAc)_2$ aqueous solution were recorded. It was found that obtained spectra pattern was not different from behavior of spectra of H_2TPP during complexation in solution and CDA membranes.^[2] Calculation of the observed rate constant (k_{obs}) was carried out for complexation reaction (4):



Table 1. Reaction rates and activation parameters of interaction reaction of H_2TPP with $Zn(OAc)_2$ in PVF – CDA membranes (H_2TPP content 0.6 wt.%).

	δ , μm	$C(Zn(OAc)_2)$, mol/l	$k_{obs} \cdot 10^4$, s^{-1}	$k_v \cdot 10^3$, $l/mol \cdot s$	ΔG^\ddagger , kJ/mol	E_a , kJ/mol	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , $J/(mol \cdot K)$
PVF (100%)	49.4	0.0139	8.39	60.3	79.9	39.6	37.1	-143.5
PVF (90%)	53.0	0.0093	2.57	27.6	81.8	69.4	66.9	-50.0
PVF (80%)	54.9	0.0113	1.54	13.7	83.6	55.7	53.2	-102.0
PVF (70%)	53.1	0.0114	1.93	16.9	83.0	64.5	62.0	-70.7
PVF (60%)	66.0	0.0087	1.69	19.5	82.7	89.7	87.2	15.0
PVF (20%)	43.6	0.0357	0.54	1.5	89.0	25.1	22.6	-223.0
PVF (10%)	44.17	0.0332	0.39	1.2	89.7	26.5	24.0	-220.4
CDA(100%)	43.7	0.0186	0.25	1.3	89.3	44.5	42.0	-158.6

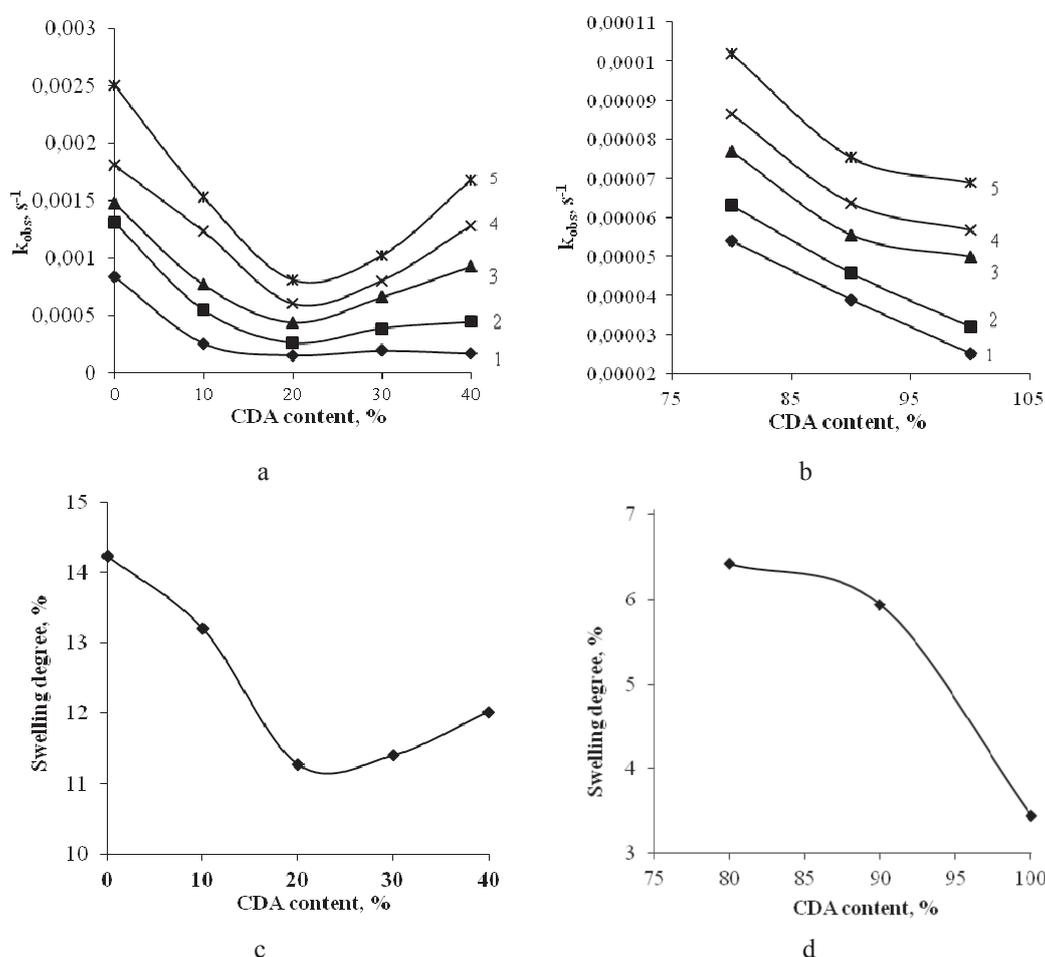


Figure 1. Dependence of rate constants at different temperatures (a, b) and the swelling degree at 298 K (c, d) for modified PVF-CDA membranes (content H_2TPP 0.6 wt.%). 1 – 298 K, 2 – 303 K, 3 – 308 K, 4 – 313 K, 5 – 318 K.

The kinetic data (Table 1 and Figure 1a, b) indicate that composition of polymer matrix significantly effect on reaction rate. Maximum values of rate constants correspond to 100% content of PVF and a minimum values – 100% content of CDA. Reaction rate constant is extremely changed with increasing of CDA content from 0% to 40%, a minimum corresponds to 20 – 30% of CDA content. Dependence of swelling degree on composition of membranes has the same character (Figure 1c, d).

In order to identify the factors that most affect on rate constant the half-time diffusion $t_{1/2}^D$ was calculated from diffusion experiment and the reaction half-time $t_{1/2}^k = 2\ln/k_{obs}$ was calculated from kinetic experiment. The results are presented in Table 2.

Table 2. Permeability coefficients, reaction half-times of H_2 TPP, half-times diffusion of $Zn(OAc)_2$ in modified polymeric matrices PVF- CDA, (H_2 TPP content 0.6 wt.%) at T = 298 K.

	$k_{obs} \cdot 10^4, s^{-1}$	$P \cdot 10^{12}, m^2/s$	$t_{1/2}^k, s$	$t_{1/2}^D, s$
PVF (100%)	8.39	3.80	826	248
PVF (90%)	2.57	3.20	2697	285
PVF (80%)	1.54	2.76	4501	339
PVF (70%)	1.93	2.52	3591	374
PVF (60%)	1.69	2.40	4101	887
PVF (10%)	0.39	0.048	17773	3781
CDA (100%)	0.25	0.004	27726	18474

The coefficient of permeability (P) decreases and the half-time diffusion ($t_{1/2}^D$) increases with increasing of CDA content in the polymer membrane. Composition of the polymer matrix has much greater influence on the value $t_{1/2}^k$: compared to "pure" PVF reaction half-time increases by 3-5 times. Data in Table 2 indicate that for investigated samples the diffusion rate is much higher than reaction rate of complex formation.

Thus, changing composition of polymer matrix, we can regulate swelling degree of polymer membrane and thus affect the reaction rate of complex formation (Figure 2). With an increase in 4 times of swelling degree the reaction

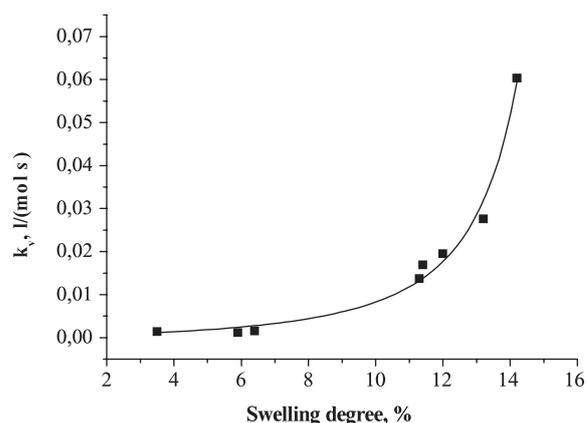


Figure 2. Dependence of the rate constant on swelling degree at 298 K for modified PVF-DCA membranes (content H_2 TPP 0.6 wt.%)

rate increases by 40 times. This fact confirms the initial assumptions about decisive influence of steric hindrance of rigid-chain polymer matrix on macrocycle deformation and reaction rate of metallation.

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