Thermal lens spectrometry as a tool for determination of stability constants of complex compounds

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The potential of thermal lens spectrometry in the determination of stability constants of complex compounds was explored using copper(I) and iron(II) complexes with 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline as examples. Thermal lens spectrometry offers advantages over conventional spectrophotometry in the determination of stability constants both in aqueous and nonaqueous media. The overall and stepwise stability constants of iron(II) tris(1,10-phenanthrolinate), copper(I) bis(2,9-dimethyl-1,10-phenanthrolinate), and copper(I) bis(1,10-phenanthrolinate) were determined at levels as low as 10^{-8}—10^{-6} mol L^{-1}.

Key words: thermal lens spectrometry, stability constants, complexation, copper(I), iron(II), 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline.

Thermal lens spectrometry (TLS) is a modern analytical method of molecular absorption spectroscopy used primarily for determining traces of various compounds. Thermal lens spectrometry combines high sensitivity, a nondestructive character, and a methodological diversity of conventional spectrophotometry.[1—4] Nevertheless, the potential of TLS as a method of investigation of reactions at nanogram levels has not been fully explored.

The determination of stability constants of complex compounds is an important problem of analytical chemistry. The development of analytical methods is accompanied by the lowering of detection limits and changes in the conditions of analytical reactions. As a result, available thermodynamic and kinetic data on these reactions can become out-dated and require refinement to provide better conditions for analytical determination at nanogram levels.[5—8] This necessitates the use of modern and highly sensitive analytical methods, among which TLS occupies a significant place. Hence, a combination of the characteristic features of TLS and the available approach to the determination of stability constants associated with the use of conventional methods becomes an important problem. The solution of this problem provides a way of extending the possibilities of TLS in both fundamental research and determination of trace amounts.

In the present study, we determined the stability constants of transition metal complexes by spectrophotometry and TLS in going from microgram concentrations of the reagents to nanogram amounts using iron(II) *tris*-(1,10-phenanthrolinate), copper(I) *bis*-(1,10-phenanthrolinate), and copper(I) *bis*-(2,9-dimethyl-1,10-phenanthrolinate) as examples. Methodological and analytical aspects of the stability constant determination by TLS are discussed with special emphasis on the advantages and limitations of this method in studies of chemical equilibria at nanogram concentrations.

Fundamentals of thermal lens spectrometry

Thermooptical methods are based on changes in the optical characteristics of the medium, which appear due to absorption of laser radiation and are quantitatively measured.[1—4] The most widely used effect, *viz.*, thermal lensing, can be characterized as a thermally induced refractive index change.[2,4] Laser irradiation of the absorbing medium (intensity profile of laser radiation is similar to a Gaussian curve) causes local heating giving rise to a temperature gradient, the maximum heating being observed at the center of the beam and the temperature gradually decreasing to room temperature with distance from the center.[1,4] An increase in the temperature leads to a refractive index change with the result that the refractive index distribution corresponds to the energy distribution in the incident beam. This gives rise to an optical element analogous in action to a diverging lens; this element is called a *thermal lens*.[2] A thermal lens, like any optical diverging lens, changes the laser beam divergence, *i.e.*, a viewer sees an increase in the beam size when looking on a screen placed in the beam path.[1,2]

In practice, thermal lens measurements are carried out with the use of various photodetectors. In principle, one can measure the broadening of the beam inducing a thermal lens. However, such experiments are associated with a number of technical problems. Because of this, *thermal lens spectrometry* makes wide use of dual-laser optical schemes, in which a powerful (as powerful as possible) laser (*excitation laser*) serves to induce a thermal

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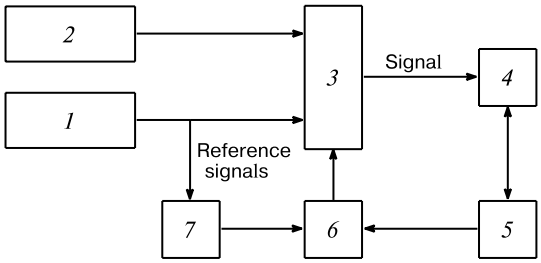

Fig. 1. Pincipal scheme of thermooptical measurements: *1*, an excitation laser; *2*, a probe laser; *3*, a system for beam focusing and convergence; *4*, a sample under study; *5*, a photodetector; *6*, a synchronization system; *7*, a reference channel photodetector.

lens, thus providing high sensitivity of measurements, and then laser radiation is rejected by an optical filter.[1,3,4] A change in the divergence of the second (*probe*) low-power (but stable) laser beam, which provides high accuracy of measurements, serves as a signal.

The principal scheme of thermooptical measurements is shown in Fig. 1. The synchronization system, which provides synchronization of the onset of the formation of a thermooptical element and the onset of signal accumulation, most commonly consists of an electromechanical chopper (for beam modulation of an excitation continuous wave laser), a controlling block, and a photodiode. The function of the reference signal is to record the current power of the excitation beam and normalize the signal to improve the accuracy of measurements.

The detector (photodiode with an aperture) is used to measure a decrease in the intensity at the center of the probe beam according to the equation

$$\vartheta = (I_{off} - I_{on})/I_{on}, \quad (1)$$

where I_{off} and I_{on} are the intensity of the probe beam without a thermal lens (either an excitation laser is switched off or its beam is shut off by a chopper) and the intensity of the thermal lens (either an excitation laser is switched on or its beam is opened), respectively.

Characteristics of thermal lens signal

A single measurement of a sample is an instrumental signal from a sample ϑ calculated from Eq. (1). The following parameter is used as an analytical thermal lens signal:

$$\theta = 2.303EA = 2.303E_0P_eA, \quad (2)$$

where P_e (W) is the power of radiation that induces a thermal lens, A is the absorbance of a sample (medium), and E_0 is the thermal-lens enhancement factor for unit power of excitation radiation (W^{-1})

$$E_0 = (-dn/dT)/(\lambda_e k). \quad (3)$$

Here λ_e is the wavelength of the excitation laser (nm), dn/dT is the temperature gradient of the refractive index (K^{-1}), and k is the thermal conductivity coefficient (mW cm^{-1} K^{-1}). The analytical signal (θ, Eq. (2)) is related to the instrumental signal (ϑ, Eq. (1)) by the equation

$$\theta = \frac{1 - \sqrt{\vartheta + 1}}{B}, \quad (4)$$

where B is the geometrical constant of the thermal lens signal

$$B = \frac{1}{2}\,\mathrm{arctg}\left(\frac{2mV}{1 + 2m + V^2}\right), \quad (5)$$

which takes into account the distance between the probe beam waist and the cell with a sample V (in units of confocal distances of the excitation laser) and the area ratio of the cross-sections of the probe and excitation beams in the sample m. The best geometrical constants m, V, and B and the accuracy of their measurement are given in Table 1.

The signal S (absorbance A measured relative to a solution of the control experiment or the thermal lens signal θ (Eq. (2)) minus the thermal lens signal of the control experiment) is used as the experimental value.

Table 1. Parameters of the dual-beam thermal lens spectrometer

Parameter	Value	
	Excitation laser*	Probe laser
Wavelength λ_e/nm	488.0 (514.5)	632.8
Focal distance of the focusing lens/mm	300	185
Confocal distance/mm	23.2 (22.0)	3.1
Laser power in the cell/mW	45—800 (80—1500)	3
Diameter of the beam waist cross-section/μm	60	25
	Optical scheme of the instrument	
Optical path length (mm)	10.1	
Cell-to-detector distance/cm	120	
Area ratio of the cross-sections of the probe and excitation beams in the cell m, Eq. (5)	2.00±0.05	
Relative distance from the excitation beam waist to the cell V, Eq. (5)	3.10±0.05	
Geometrical constant of the spectrometer B, Eq. (5)	0.352±0.006	

*The values for the wavelength of 514.5 nm are given in parentheses.

The parameter calculated from Eq. (6) is used as the sensitivity coefficient of thermal lens measurements.

$$\zeta = \theta/c = (2.303E_0P_eA)/c = 2.303E_0P_e\varepsilon l. \quad (6)$$

Calculations of overall stability constants

Competitive ligand complexation

The formation—dissociation reactions of $[Fe(Phen)_3]^{2+}$ (Phen is 1,10-phenanthroline, Scheme 1)[9–11] and $[Cu(dmp)_2]^+$ (dmp is 2,9-dimethyl-1,10-phenanthroline, Scheme 2)[12] in acidic solutions were studied.

Scheme 1

$$Fe^{2+} + 3\ Phen \overset{i}{\rightleftharpoons} [Fe(Phen)]^{2+} + 2\ Phen \overset{i}{\rightleftharpoons} [Fe(Phen)_2]^{2+} + Phen \overset{ii}{\rightleftharpoons} [Fe(Phen)_3]^{2+}$$

i. Rapidly. *ii*. Slowly.

Scheme 2

$$Cu^+ + 2\ dmp \rightleftharpoons [Cu(dmp)]^+ + dmp \rightleftharpoons [Cu(dmp)_2]^+$$

The reactions were carried out in the presence of a large excess of the reagent at low pH (<3.5). Under these conditions, ligand protonation occurs as a competitive reaction. The equilibrium concentration of the ligand L (Phen or dmp) was determined according to the equation:

$$[L] = \frac{c_L}{1 + [H^+]K_b}, \quad (7)$$

where K_b is the equilibrium constant of ligand protonation; stepwise complexation was ignored. The equilibrium concentration was determined on the assumption that $c_L \gg [ML_z^{q+}]$ (M = Cu^I, Fe^{II}), which is necessary for Eq. (7) to be fulfilled:

$$[ML_z^{q+}] = \frac{\beta_{z(M,L)}c_M[L]^z}{1 + \beta_{z(M,L)}[L]^z}. \quad (8)$$

In the presence of a large excess of the ligand and at low pH, the consumption of the ligand for complex formation can be ignored. The theoretical signal was calculated by the equation:

$$S = \frac{[ML_z^{q+}]}{c_M}S_{max}, \quad (9)$$

where S_{max} is the analytical signal on condition that $c_M = [ML_z^{q+}]$. The stability constants $\beta_{m(M,L)}$ were calculated from the segment intercepted by the line

$$\gamma \equiv \lg\frac{S}{S_{max} - S} = \lg\beta_{z(M,L)} + z\lg[L] \quad (10)$$

on the *Y* axis; the concentration [L] was calculated from Eq. (7). The number of coordinated ligands z was calculated from the line slope. The stability constants were more precisely evaluated by substituting the stoichiometric value $z = 2$ (for $[Cu(dmp)_2]^+$) or $z = 3$ (for $[Fe(Phen)_3]^{2+}$) into Eq. (10):

$$\log\beta_{2(Cu,dmp)} = \gamma - 2\log[dmp], \quad (11)$$

$$\log\beta_{3(Fe,Phen)} = \gamma - 3\log[Phen]. \quad (12)$$

Competitive metal complexation

For the competitive reaction at the complex-forming metal atom, we studied complexation of copper(I) with Phen in a 4 : 1 DMSO—MeCN mixture:[13]

$$[Cu(MeCN)_4]^+ + 2\ Phen \rightleftharpoons [Cu(Phen)_2]^+ + 4\ MeCN,$$

which was accompanied by competitive complexation of copper(I) with MeCN:

$$Cu^+ + 4\ MeCN \rightleftharpoons [Cu(MeCN)_4]^+.$$

When acetonitrile is in large excess ($c_{MeCN} \gg c_{Cu}$), it is reasonable to assume that $[MeCN] = c_{MeCN}$. The stability constant $\log\beta_{2(Cu,Phen)}^{(DMSO)}$ was calculated from the segment intercepted by the line in the coordinates

$$\lg\frac{c_{MeCN}^4\theta/\zeta_2}{c_{Cu(MeCN)_4} - \theta/\zeta_2} = \lg\beta_{2(Cu,Phen)}^{(DMSO)} + z\lg(c_{Phen} - 2\theta/\zeta_2) \quad (13)$$

on the *Y* axis. The stability constant in an aqueous medium, $\log\beta_{2(Cu,Phen)}^{(aq)}$, was calculated on the assumption that $\beta_{4(Cu,MeCN)}c_{MeCN}^4 \gg 1$:

$$\lg\frac{\beta_{4(Cu,MeCN)}c_{MeCN}^4\theta/\zeta_2}{c_{Cu(MeCN)_4} - \theta/\zeta_2} = \lg\beta_{2(Cu,Phen)}^{(aq)} + z\lg(c_{Phen} - 2\theta/\zeta_2). \quad (14)$$

The coefficient ζ_2, which is equal to the theoretical signal of a $[Cu(Phen)_2]^+$ solution with a concentration of 1 mol L^{-1}, was calculated by the equation

$$\zeta_2 = 2.303\varepsilon_{[Cu(Phen)_2]}lE_0P_e. \quad (15)$$

Assuming the stoichiometric value $z = 2$, the overall stability constants of $[Cu(Phen)_2]^+$ in a 4 : 1 DMSO—MeCN mixture and water were calculated from the equations

$$\beta_{2(Cu,Phen)}^{(DMSO)} = \frac{c_{MeCN}^4\theta/\zeta_2}{(c_{Cu(MeCN)_4} - \theta/\zeta_2)(c_{Phen} - 2\theta/\zeta_2)^2}, \quad (16)$$

$$\beta_{2(Cu,Phen)}^{(aq)} = \beta_{2(Cu,Phen)}^{(DMSO)}\beta_{4(Cu,MeCN)}. \quad (17)$$

Calculations of stepwise stability constants

Copper(I)—1,10-phenanthroline

To determine the first-step stability constants, we used an approximation, according to which the only homoleptic complex $[Cu(MeCN)_2(Phen)]$ is formed by the reaction

$$[Cu(MeCN)_4]^+ + Phen \overset{K_{1(Cu,Phen)}^{(DMSO)}}{\rightleftharpoons} [Cu(MeCN)_2(Phen)]^+ + 2\ MeCN,$$

which is true for solutions containing copper in a low concentration and small amounts of 1,10-phenanthroline ($c_{Phen} \approx c_{Cu}$). In addition, $c_{MeCN} \gg c_{Cu}$. Hence, we assumed that $[MeCN] = c_{MeCN}$. The first-step stability constants of the complex in a 4 : 1 DMSO—MeCN mixture and water were calculated from the equations:

$$K_{1(Cu,Phen)}^{(DMSO)} = \frac{c_{MeCN}^2 \theta/\zeta_1}{(c_{Phen} - \theta/\zeta_1)(c_{Cu(MeCN)_4} - \theta/\zeta_1)}, \quad (18)$$

$$K_{1(Cu,Phen)}^{(aq)} = K_{1(Cu,Phen)}^{(DMSO)} \beta_{2(Cu,MeCN)}. \quad (19)$$

The ζ_1 coefficient, which is equal to the theoretical thermal lens signal of a solution containing the $[Cu(MeCN)_2(Phen)]^+$ complex in a concentration of 1 mol L^{-1}, was calculated by the equation

$$\zeta_1 = 2.303 \varepsilon_{[Cu(MeCN)_2Phen]} l E_0 P_e. \quad (20)$$

To estimate the second-step stability constants, we used an approximation, according to which copper is present only as the $[Cu(MeCN)_2Phen]^+$ and $[Cu(Phen)_2]^+$ complexes:

$$[Cu(MeCN)_2Phen]^+ + Phen \overset{K_{2(Cu,Phen)}^{(DMSO)}}{\rightleftharpoons} [Cu(Phen)_2]^+ + 2\ MeCN,$$

which is true for solutions containing an excess amount of Phen. The second-step stability constants in a 4 : 1 DMSO—MeCN mixture and water were calculated according to the following equations:

$$K_{2(Cu,Phen)}^{(DMSO)} = X/(Y \cdot Z), \quad (21)$$

$$X = \frac{\theta - \zeta_1 c_{Cu(MeCN)_4}}{\zeta_2 - \zeta_1} c_{MeCN}^2,$$

$$Y = c_{Cu(MeCN)_4} - \frac{\theta - \zeta_1 c_{Cu(MeCN)_4}}{\zeta_2 - \zeta_1},$$

$$Z = c_{Phen} - \frac{\theta - \zeta_1 c_{Cu(MeCN)_4}}{\zeta_2 - \zeta_1} - c_{Cu(MeCN)_4},$$

$$K_{2(Cu,Phen)}^{(aq)} = K_{2(Cu,Phen)}^{(DMSO)} \frac{\beta_{4(Cu,MeCN)}}{\beta_{2(Cu,MeCN)}}, \quad (22)$$

where ζ_1 and ζ_2 were calculated from Eqs (20) and (15), respectively.

Copper(I)—2,9-dimethyl-1,10-phenanthroline

The stepwise stability constants $K_{1(Cu,dmp)}$ and $K_{2(Cu,dmp)}$ were calculated by Yatsimirsky's method.[5,14,15] We derived the equations using the following approximations: (1) complexation occurs stepwise and the complexes are in the equilibrium state, (2) only $[Cu(dmp)]^+$ and $[Cu(dmp)_2]^+$ contribute to absorption, whereas all other components of the system show no significant adsorption at the operating wavelength. The stability constants were calculated according to the following equations:

$$K_{1(Cu,dmp)} = (a_1 b_1 + a_2 b_2)/(a_1 b_2 + b_1^2), \quad (23)$$

$$K_{2(Cu,dmp)} = a_2(1 + b_1)/(a_1 b_1 + a_2 b_2), \quad (24)$$

where the a_1 and a_2 parameters were evaluated on the assumption that the total concentration of the ligand tends to zero:

$$a_1 = \lim_{c_L \to 0} \frac{S}{c_M l [L]}$$

and

$$a_2 = \lim_{c_L \to 0} \left[\left(\frac{S}{c_M l [L]} - a_1 \right) \Big/ [L] \right], \quad (25)$$

and the b_1 and b_2 parameters were evaluated on condition that $[L] \to \infty$:

$$b_1 = \lim_{[L] \to \infty} \frac{S}{c_M l}$$

and

$$b_2 = \lim_{[L] \to \infty} \left(\frac{S}{c_M l} - b_1 \right) [L]. \quad (26)$$

In addition to Yatsimirsky's method, we calculated the stepwise stability constants of the copper(I) complexes from the experimental data, and solved the reverse problem, *i.e.*, calculated the dependence of the degree of complexation on the excess amount of the reagent in solution, using a polynomial least-squares method.

Experimental

Experiments were carried out on a dual-beam dual-laser thermal lens spectrometer.[16,17] The thermal lens was induced in a cell with an Innova 90-6 argon ion laser (Coherent, USA) at λ_e = 488.0 and 514.5 nm (TEM_{00} mode). An SP-106-1 helium neon laser (Spectra Physics, USA) with λ_p = 632.8 nm (4 mW in a cell with a sample, TEM_{00} mode) was used as the probe laser. The signal (intensity at the center of the probe beam) from the

photodiode was passed through an amplifier and directed to an ADC—DAC (analogue-to-digital converter and a digital-to-analogue converter) board installed on an IBM PC/AT. Measurements were synchronized on the computer using a specially designed program package.[16] Thermal lens measurements were carried out in quartz cells with a 1-cm optical path length. The wavelengths of the excitation laser (488.0 and 514.5 nm) were chosen taking into account the maximum sensitivity of measurements (molar absorptivities of the complexes and laser radiation power). The characteristics of the thermal lens device are given in Table 1. The curve of the instrumental error of a thermal lens spectrometer is described by the following equation:

$$\delta_{TLS} = \frac{0.27\theta\sqrt{(12\theta^2 - 675)/[\theta^3(8.1\theta - 650)]}}{0.21\sqrt{-\theta(8.1\theta - 650)} - 1.9\theta}. \qquad (27)$$

Spectrophotometric measurements were carried out on an SF-46 spectrophotometer using quartz cells (l = 1 cm). The copper content in the complex with MeCN was determined on a DR/2010 portable microprocessor-controlled spectrophotometer (HACH, USA). A universal EV-74 ionometer equipped with a glass indicator electrode and a silver chloride reference electrode was used to measure pH. The accuracy of measurements of pH was ±0.05.

The glassware (AO Khimlaborpribor, Klin, Russia) were made of a P2-20-14/23 glass (content: SiO_2, 74%; Al_2O_3, 5%; B_2O_3, 8%; CaO + MgO, 1.2%; Na_2O, 5%; K_2O, 2.8%; BaO, 4.0%; Fe_2O_3, at most 0.20%; SO_3, at most 0.40%; Sb_2O_3, at most 0.40%).[18]

The geometry of the Phen and dmp molecules and their complexes with copper(I) was calculated by the PM3 method (CS MOPAC, CambridgeSoft Corp., Cambridge, MA, USA). The electron densities in the molecules of the reagents were calculated using the CS Chem3D Pro® program package (CambridgeSoft Corp., Ver. 5.0).

The following solvents were used: bidistilled deionized water (Milli-Q, Millipore ultrapure water system, France: the specific resistance was at least 18 MOhm cm; the concentration of organic impurities was at most 5 ng mL^{-1}; the metal contents were lower than the following values: Cu, $5 \cdot 10^{-9}$%; Fe, $2 \cdot 10^{-9}$%; Co, $2 \cdot 10^{-10}$%; Ni, $7 \cdot 10^{-9}$%); rectified ethanol was purified by double distillation (t_b = 78.4 °C) according to a known procedure;[19] MeCN was of reagent grade; DMSO was a pharmaceutical material, which was purified from water by drying over $CaCl_2$ or BaO during a period of time from 1 h to one week followed by vacuum distillation (t_b = 190 °C, t_m = 18 °C). The thermal lens signals of the solvents and the calculated thermal-lens enhancement factors under the experimental conditions used (Eq. (2)) are given in Table 2.

The following reagents were used: copper(II) sulfate pentahydrate (analytical grade); a standard sample with iron(III) content of 0.1 g cm^{-3} (GSO 5219-90); concentrated aqueous ammonia (high-purity grade); ascorbic acid (pharmaceutical material); sodium perchlorate (analytical grade); copper(II) oxide (analytical grade); copper(I) oxide (analytical grade); 57% perchloric acid solution (reagent grade); potassium hydroxide (analytical grade); concentrated sulfuric acid (reagent grade); potassium sodium tartrate tetrahydrate (analytical grade); 1,10-phenanthroline hydrochloride (high-purity grade); 1,10-phenanthroline monohydrate (analytical grade); 2,9-dimethyl-1,10-phenanthroline hemihydrate (analytical grade). The copper(I) complex with acetonitrile $[Cu(MeCN)_4]ClO_4$ was synthesized according to a known procedure.[21]

Determination of stability constants in a copper(I)—2,9-dimethyl-1,10-phenanthroline system. A solution of potassium sodium tartrate (2 mL, 0.01 mol L^{-1}), a solution of ascorbic acid (1 mL, 0.001 mol L^{-1}), and a solution of 2,9-dimethyl-1,10-phenanthroline (2 mL) in 50% aqueous ethanol (stoichiometric excesses over copper in the final solution were 0.5—70) were added to a solution containing the required amount of copper(II) (the final concentration was $1 \cdot 10^{-4}$ mol L^{-1} or $1 \cdot 10^{-5}$—$1 \cdot 10^{-7}$ mol L^{-1}). The required pH (0—6.5) in the solution was achieved by adding sulfuric acid (0.001—5 mol L^{-1}). The volume of the solution was increased to 10 mL by adding distilled water. The solution was kept on a warm water bath (at 60 °C) for 30 min and then cooled to room temperature. Spectrophotometric measurements were carried out at 456 nm relative to a solution from the control experiment. Thermal lens measurements were carried out at 488.0 nm.

Determination of stability constants in a copper(I)—1,10-phenanthroline system. A solution of 1,10-phenanthroline in DMSO (stoichiometric excesses over copper in the final solution were 0.5—100) was added to a solution of $[Cu(MeCN)_4]ClO_4$ (2 mL, $1.2 \cdot 10^{-3}$ and $6.3 \cdot 10^{-6}$ mol L^{-1}, respectively), containing MeCN and DMSO in a ratio of 1 : 4. The volume of the solution was brought to 4 mL by adding a mixture of MeCN and DMSO (1 : 4). All solutions contained ascorbic acid at a concentration of $6.3 \cdot 10^{-3}$ mol L^{-1}. The absorbance was measured at 435 nm. Thermal lens measurements were carried out at 488.0 nm.

Determination of stability constants in an iron(II)—1,10-phenanthroline system. A solution of ascorbic acid (1 mL) with a

Table 2. Thermal-lens enhancement factors $E = E_0P_e$ (Eq. (2)) and thermal lens signals of the solvents used (after purification), T = 293 K

Solvent	λ_e = 488.0 nm, P_e = 0.12 W		λ_e = 514.5 nm, P_e = 0.20 W	
	E	Signal	E	Signal
Water	19.55±0.04	0.0010±0.0006	30.88±0.05	0.0010±0.0005
EtOH	308.6±0.1	0.020±0.008	487.4±0.1	0.020±0.007
DMSO	630±10	0.10±0.04	990±10	0.15±0.06
MeCN	580±5	0.010±0.007	910±5	0.010±0.005

Note: The thermal-lens enhancement factors were taken from the literature[4] (water, EtOH) or calculated from the data published in the study.[20]

concentration of $7 \cdot 10^{-7}$—$7 \cdot 10^{-3}$ mol L^{-1} (a tenfold stoichiometric excess over iron in the final solution) and a solution of 1,10-phenanthroline monohydrate (stoichiometric excesses over iron in the final solution were 0.5—300) were added to a solution of iron(III) (1 mL, $7 \cdot 10^{-8}$—$7 \cdot 10^{-4}$ mol L^{-1}). The required pH was obtained by adding a perchloric acid solution to the corresponding concentration. The volumes of the solutions were brought to 10 mL by adding distilled water. The absorbance and thermal lens signals were measured at 514.5 nm.

Results and Discussion

Requirements for systems and methods of investigation for calculation of stability constants

Let us estimate the optimum concentration level of metals and the maximum stability constant that is possible to determine by spectrophotometry and thermal lens spectrometry taking into account that the reasonable instrumental error should be at most 10%. At a 50% degree of complexation, the error in determination of the $[ML_z]/[M]$ ratio is minimum by definition (if the absolute error in determination of the concentration of the complex is constant). This point is determined by an equilibrium concentration of a free ligand equal to half the stoichiometric concentration.

Spectrophotometry is characterized by an instrumental error of ±10% at an absorbance of 0.05.[22] For the ML_z complex with $\varepsilon = 1 \cdot 10^4$ L mol^{-1} cm^{-1}, the optimum concentration $c_M = n \cdot 10^{-5}$ mol L^{-1}. Assuming that an excess amount of the ligand ($c_L = 10c_M$) is present under the experimental conditions, the apparent stability constant (in the conditions used) $\beta_{z(M,L)} \leq 10^{4z}$.

At $\theta = 0.015$, the instrumental error of TLS is ±10% (Eq. (27)). In aqueous solutions (in the experimental conditions used), $\theta/A = 2.303E_0P_e \geq 25$, whence it follows that $c_M \approx n \cdot 10^{-7}$ mol L^{-1} and $\beta_{z(M,L)} \leq 10^{6z}$. In organic solvents, $\theta/A = 2.303E_0P_e \geq 300$ (see Table 2), whence it follows that $c_M = n \cdot 10^{-8}$ mol L^{-1} and $\beta_{z(M,L)} \leq 10^{7z}$. Therefore, thermal lens spectroscopy allows one to determine the stability constants with the use of solutions containing complexes in concentrations two—three orders of magnitude lower than those required for conventional spectrophotometry and gives estimates of the apparent stability constants in a broader range.

Choice of systems for investigation

The restrictions on the above-mentioned maximum stability constants determined from experiments can be overcome by considering systems involving a competitive reaction with metal or a ligand. In this case, the apparent stability constants are determined experimentally, whereas the thermodynamic constants are calculated from the equilibrium constant of the competitive reaction.

The iron(II)—Phen mixture is a system of choice for examining the possibilities of TLS, because its absorption maximum ($\lambda_{max} = 510$ nm, $\varepsilon_{max} = 1.11 \cdot 10^4$)[23] is virtually equal to the main generation wavelength of an Ar^+ laser (514.5 nm), while the free ligand shows no adsorbtion in this region. The $[Fe(Phen)_3]^{2+}$ complex is thermodynamically stable, and the stability constants were confirmed by voluminous data obtained by different methods[24—26] (Table 3).

Table 3. Stability constants of iron(II) complexes with Phen

Method	Concentration range /mol L^{-1}	$\log\beta_{3(Fe,Phen)}$
Kinetic[10]	—	21.5
Electromotive force[9]	—	21.3
Spectrophotometry and potentiometry[27,28]	—	21.3
Spectrophotometry (interphase distribution)[23]	—	21.14
Spectrophotometry	$n \cdot 10^{-5}$ ($n = 5$)	21.5±0.3
	$n \cdot 10^{-6}$ ($n = 5$)	21.5±0.2
Thermal lens spectrometry, $\lambda_e = 514.5$ nm, $P_e = 90$ mW	$n \cdot 10^{-7}$ ($n = 11$)	21.3±0.1
	$n \cdot 10^{-8}$ ($n = 5$)	20.8±0.6

Note. $T = 293$ K ($P = 0.95$).

For the $[Fe(Phen)_3]^{2+}$ and $[Cu(dmp)_2]^+$ complexes, we used protonation of the reagent as a competitive reaction. These compounds offer the following advantages: the protonation constants of these compounds have been determined with high accuracy and were confirmed by independent methods,[24—26] and the equilibrium concentration of hydroxonium ions in solution can be determined by direct measurements. The $[Cu(Phen)_2]^+$ complex is rapidly oxidized in aqueous and aqueous-organic solutions. Hence, we used a 4 : 1 DMSO—MeCN aprotic mixture as the solvent. The reaction at the complex-forming metal atom giving copper(I) complexes with MeCN served as a competitive reaction.

Determination of overall stability constants in aqueous solutions

The influence of the solvent composition on the thermooptical effects plays the key role. However, aqueous solutions are unfavorable because of a small temperature gradient of the refractive index and high thermal conductivity.[1,3,4] The highest sensitivity of thermal lens measurements, *i.e.*, the best E_0 coefficient (Eq. (3)), is achieved in organic media characterized by a large temperature gradient of the refractive index and low thermal conductivity. However, water is more available as the solvent, can easily be purified, and serves as a convenient reaction medium. In addition, short-period vibrations of the thermal lens signal, which directly affect reproducibility of measurements, are substantially smaller in aqueous solutions than in organic media.[6] For this reason, we

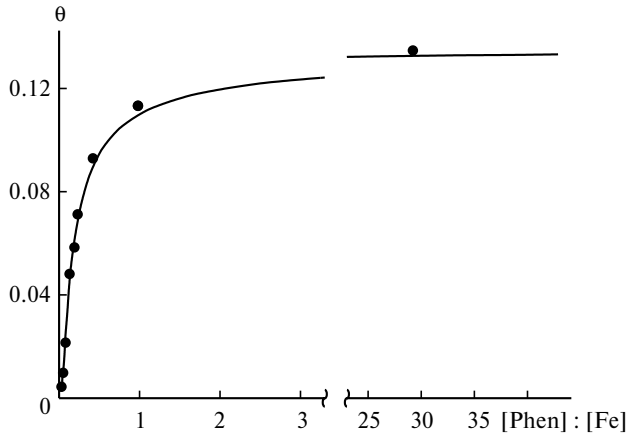

Fig. 2. Plot of the thermal lens signal in an iron(II)—Phen system ($c_{Fe} = 7 \cdot 10^{-7}$ mol L^{-1}) in the presence of a tenfold molar excess of ascorbic acid *vs*. the reactant concentration in an aqueous solution, pH 4.2; experimental (dotted curve) and calculated (solid curve) data; λ_e = 514.5 nm; P_e = 45 mW. The stability constants are given in Table 3.

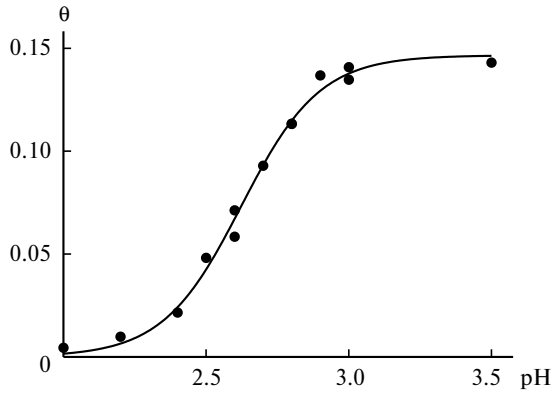

Fig. 3. Plot of the thermal lens signal of an aqueous iron(II) solution ($7 \cdot 10^{-7}$ mol L^{-1}) in the presence of 1,10-phenanthroline ($3 \cdot 10^{-5}$ mol L^{-1}) and ascorbic acid ($7 \cdot 10^{-6}$ mol L^{-1}) *vs*. pH; experimental (dotted curve) and calculated (solid curve) data, λ_e = 514.5 nm, P_e = 45 mW. The stability constants are given in Table 3.

determined the stability constants of $[Fe(Phen)_3]^{2+}$ and $[Cu(dmp)_2]^{+}$ in aqueous solutions.

For the iron(II) complexes, the stability constants ($n \cdot 10^{-5}$ and $n \cdot 10^{-7}$ mol L^{-1} determined by spectrophotometry and TLS, respectively) are equal to each other and to the corresponding values published in the literature[9,10,23,25,27,28] (see Table 3). The plots of the thermal lens signal *vs*. the metal to reagent ratio calculated by Eq. (9) from the stability constants (Fig. 2) and the plots of the concentration of the complex *vs*. pH (Fig. 3) agree well with the experimental data. These results were obtained throughout the concentration range used, $n \cdot 10^{-8}$—$n \cdot 10^{-6}$ mol L^{-1}. A high accuracy of the stability constants of $[Fe(Phen)_3]^{2+}$ determined by TLS at a level of $n \cdot 10^{-7}$—$n \cdot 10^{-6}$ mol L^{-1} (see Table 3) is attributable to the fact that the measurements were performed in substantially more dilute solutions than those used in spectrophotometry, which better corresponds to the ideal solution approximation.[5] In addition, the $[Fe(Phen)_3]^{2+}$ concentration range under study corresponds to the region of the lowest instrumental error of thermal lens measurements (Eq. (27)).

A comparison of the stability constants of the copper(I) complexes with dmp ($\log\beta_{2(Cu,dmp)}$ = 19.1, Table 4) and Phen ($\log\beta_{2(Cu,Phen)}$ = 15.8, Table 5) demonstrates that they differ from each other by more than three orders of magnitude. However, the introduction of the Me groups at positions 2 and 9 increases steric selectivity of dmp to copper(I) compared to Phen [5,25] and should not affect substantially stability of the complex only due to the inductive effect. This is confirmed by calculations of the geometry and the charge density distributions for Phen and dmp and their complexes with copper(I).[7]

Table 4. Stability constants of copper(I) complexes with dmp

Method	Copper concentration/mol L^{-1}	Calculation method	$\log\beta_{2(Cu,dmp)}$	$\log K_{1(Cu,dmp)}$	$\log K_{2(Cu,dmp)}$
Potentiometry[12]	$n \cdot 10^{-4}$	—	19.1		
Spectrophotometry	$n \cdot 10^{-4}$ (n = 10) pH 1.30	—	16.2±0.2	—	—
Thermal lens spectrometry	$n \cdot 10^{-5}$ (n = 10) pH 2.40	Without consideration for stepwise complexation	16.2±0.2	—	—
		Yatsimirsky's method	15.3±0.8	7.8±0.5	7.5±0.5
		Parametric method	15.4±0.5	7.9±0.3	7.5±0.3
	$n \cdot 10^{-6}$ (n = 5) pH 3.15	Without consideration for stepwise complexation	16.0±0.5	—	—
		Yatsimirsky's method	15.5±0.9	7.9±0.5	7.6±0.5
		Parametric method	15.3±0.6	7.8±0.3	7.5±0.3

Note. λ = 456 nm (spectrophotometry); λ_e = 488.0 nm, P_e = 90 mW; T = 293 K (TLS) (n = 5—10, P = 0.95).

Table 5. Stability constants of copper(I) complexes with Phen in a DMSO—MeCN solution (4 : 1)

Method	c_{Cu} /mol L^{-1}	Calculation method	$\log\beta_{2(Cu,Phen)}^{(DMSO)}$	$\log K_{1(Cu,Phen)}^{(DMSO)}$	$\log K_{2(Cu,Phen)}^{(DMSO)}$
Spectrophotometry[13]	$n\cdot10^{-4}$	Kinetic data	12.9	—	—
Spectrophotometry	$n\cdot10^{-4}$ (n = 10)	Without consideration for stepwise complexation	13.5±0.5	—	—
Thermal lens spectrometry	$n\cdot10^{-6}$ (n = 8)	Without consideration for stepwise complexation	11.7±0.2	—	—
		Yatsimirsky's method	11.1±0.8	5.8±0.4	5.3±0.4
		Parametric method	11.3±0.6	5.9±0.3	5.4±0.3

Note. λ_e = 488.0 nm, P_e = 90 mW, T = 293 K (P = 0.95).

Spectrophotometric measurements (Fig. 4, *a*) revealed that the average number of the ligands z = 2.1±0.1 (see Eq. (10), n = 10, P = 0.95). Calculations by Eq. (11) gave $\log\beta_{2(Cu,dmp)}$ = 16.2±0.2 (see Table 4). The number of the ligands estimated by TLS according to Eq. (10) in the concentration range of $n\cdot10^{-6}$—$n\cdot10^{-5}$ mol L^{-1} was 2.0±0.2 (n = 5; P = 0.95). The stability constants evaluated by TLS according to Eq. (11) differ slightly from each other and from the stability constant determined by spectrophotometry (see Table 4). The calculated plots of the concentration of the complex *vs.* pH (Eq. (7)) and the reactant to metal ratios (Eq. (9)) are also in good agreement with the experimental dependences throughout the concentration range used (see Fig. 4). On the whole, the stability constant is much closer to $\log\beta_{2(Cu,Phen)}$ = 15.8 published in the literature[12] and to the value obtained in the present study (see below). Therefore, a decrease in the concentration of the reagents from $n\cdot10^{-5}$—$n\cdot10^{-4}$ mol L^{-1} to $n\cdot10^{-8}$—$n\cdot10^{-6}$ mol L^{-1} is not accompanied by substantial changes in complexation of iron(II) with Phen and of copper(I) with dmp.

At the same time, a comparison of the results of thermal lens determination of the stability constants and analytical determination under the same conditions[8,29] (c_{Fe} = $n\cdot10^{-7}$ mol L^{-1} and c_{Cu} = $n\cdot10^{-7}$ mol L^{-1}) shows that reproducibility of thermal lens measurements of the stability constants (reagent saturation curves, Eqs (10) or (11) and (12)) is better than that of analytical methods (calibration curves).[8,29,30] This is attributable to the fact that the signal of the control experiment θ_0, which is determined by nonselective absorption of the reagents and the solvent, has virtually no effect on the reagent saturation curve lying at high values of the signal and, consequently, has almost no effect on the final stability constant compared to the effect of the free term of the calibration curve on its slope (see Ref. 22, Eq. (9.21)).

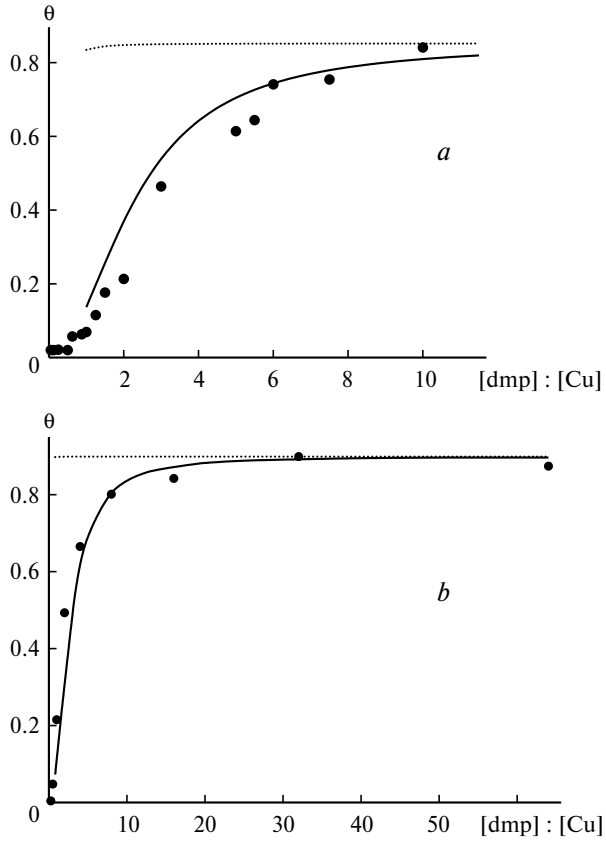

Fig. 4. Plot of the analytical signal (θ) in a copper(I)—dmp system *vs.* the reactant concentration in an aqueous solution; experimental (dotted curve) and calculated data obtained in the present study, $\log\beta_{2(Cu,dmp)}$ = 16.2 (solid curve), lit. data[12]: $\log\beta_{2(Cu,dmp)}$ = 19.1 (dashed curve). *a*, Spectrophotometry (c_{Cu} = $1\cdot10^{-4}$ mol L^{-1}, pH 1.30, λ = 456 nm); *b*, thermal lens spectrometry (c_{Cu} = $1\cdot10^{-5}$ mol L^{-1}, pH 2.40, λ = 488.0 nm; P_e = 90 mW.). The stability constants are given in Table 4.

Determination of stability constants in nonaqueous solutions

As mentioned above, the temperature gradient of the refractive index in most nonaqueous media is higher than that in water.[4] Therefore, the use of thermal lens spectrometry in nonaqueous solutions for the determination of stability constants holds considerable promise due to higher instrumental sensitivity of measurements. In the present study, we performed such thermal lens measure-

ments to determine the stability constants of the copper(I)—Phen complex in DMSO—MeCN mixtures. The formation of the copper(I) complexes with MeCN served as a competitive reaction.

The advantages of this approach are that the concentration of the free ligand in solution is a known and constant value. Good solubility of the complex is provided by DMSO, whereas MeCN, being simultaneously the ligand and solvent, increases resistance of the $[Cu(Phen)_2]^+$ complex to oxidation with atmospheric oxygen.[30] We used a 4 : 1 DMSO—MeCN mixture in the presence of an excess of ascorbic acid ($6.3 \cdot 10^{-3}$ mol L^{-1}) to prevent oxidation of copper(I). At higher concentrations of MeCN, the solubility of the complex substantially decreases.

Under the conditions used, the competitive reaction plays a substantial role at $[Cu(MeCN)_4]/[Phen] < 1$. The stability constant calculated from the spectrophotometric data (Eqs (14) and (16)), $\log\beta_{2(Cu,Phen)}^{(DMSO)} = 13.5 \pm 0.5$ ($n = 10$; $P = 0.95$), agrees well with the only known reliable constant for the system under consideration:[13] $\log\beta_{2(Cu,Phen)}^{(DMSO)} = 12.9$. The stability constant determined by thermal lens spectrometry (see Fig. 4, *b*) according to Eq. (14) is $\log\beta_{2(Cu,Phen)}^{(DMSO)} = 11.7 \pm 0.2$; $z = 1.5 \pm 0.4$ ($n = 8$; $P = 0.95$).

A comparison of the saturation curves (see Figs 4, *b* and 5, *b*) shows that, as expected, the thermal lens signal in a nonaqueous solution is higher than that in aqueous solutions, while the reproducibility of measurements remains at the same level. As a result, the accuracy of the stability constants for $[Cu(Phen)_2]^+$ determined at the same concentration level ($n \cdot 10^{-6}$ mol L^{-1}) is substantially higher (*cf.* Tables 4 and 5) and is comparable with the accuracy of the estimates of $\beta_{3(Fe,Phen)}$ (see Table 3) in spite of the fact that the molar absorptivity of the iron complex is much higher.

Having reliable estimates of $\beta_{2(Cu,MeCN)}$ and $\beta_{4(Cu,MeCN)}$, the overall stability constants for $[Cu(Phen)_2]^+$ in water ($\beta_{2(Cu,Phen)}^{(aq)}$) can be evaluated from Eq. (17). The stability constants of the acetonitrile copper complex in DMSO are lacking in the literature. Because of this, we performed calculations with the use of the stability constants of this complex in 2-butanol ($\log\beta_{2(Cu,MeCN)}^{(2\text{-BuOH})} = 3.9$; $\log\beta_{4(Cu,MeCN)}^{(2\text{-BuOH})} = 5.1$)[31] because this solvent does not form complexes with copper(I) and its dielectric permeability and orientational polarizability are most close to those of DMSO. The value of $\beta_{2(Cu,Phen)}^{(aq)}$ agrees well with those published in the literature[12] (Table 6) and with $\beta_{2(Cu,dmp)}$ (see Table 4).

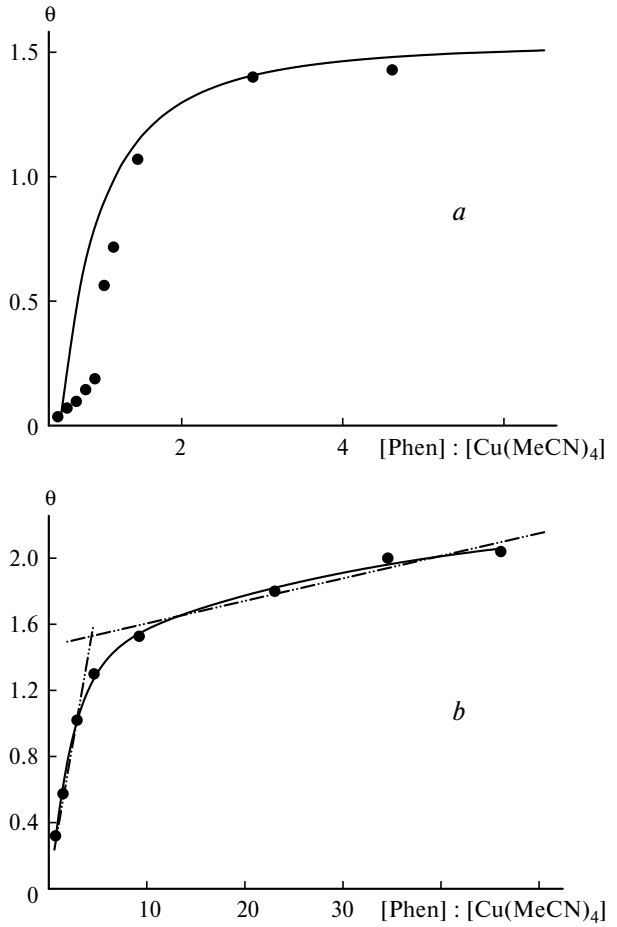

Fig. 5. Plot of the analytical signal (θ) in a copper(I)—Phen system *vs.* the reactant concentration in a 4 : 1 DMSO—MeCN mixture, the concentration of ascorbic acid was $6.3 \cdot 10^{-3}$ mol L^{-1}; *a*, spectrophotometry, $\lambda = 488.0$ nm, $c_{Cu} = 6 \cdot 10^{-4}$ mol L^{-1}, *b*, thermal lens spectrometry, $\lambda_e = 488.0$ nm, $P_e = 90$ mW, $c_{Cu} = 2 \cdot 10^{-6}$ mol L^{-1}. The stability constants are given in Table 5.

Table 6. Stability constants of copper(I) complexes with Phen in water

Method	c_{Cu} /mol L^{-1}	Calculation method	$\log\beta_{2(Cu,Phen)}^{(aq)}$	$\log K_{1(Cu,Phen)}^{(aq)}$	$\log K_{2(Cu,Phen)}^{(aq)}$
Potentiometry[12]	$n \cdot 10^{-4}$	Kinetic data	15.8	—	—
Thermal lens	$n \cdot 10^{-6}$	Without consideration	16.8±0.3	—	—
spectrometry	($n = 8$)	for stepwise complexation			
		Yatsimirsky's method	16.2±0.9	9.7±0.4	6.5±0.5
		Parametric method	16.4±0.6	9.8±0.3	6.6±0.4

Note. $\lambda_e = 488.0$ nm, $P_e = 90$ mW, $T = 293$ K ($P = 0.95$).

Determination of stepwise stability constants

In spite of systematic studies of complexation, data on the stepwise stability constants for complexes with even widely used ligands are often lacking in the literature.[5,30,32] The overall stability constants of the complexes and analysis of the correlation dependences for the known stability constants of transition metal complexes with Phen and its derivatives[5—7,23,26—28,30,32,33] suggest that the stepwise stability constants can be determined under the conditions used. However, the spectrophotometric ligand saturation curves are either strongly distorted (see Fig. 5, *a*) or little informative (see Fig. 4, *a*). Hence, it is practically impossible to determine stepwise stability constants from spectrophotometric data. We determined these constants in the systems under consideration by TLS.

A comparison of the spectrophotometric (see Figs 4, *a* and 5, *a*) and thermal-lens saturation curves (see Figs 4, *b* and 5, *b*) shows that they differ substantially from each other, which is attributable to the effect of stepwise complexation of copper in this system at lower concentration levels.[7]

For $[Cu(Phen)_2]^+$, the ligand saturation curve clearly shows two regions with different slopes (see Fig. 5, *b*) characterized by a ratio of 1 : 2. This is evidence that under the conditions of thermal lens measurements, it is possible to observe stepwise complexation in the system under consideration. The stability constants are given in Table 5. These constants agree well with each other, and the $\log K_{1(Cu,Phen)}/\log K_{2(Cu,Phen)}$ ratio correlates with the analogous ratios for the copper(II) and nickel(II) complexes with Phen.[24,25] The overall stability constant determined from these calculations differs insignificantly from that calculated by Eq. (16) (see Table 5). Analogously to the calculation of the overall stability constant, we estimated the stepwise stability constants of this complex in aqueous solutions (Eqs (19) and (22), see Table 6). Therefore, we succeeded in determining the stepwise stability constants due to the use of more dilute solutions in the presence of a larger relative excess of the competitive ligand without changes in the solution composition.

For the $[Cu(dmp)_2]^+$ complex, stepwise complexation under the same conditions is less pronounced (see Fig. 4, *b*). To compare the results, we used the following two approaches: Yatsimirsky's method (Eqs (23)—(26)) and the determination of the $K_{1(Cu,dmp)}$ and $K_{2(Cu,dmp)}$ constants from the polynomial regression of the saturation curves. The results are given in Table 4. Both approaches gave values, which insignificantly differ from each other. For the copper concentrations of $1 \cdot 10^{-5}$ and $1 \cdot 10^{-6}$ mol L^{-1}, the results of calculations are equal in accuracy (see Table 4).

A comparison with the results for the $[Cu(Phen)_2]^+$ complex demonstrates that the error in determination of the stepwise constants for $[Cu(dmp)_2]^+$ is higher. This is associated with both a rather small number of measurements and the assumptions of Yatsimirsky's method, which employs an approximation of the dependences to a particular value of one of the parameters (Eqs (23) and (24)). Nevertheless, $\log\beta_{2(Cu,dmp)} = 15.3 \pm 0.8$ ($n = 8$; $P = 0.95$) determined by this method is consistent with $\log\beta_{2(Cu,dmp)} = 16.0 \pm 0.5$ calculated by Eq. (11).

Due to good reproducibility of the reactant saturation curve (see Fig. 4, *b*), the second approach can be extended to the determination of three unknowns, *viz.*, the $K_{1(Cu,dmp)}$ and $K_{2(Cu,dmp)}$ constants and the protonation constant of 2,9-dimethyl-1,10-phenanthroline. These three constants can be simultaneously determined only if pH is lower than $pK_{a(dmp)}$ by no more than 1—2 (Eq. (8)), and all stability constants were determined under these conditions. Although in this case the error in determination is higher, this approach allows one to determine all three parameters from the results of a single experiment without additional measurements. The resulting stepwise stability constants ($\log K_{1(Cu,dmp)} = 8 \pm 1$ and $\log K_{2(Cu,dmp)} = 7 \pm 1$) differ insignificantly from those evaluated as described above (see Table 4), and $pK_{a(dmp)}$ is 5.8 ± 0.5 ($n = 8$; $P = 0.95$), which is in good agreement with the data published in the literature.[25,34]

Therefore, processing of the spectrophotometric saturation curves for copper(I) *bis*-(1,10-phenanthrolinate) and copper(I) *bis*-(2,9-dimethyl-1,10-phenanthrolinate) did not allow us to determine the stepwise stability constants with reasonable accuracy. To the contrary, the stepwise constants can be determined by thermal lens measurements in dilute solutions with satisfactory accuracy.

As a practical result, it should be noted that the differences in the observed reactant saturation curves for the two methods used are associated not with changes in the overall stability constants but with a higher effect of stepwise complexation at lower concentration levels of metals and, consequently, of the complex. We used this fact to develop procedures for the determination of iron using Phen[8] and of copper using Phen [30] and dmp.[29] In all cases, the detection limits were $n \cdot 10^{-9}$—$n \cdot 10^{-8}$ mol L^{-1}.

* * *

To summarize, the stability constants in the systems under study were determined by two methods, *viz.*, by spectrophotometry ($n \cdot 10^{-5}$—$n \cdot 10^{-4}$ mol L^{-1}) and thermal lens spectrometry ($n \cdot 10^{-8}$—$n \cdot 10^{-6}$ mol L^{-1}). The results of determination demonstrate that TLS offers a number of advantages. 1. Reproducibility of the results of thermal lens measurements of stability constants is higher than that achieved by spectrophotometry. This is attributable to the fact that low concentration levels of the reagents better correspond to the ideal solution approximation. As a result, the use of TLS makes it possible to refine the stability constants. 2. Low working concentrations

($n \cdot 10^{-8}$—$n \cdot 10^{-6}$ mol L^{-1}) employed in TLS allows the determination of the stepwise stability constants in systems, where they cannot be determined by conventional methods.

In addition to the determination of the fundamental characteristics, which is of interest by itself, thermal lens spectrometry enables one to obtain results of practical importance. The parameters of analytical reactions determined in the present study make it possible to choose the optimum conditions for analytical reactions at trace levels, which, in turn, can help in developing highly sensitive procedures of thermal lens determination and substantially decreasing the detection limits and minimal detectable concentrations.

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