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Specific Features of the Formation of Zinc and Cadmium Complexes with Tetraphenylporphine in Amphiprotic Media

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Abstract—The kinetics of the complex formation reactions of tetraphenylporphine with zinc and cadmium acetates in mixed solvents containing alcohols and inert diluents was studied by electronic absorption spectroscopy. The dependences of the rate constant on the binary solvent composition have an extreme character, which is universal in the temperature range 298–313 K for different salts, alcohols, and weakly solvating diluents. The electric conductivity of zinc acetate solutions was measured in a wide range of compositions of alcohol–chloroform binary solvents. The electric conductivity increased with an increase in the content of alcohols.

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Alcohols as polar solvents with amphiprotic (donor and acceptor) properties are a suitable low-molecular-weight model of the inner region of biomolecules, such as hemoglobin, nucleic acids, and enzymes [1]. This fact is responsible for the importance of studying the reactivity of macrocycles both in neat alcohol and its various mixtures with inert diluents, which makes it possible to control the solvation power of a medium.

Previously, the kinetics of complex formation reactions of etioporphyrin [2–4] and tetraphenylporphine (H_2TPP) [7] with metal salts was studied in different solvents: alcohols with different structures, acetic acid, benzene, and ethanol and their mixtures with carbon tetrachloride. Of special interest are studies dealing with the effect of the binary solvent on the kinetics of formation of metalloporphyrins where it was attempted to determine the contribution of solvation effects to the kinetic parameters of the reaction. For the binary solvent ethanol–CCl_4, a smooth decrease in the reaction rate constant with an increase in the concentration of the nonpolar component (the maximal CCl_4 content was 90 vol %) was observed [2, 3]. This is accompanied by an increase in the reaction activation energy and entropy in the range of CCl_4 concentrations of 40–90 vol %. This fact was explained from the standpoint of resolvation or a change in the composition of the solvation shells of both the metal salt and porphyrin. In addition, experimental data were obtained on the kinetics of formation of cadmium etioporphyrin in the ethanol–benzene binary solvent (the maximal benzene content was 0.6 mol fractions). A smooth decrease in the reaction rate constant was observed as the fraction of the nonpolar component of the solvent mixture increased. Unfortunately, in these works, no experimental data were reported for the range of high contents of the nonpolar component of the binary solvent, which prevents us from assessing the general kinetic pattern of the process under consideration. The assumption that changes in the solvation shells of the salt and porphyrin caused by varying the composition of the solvent have considerable effect on the reaction kinetics was not confirmed by experimental methods.

EXPERIMENTAL

Tetraphenylporphine H_2TPP, synthesized as described in [5], was additionally purified on Al_2O_3 of activity IV. Cadmium and zinc acetates ($Cd(AcO)_2$ and $Zn(AcO)_2$) were preliminarily calcined. To study the complexation reaction, aliphatic alcohols (methanol, ethanol, propanol) and weakly solvating solvents (diluents) (chloroform and dichloroethane) were used. The solvents were purified by common procedures [8].

Electronic absorption spectra were recorded on a PerkinElmer Lambda 20 UV/VIS scanning spectrophotometer with a wavelength setting accuracy of 0.1 nm. The wavelength setting reproducibility was ±0.05 nm. The photometric accuracy was ±0.003. For taking measurements at different temperatures, a Peltier temperature control accessory was used, which allows one to record spectra in the temperature range 15–45°C with an accuracy of ±0.15°C. All measurements were carried out in standard quartz cells with an optical pathlength of 1 cm.

Conductometric measurements were carried out on an INSTEK LCR-817 instrument in a thermostated cell with platinum electrodes at 298 ± 0.02 K. The error of determination of electric conductivity was no more than 3%.

RESULTS AND DISCUSSION

The complex formation of H_2TPP with zinc and cadmium acetates was studied in mixed solvents contain-

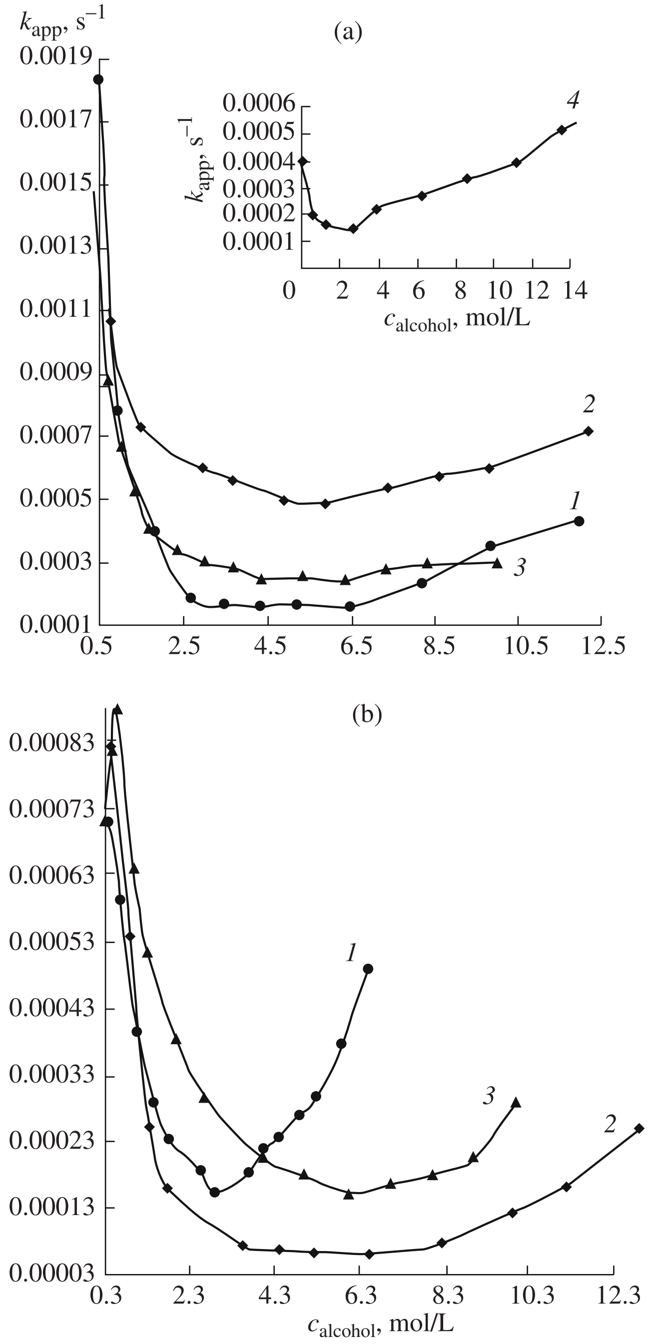

Fig. 1. Apparent rate constant of the complex formation reaction between (a) $Zn(OAc)_2$, (b) $Cd(OAc)_2$, and (c) H_2TPP vs. the alcohol content in the binary solvent. (*1*) methanol–chloroform, (*2*) ethanol–chloroform, (*3*) propanol–chloroform, and (*4*) methanol–dichloroethane.

ing alcohols and inert diluents (chloroform and dichloroethane) in the entire concentration range.

$$H_2TPP + Zn(AcO)_2 \longrightarrow ZnTPP + 2AcOH$$

The apparent rate constants k_{app} for the pseudo-first-order reaction were calculated for the initial H_2TPP concentration 5×10^{-5} mol/L, and the Zn^{2+} and Cd^{2+} acetate concentrations met the pseudo-first-order conditions. The plots of the rate constant of the complex formation reaction versus the binary solvent composition have an extreme character, which is universal since it is observed in the temperature range 298–313 K for different salts (Zn, Cd), alcohols (methanol, ethanol, *n*-propanol), and low-polarity diluents (chloroform, dichloroethane) (Fig. 1).

It is worth noting that, despite the universal character of the kinetic parameters of the porphyrin complex formation reaction, we failed to find literature data obtained for the entire range of compositions of alcohol-containing binary solvents. Therefore, the available literature data on the kinetics of the formation of metalloporphyrins in mixed solvents [2–4, 7, 8] prevent us from formulating the reasons for the extreme character of the curves.

The activation parameters of the complex formation reaction were obtained from the plots of the logarithm of the rate constant for the reaction of coordination of H_2TPP to zinc and cadmium acetates in binary solvents ethanol–chloroform of various compositions (Fig. 2). The data in the table show that, at low alcohol contents in the mixture, the parameters for the zinc and cadmium salts are the same. With an increase in the alcohol concentration, the kinetic parameters become different, which is accompanied by the compensation effect of the enthalpy and entropy contribution to the rate constant of the process. However, it is evident that the acceleration of the complex formation reaction at a high alcohol concentration is mainly caused by a decrease in the activation enthalpy.

Taking into account the composition of the participants of the reaction, we may assume that the reasons for the extreme character of the curves (Fig. 1) can be very different and determined by the specific features of the solvation of the porphyrin, cadmium and zinc salts, and transition state; salt dissociation in mixed solvents; and the associative state of the solvents. It is evident that the possible salt dissociation, which radically changes the nature of the complex-forming compound, from a neutral molecule to a ionic one, is expected to have the strongest disturbing effect on the reaction system [8].

Taking into account the high sensitivity of the electric conductivity of solutions to the appearance of charged particles, we measured the electric conductivity of zinc acetate solutions in a wide range of compositions. The salt concentration corresponded to its content in the kinetic experiment. The data in Fig. 3 show that the conductivity of the solution monotonically increases with an increase in the alcohol content and in its dielectric constant (methanol > ethanol > *n*-propanol). At the same time, the monotonic increase in the conductivity allows us to assume that salt dissociation can have an effect on the acceleration of complex formation at high alcohol concentrations; however, this in no way explains the existence of the descending branch

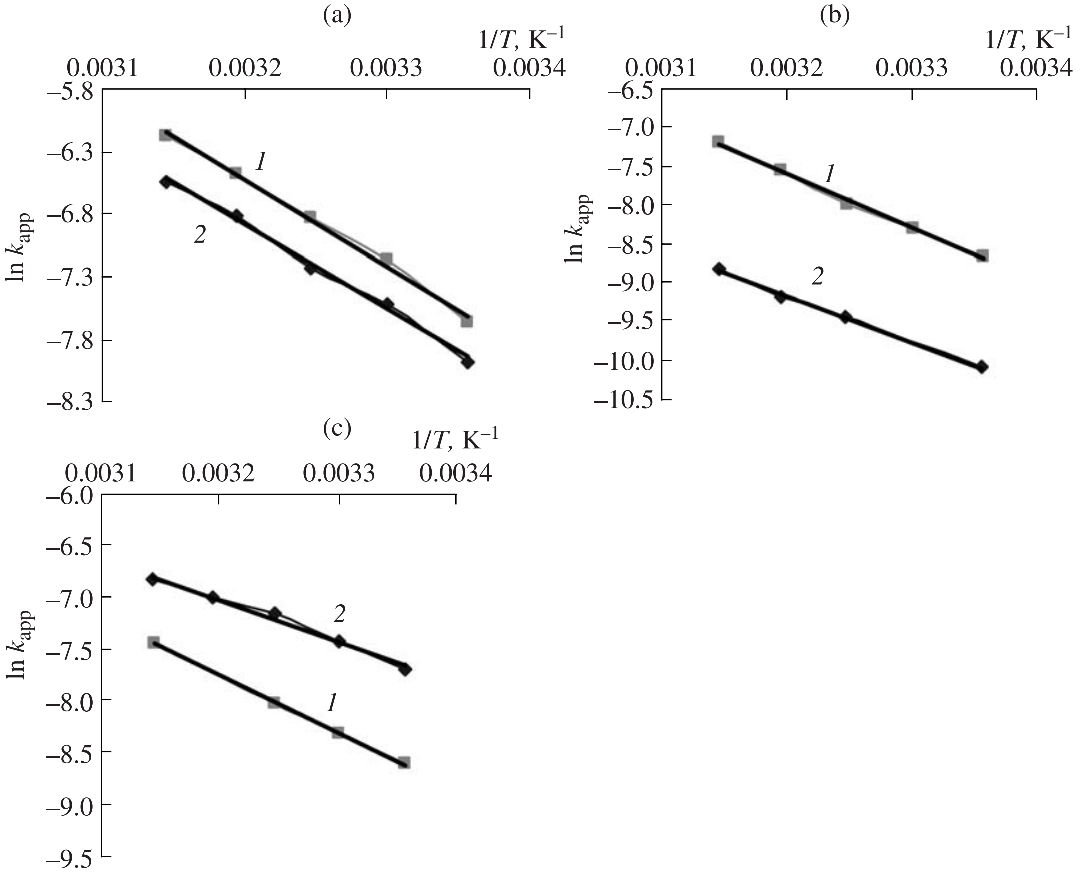

Fig. 2. Logarithm of the rate constant vs. inverse temperature for the reaction of metallization of H_2TPP with (*1*) $Zn(OAc)_2$ and (*2*) $Cd(OAc)_2$ in the binary solvent ethanol–chloroform. The ethanol content: (a) 0.94, (b) 5.20, and (c) 12.0 mol/L. The concentration of $Zn(OAc)_2$ 1.4×10^{-4}, $Cd(OAc)_2 - 9.9 \times 10^{-4}$ mol/L, respectively.

Activation parameters of the metallization reaction of H_2TPP in ethanol at 25°C

Salt	Alcohol concentration, mol/L	Reaction rate constant, L mol^{-1} s^{-1}	Activation energy E_a, kJ/mol	ΔH, kJ/mol	ΔS, J/(mol K)	ΔG, kJ/mol
$Zn(OAc)_2$	0.94	0.35	57.7	55.2	–68.23	75.6
	5.2	0.13	58.7	56.2	–73.45	78.1
	12.0	0.14	46.0	43.5	–115.3	77.9
$Cd(OAc)_2$	0.94	0.34	56.5	54.0	–72.57	75.7
	5.2	0.04	49.3	49.3	–113.95	80.9
	12.0	0.46	33.7	31.2	–146.49	74.9

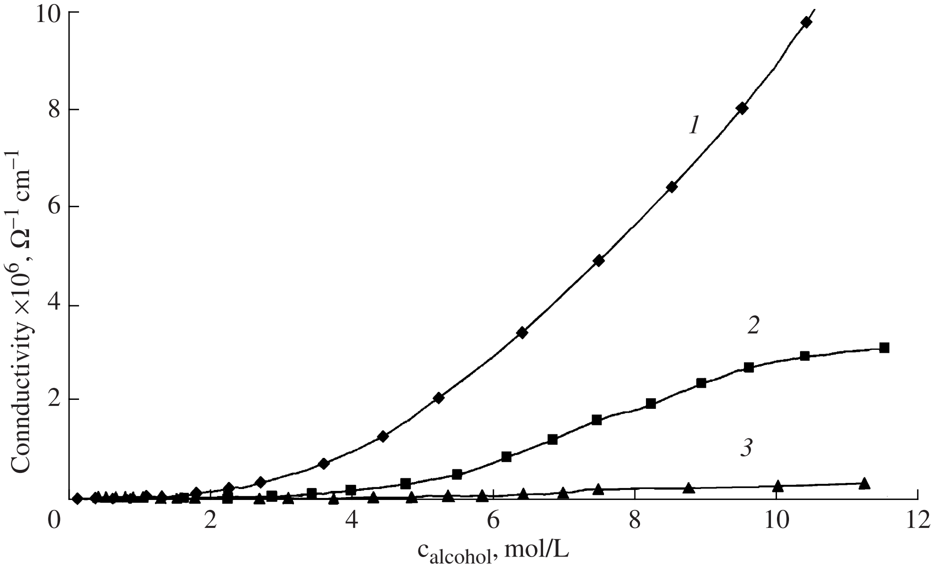

Fig. 3. Electric conductivity of $Zn(OAc)_2$ ($c_{Zn(OAc)_2} = 1.548 \times 10^{-3}$ mol/L) vs. the alcohol concentration in the binary solvent (*1*) methanol–chloroform, (*2*) ethanol–chloroform, and (*3*) *n*-propanol–chloroform.

of the curves (Fig. 1) and, hence, their extreme character.

Thus, the dependence $k_{app} = f(c_{alcohol})$ is presumably related to the specific features of either the solvation states of porphyrin and Zn and Cd acetates or the transition state of the complexation reaction.

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