Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 860–864. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 916–920.

Spectropotentiometric Study of Complexation Equilibrium in the System H_2TAPBr_4, H_2TAPCl_4–$(CH_3COO)_2Cd$–$HClO_4$–DMSO at 298 K

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Received November 2, 1999

Abstract — A procedure was suggested for direct measurement of the equilibrium constant of complex formation of porphyrins $MX_2 + H_2P \rightleftarrows MP + 2HX$, based on providing conditions under which the direct reaction is suppressed and the reverse reaction is facilitated. The procedure is applicable to complexation of Cd^{2+} with tetrachloro- and tetrabromotetraazaporphyrins in DMSO in the presence of $HClO_4$.

Formation of metal porphyrins in organic solvents is schematically described by the equation

$$MX_2 + H_2P \overset{K_e}{\rightleftarrows} MP + 2HX. \quad (1)$$

The equilibrium constant of this reaction is

$$K_e = \frac{[MP][HX]^2}{[MX_2][H_2P]}, \quad (2)$$

where H_2P is a porphyrin, MP is its metal complex, MX_2 is the salt of metal X, and HX is an acid.

In most cases, the forming metal porphyrins are so stable that determination of the equilibrium constant is difficult. With the majority of *d*-metal salts in solutions, reaction (1) is practically irreversible [1]; therefore, direct thermodynamic methods for studying equilibria are unsuitable. Nevertheless, a few attempts were made to choose conditions for providing reversibility of reaction (1) by suppressing the direct reaction and facilitating the reverse reaction, with the aim to determine the equilibrium constant [Eq. (2)]. Adeyemo and Krishnamurthy [2] performed reaction (1) at a constant ionic strength in aqueous solution with sulfonated tetraphenylporphine and $Hg(NO_3)_2$. Shamim and Hambright [3] studied a series of water-soluble porphyrins in the form of iodides and perchlorates, prepared their cadmium complexes, and selected conditions for reaction (1) in aqueous solution. The complicating factors in these cases are association of porphyrins and hydrophobic interactions of the organic moiety with water. These interactions make difficult rigorous comparative characterization of the complexes. Furthermore, the structure of labile mercury complexes is still the matter of discussion. Study of equilibrium (1) in a series of solvents is complicated by occurrence of acid–base equilibria (3)–(6):

$$H_2P = HP^- + H^+, \quad (3)$$

$$HP^- = P^{2-} + H^+, \quad (4)$$

$$H_3P^+ = H_2P + H^+, \quad (5)$$

$$H_4P^{2+} = H_3P^+ + H^+. \quad (6)$$

The cations H_3O^+ and H_4P^{2+} of tetrabromo- and tetrachlorotetraazaporphyrins are indifferent to coordination with M^{2+}, and the anionic species HP^- and P^{2-} forming under rigorous conditions can react with very high rates. The complexing power of metal solvate complexes decreases with decreasing pH. As a result, the current concentrations of H_2P, M^{2+}, and MP are complex functions of pH. In this work for studying the complexation equilibrium we chose cadmium acetate, DMSO as solvent, and tetrabromo- and tetrachlorotetraazaporphines (H_2TAPBr_4 and H_2TAPCl_4, respectively), whose complexation with cadmium was not studied previously. Bromine- and chlorine-substituted tetraazaporphyrins exhibit a low proton affinity, and their cadmium complexes show a low kinetic and thermodynamic stability. DMSO is an aprotic polar solvent; it readily dissolves the chosen porphyrins, and their chemical modification to enhance the solubility is not required.

Complexation of Cd^{2+} with H_2TAPBr_4 and H_2TAPCl_4 was studied by spectropotentiometric titration [4] using a cell shown in Fig. 1. The experimental results and the pK_e values calculated from them are listed in the table. The electronic absorption spectra of the chloro and bromo derivatives (they practically coincide) are shown in Fig. 2. The mean values

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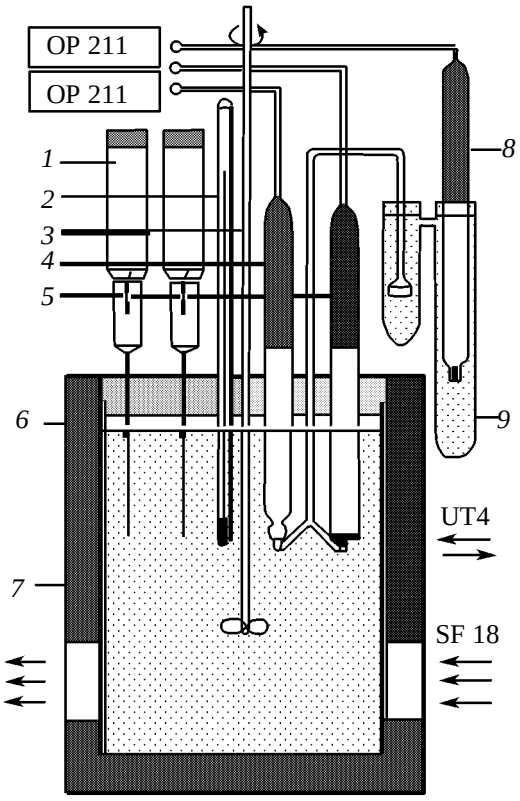


Fig. 1. Scheme of the spectropotentiometric cell: (*1*) dosing microsyringes (scale division 6×10^{-4} ml); (*2*) mercury thermometer (scale division 0.02 K); (*3*) power-driven stirrer; (*4*) glass electrode; (*5*) ion-selective electrode; (*6*) temperature-controlled glass optical cell, *V* 100 cm^3, *l* 3.3 cm; (*7*) temperature-controlled jacket; (*8*) reference electrode; and (*9*) liquid junction.

of the equilibrium constants K_e for $CdTAPBr_4$ and $CdTAPCl_4$ are 1.07×10^{-4} and 4.90×10^{-6} mol l^{-1}, respectively.

Tetrahalotetraazaporphyrins are aromatic macrocycles with a stable multicontour π-electron system. Continuous π,π overlap throughout the macrocycle, involvement of lone electron pairs of halogen and intracyclic nitrogen atoms in *n*–π conjugation, and increase in the number of π electrons in the conjugated system due to *meso*-nitrogen atoms enhance the conformational rigidity of H_2PX_4 molecules [1, 5]. The more rigid the molecule, the greater the polarity of NH groups and complexing power of H_2PX_4 [6–8]. Halogenation of the β-pyrrole positions in porphyrins causes significant changes in the structure and reactivity of porphyrins. The polarity and chemical activity of NH bonds increase, which is manifested in the capability of polybrominated porphyrins, especially tetraazaporphyrins, to enter into strong acid–base interactions with electron-donor solvents such as DMSO, DMF, pyridine, piperidine, and imidazole with formation of sandwich solvates of the porphyrin dianion [9]. For example, $H_2TAP(\beta\text{-}Br)_8$ forms with these solvents acidic solvation salts $[SH^+\cdots TAPBr_8^{2-}\cdots SH^+]$ with peculiar properties.

Polarization of NH bonds in porphyrins due to halogenation in the pyrrole rings sharply accelerates complexation with *d*-metal salts. Such porphyrins, especially tetraazaporphyrins activated with strong electron-withdrawing substituents (Br, Cl, SO_2OH, etc.) enter into complexation (1) even with *p*- (Al^{3+}) and *s*-metal (Mg^{2+}) salts [10, 11]. For common porphyrins this reaction is unknown. The stability of

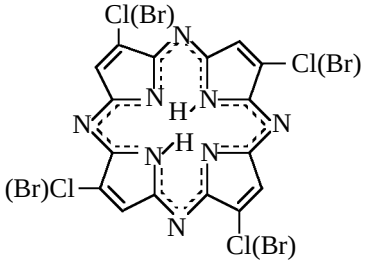
Experimental optical densities in the half-conversion point ($A_{1/2}$) and calculated values of pCd = $-\log[Cd^{2+}]$ and pK_e

$CdTAPCl_4$				$CdTAPBr_4$			
pH	pCd	$A_{1/2}$	pK_e	pH	pCd	$A_{1/2}$	pK_e
4.26	3.25	0.54	5.48	4.13	4.25	1.06	4.20
4.21	3.10	0.54	5.53	3.94	4.10	1.05	3.97
4.13	3.07	0.54	5.40	3.88	4.03	1.04	3.92
4.09	3.05	0.54	5.34	3.86	3.98	1.04	3.93
4.05	3.00	0.54	5.31	3.84	3.92	1.04	3.95
4.04	2.97	0.54	5.30	3.83	3.89	1.04	3.96
4.02	2.93	0.54	5.33	3.82	3.86	1.04	3.97
4.01	2.92	0.54	5.32	3.78	3.85	1.04	3.90
3.99	2.90	0.54	5.30	3.80	3.84	1.04	3.95
3.98	2.85	0.54	5.34	3.79	3.81	1.04	3.96
3.96	2.81	0.54	5.34	3.78	3.79	1.04	3.96
3.94	2.78	0.54	5.33	3.78	3.77	1.04	3.98
3.91	2.71	0.54	5.35	3.77	3.75	1.04	3.98
3.89	2.69	0.53	5.33	3.75	3.72	1.04	3.97
3.86	2.62	0.53	5.34	3.74	3.70	1.04	3.97
3.84	2.59	0.53	5.33	3.73	3.68	1.03	3.96
3.83	2.58	0.53	5.33	3.73	3.66	1.03	3.98
3.81	2.55	0.53	5.32	3.73	3.64	1.03	4.00
3.80	2.52	0.53	5.33	3.72	3.63	1.03	3.97
3.79	2.49	0.53	5.34	3.71	3.61	1.03	3.98
3.77	2.46	0.53	5.33	3.70	3.59	1.03	3.99
3.74	2.40	0.53	5.33	3.69	3.57	1.03	3.98
3.72	2.38	0.53	5.32	3.68	3.54	1.03	3.99
3.70	2.35	0.53	5.31	3.67	3.53	1.03	4.00
3.67	2.32	0.53	5.28	3.66	3.52	1.03	3.99
3.64	2.30	0.53	5.24	3.65	3.49	1.03	4.00
3.61	2.27	0.53	5.21	3.63	3.41	1.03	4.02
3.57	2.24	0.53	5.14	3.57	3.32	1.03	4.00
3.55	2.23	0.53	5.13	3.55	3.31	1.03	3.97
3.52	2.21	0.53	5.09	3.55	3.29	1.03	3.99

metal complexes with brominated azaporphyrins also changes [6, 12].

The inductive electronic effect of Cl and Br apparently causes polarization of the $C^{\beta}=C^{\beta}$ bonds, which is transferred via the π-conjugated system to the NH bonds. Their polarization decreases the extent of inhibition of complexation (1) by the effect of the macrocycle rigidity and in the case of azaporphyrins suppresses the geometric constituent of the macrocyclic effect [8]. Published data [13] show that the coordinating power of porphyrins with the active NH bond strongly depends on the nature of the solvent. Thus, pyridine and other strongly basic solvents accelerate reaction (1) with halo derivatives of tetraazaporphyrin H_2TAPX_n, whereas carboxylic acids suppress this reaction, affecting the state of the NH groups [13].

The relatively significant dependence of the equilibrium (1) constant on the nature of the halogen is due to the stronger polarization of the σ-electron system of the macroring under the action of chlorine as compared to bromine.



We can expect that in porphyrins, similar to arenes, chlorine, as compared to bromine, exerts a stronger negative inductive effect (*–I*) and a weaker positive effect due to *n–p* conjugation (*+C*). Therefore, the electronic shift toward the chlorine atom will be stronger as compared to bromine. These electronic effects in the porphyrin molecule accelerate complexation reaction (1) and most frequently stabilize the complex [14, 15], i.e., slow down the reverse reaction in equilibrium (1). As a result, the equilibrium constants of formation of the Cd tetraazaporphyrin complexes increase.

EXPERIMENTAL

H_2TAPBr_4 and H_2TAPCl_4 were prepared according to [16, 17]. Chemically pure grade DMSO was stored for 12 h over NaOH and vacuum-distilled (2–3 mm) from NaOH. Pure grade tetraethylammonium chloride was purified by double recrystallization from acetone and vacuum-dried (1.33 Pa) for a day at room temperature.

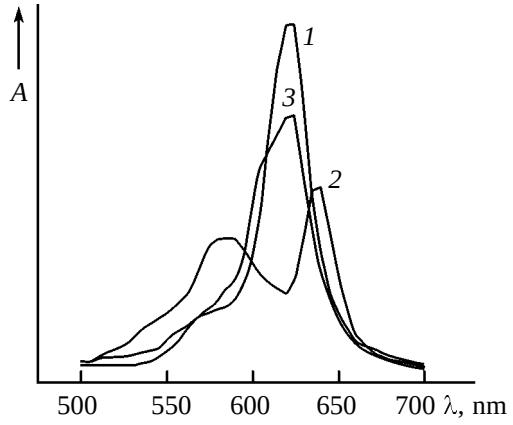


Fig. 2. Electronic absorption spectra of (*1*) CdP, (*2*) H_2P, and (*3*) reaction mixture $[H_2P]/[CdP] = 1$.

Tetraethylammonium perchlorate was prepared by precipitation from 8.75 M aqueous $HClO_4$ (chemically pure grade) with tetraethylammonium chloride purified as described above. Tetraethylammonium perchlorate was recrystallized from ice-cold water to negative reaction for Cl. The titrants were prepared from 8.75 M aqueous $HClO_4$ (chemically pure grade) and cadmium acetate (pure grade) in DMSO.

The electronic absorption spectra were recorded with an SF-18 spectrophotometer. Potentiometric measurements were performed in a pH-metric cell.

ESL-43-07 glass electrode	Test solution of DMSO	0.01 M Et_4NClO_4 in DMSO	Ag/AgCl, Et_4NCl_{sat} in DMSO

The pH of solutions in DMSO was measured with an ESL-43-07 glass electrode which was soaked for 7 days in water to attain stable readings and stored in water between measurements. The EVL-1M3 silver chloride reference electrode was filled with a saturated solution of tetraethylammonium chloride in DMSO. The liquid junction was filled with a 0.01 M solution of tetraethylammonium perchlorate in DMSO. The test solution was temperature-controlled to within 0.02 K with a UT4 liquid thermostat.

The pH-metric cell was calibrated at 298 K in 0.05 M dimethyl sulfoxide buffer solutions [18]: *o*-nitrobenzoic acid–sodium *o*-nitrobenzoate (pH 6.99); picric acid–sodium picrate (pH 1.00); and benzoic acid–lithium benzoate (pH 9.59). The coefficients of the calibration equation were found from three series of measurements.

$$E = 441.45 - 59.58\text{pH}; \; r \; 0.999. \qquad (7)$$

Spectropotentiometric titration. A glass cell was charged with 75 ml of a $\sim 2 \times 10^{-5}$ M solution of H_2TAPX_4 in DMSO. The solution was kept for 0.5–1 h at 298 K to attain stable readings of the pH meter, after which its spectrum was recorded. Then a solution of $(CH_3COO)_2Cd$ was added from a microsyringe to attain complete formation of the complex (monitoring by electronic absorption spectra). Then the solution was acidified with $HClO_4$ to the half-conversion state, $[H_2P]/[CdP] = 1$. This state was attained at half absorption of the colored system ($A_{1/2}$), monitored spectrophotometrically, and preliminarily estimated from the known molar extinction coefficients ε for each porphyrin. The spectrum was taken, and the potential was recorded.

The titration procedure included the following stages: (1) shift of equilibrium (1) by adding $HClO_4$ in amounts corresponding on the average to $0.06A_{1/2}$; (2) restoration of the initial value of $A_{1/2}$ by adding $(CH_3COO)_2Cd$, taking into account dilution; (3) shift of equilibrium (1) by adding $(CH_3COO)_2Cd$; (4) restoration of the initial value of $A_{1/2}$ with an $HClO_4$ solution; and (5) repetition of cycle (1)–(4).

In each stage, after attainment of the equilibrium, we recorded the electronic absorption spectrum and the potential E. The total change in the solution volume by the end of titration did not exceed 1%.

Dilution was taken into account by Eq. (8):

$$A_{1/2} = \frac{0.5A_{max}(1 + \varepsilon_{min}/\varepsilon_{max})}{1 + V/V_0}, \quad (8)$$

where $A_{max} = A_{CdP}$, $\varepsilon_{min} = \varepsilon_{H_2P}$, $\varepsilon_{max} = \varepsilon_{CdP}$ (at λ 620 nm), V_0 is the initial volume, and V is the total increase in volume. Formula (8) can be readily deduced by simple transformations.

From the electronic absorption spectrum (Fig. 2) follows expression (9):

$$A_{1/2} = 0.5\ A_{max} - A_{min}) + A_{min} = 0.5(A_{max} + A_{min}). \quad (9)$$

By equating the right sides of Eqs. (10) (Lambert–Beer law), we obtain Eq. (11):

$$C_0 = A_{max}/(\varepsilon_{max}l),\ C_0 = A_{min}/(\varepsilon_{min}l), \quad (10)$$

$$A_{min} = A_{max}\varepsilon_{min}/\varepsilon_{max}. \quad (11)$$

By combining Eqs. (9) and (11), taking into account dilution, we obtain Eq. (8). By transforming Eq. (2) into the logarithmic form, we obtain expression (12) for calculating pK_e:

$$pK_e = 2pH - 2pCd + \log([H_2P]/[CdP]). \quad (12)$$

Here $pCd = -\log[Cd^{2+}] = -\log\{(M_0\Sigma V)/(\Sigma V_1 + V_0) - [CdP]\}$, where M_0 is the cadmium acetate concentration in DMSO (M), ΣV is the total increase in the volume of the titrant $(CH_3COO)_2Cd$, ΣV_i is the total inctease in the volume due to addition of $HClO_4$ and $(CH_3COO)_2Cd$, and V_0 is the initial volume. In Eq. (12), $[H_2P]$ and $[CdP]$ in the half-conversion point are calculated by Eqs. (13) and (14):

$$[H_2P] = \frac{A_0^{H_2P}}{\varepsilon_{H_2P}l} - [CdP], \quad (13)$$

$$[CdP] = \frac{A_0\varepsilon_{H_2P} - A_\tau\varepsilon_{CdP}}{\varepsilon_{H_2P} - \varepsilon_{CdP}} \frac{l}{\varepsilon_{CdP}l}. \quad (14)$$

Here $A_0^{H_2P}$ is the initial optical density of the porphyrin, A_0 is the initial optical density of CdP, A_τ is the current optical density, and l is the cell thickness.

For the chloro derivative of tetraazaporphine, ε_{H_2P} 7076 and ε_{CdP} 20 260, and for the bromo derivative, ε_{H_2P} 5076 and ε_{CdP} 20 191 l mol^{-1} cm^{-1} at λ 620 nm (cell thickness 3.3 cm).

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