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Thermal-Lens Spectrometric Study of Processes in Two-Phase Systems: Extraction Determination of Copper As Diethyldithiocarbamate

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Abstract—The metrological characteristics of the extraction–thermal-lens determination of copper as diethyldithiocarbamate have been determined. The smallest reagent : metal ratio ensuring 100% extraction is 60 : 1. The copper detection limit is 8×10^{-9} mol/l. Copper(II) extraction with zinc diethyldithiocarbamate had been investigated in an unagitated system. The formation rate of the copper complex in chloroform is governed by two processes, namely, the diffusion of copper(II) across the interface and the substitution of copper for zinc in zinc diethyldithiocarbamate. The signal from copper(II) diethyldithiocarbamate in the organic phase was measured as a function of the distance between the measurement point and the interface. The diffusion of the complex forming in the organic phase exerts no effect on the formation of this complex. The experimental data pertaining to the “diffusion-controlled” portion of the thermal-lens signal curve are consistent with the model based on Fick’s equation.

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Dithiocarbamates are wisely used as reagents in organic synthesis, medicine, biology, and other fields of science [1–4]. Furthermore, pesticides of the carbamate family have almost replaced DDT, lindane, and other familiar pesticides [5, 6]. Metal carbamates are highly bioactive. Their polarity ranges between medium and high. Under environmental conditions, some of them turn into substances with a still higher polarity and toxicity [4]. However, dithiocarbamate complexes have not been adequately studied. In particular, the literature contains no distribution constant data for these complexes in water–organic phase systems. Furthermore, the spectrophotometric detection of dithiocarbamates is insufficiently sensitive [7, 8].

Fluorimetry is a very sensitive method, but it requires a complicated sample preparation technique for obtaining fluorescing analytical species of dithiocarbamates [9, 10].

The extra advantages of photothermal spectrometric methods, primarily thermal-lens spectrometry, are high sensitivity and nondestructivity. The potential of thermal-lens spectrometry is most clearly seen in fundamental studies, particularly in the investigation of reactions at low reactant concentrations [11–13], including two-phase systems [14].

This work is devoted to carbamate complex formation and extraction. Specifically, we report a thermal-lens spectrometric study of the model system copper(II) diethyldithiocarbamate–water–chloroform.

EXPERIMENTAL

Instruments. Thermal-lens measurements were carried out with a dual-beam two-laser spectrometer [15]. A thermal lens was induced in the cell using an argon ion laser (Innova 90-6, Coherent, United States; $\lambda = 514.5$ nm; TEM_{00} mode). The probing laser was a He–Ne one (SP-106-1, Spectra Physics, United States; $\lambda = 632.8$ nm; TEM_{00} mode). The most important characteristics of the spectrometer are listed in the table. The thermal-lens signal was measured using quartz cells with an optical path length of 1 cm. The residual copper(II) concentration in water was determined by atomic absorption spectroscopy on an AAS-3 spectrometer (Carl Zeiss, Germany) using electrothermal atomization.

Solvents and reagents. The solvents were chloroform (spectrophotometric grade), deionized water (Milli-Q, resistivity 5 MΩ cm, pH 5.8), which were used as-received. The reagents were sodium diethyldithiocarbamate (hereafter, NaDDC; analytical grade), copper(II) oxide (analytical grade), zinc nitrate hexahydrate (analytical grade), and concentrated HNO_3 (reagent grade). The base solution of copper was obtained by completely dissolving CuO (0.040 g) in a mixture of concentrated HNO_3 (5 ml) and distilled water (5 ml) heated in a water bath. The resulting solution was cooled and was adjusted to 100 ml with distilled water. The ultimate copper concentration was 5×10^{-3} mol/l.

Configuration parameters of the dual-beam thermal-lens spectrometer

Inducing laser	Wavelength (λ_e, nm)	514.5
	Focal length of the focusing lens (f_e, mm)	300
	Confocal length ($z_{c,\,e}$, mm)	6.4
	Laser radiation power in the cell (P_e, mW)	80–500
	Beam waist diameter ($2 \times \omega_{0e}$, μm)	64.5
Probing laser	Wavelength (λ_e, nm)	632.8
	Focal length of the focusing lens (f_e, mm)	185
	Confocal length ($z_{c,\,e}$, mm)	0.9
	Laser radiation power in the cell (P_e, mW)	3
	Beam waist diameter ($2 \times \omega_{0e}$, μm)	27
Geometric parameters	Optical path length (l, μm)	100
	Distance between the cell and the detector (cm)	180
	Ratio of the cross-sectional areas of the probing and inducing beams in the cell (m)	2.85
	Relative distance between the waist of the inducing beam and the cell (V)	3.93
	Chopping frequency (ψ, Hz)	2

Synthesis and properties of zinc diethyldithiocarbamate. $Zn(NO_3)_2 \cdot 6H_2O$ (0.1045 g) and NaDDC (0.235 g) were dissolved in distilled water (50 ml). The solution was stirred, and the resulting white precipitate of the zinc complex was vacuum-filtered, washed with distilled water, and dried at 100–110°C. The product was stored in a glovebox at room temperature. The $Zn(DDC)_2$ complex is white, readily soluble in chloroform, and stable in the dark for a long time. The base solution of the complex (0.0115 mol/l) was prepared by dissolving the reagent (0.0209 g) in chloroform (5 ml). The working solution of the complex (4.6×10^{-5} mol/l) was prepared immediately before the experiment by adding 40 μl of the base solution to 10 ml of chloroform. The absorption spectrum of zinc diethyldithiocarbamate in chloroform is in agreement with the literature [7]. Based on the spectral properties of copper(II) diethyldithiocarbamate and on the characteristics of the thermal-lens spectrometer, the thermal lens–inducing wavelength was chosen to be $\lambda_e = 514.5$ nm.

Procedure 1: extraction–thermal-lens determination of copper. The calibration plot for copper(II) diethyldithiocarbamate concentrations between 2×10^{-7} and 1.5×10^{-5} mol/l was constructed as follows. The working solution of copper nitrate (2.5×10^{-5} mol/l, 20 μl to 1.5 ml) was diluted with distilled water to 3 ml. the working solution of zinc diethyldithiocarbamate in chloroform was added, and the copper complex was extracted for 2 min. Forty minutes after phase separation, the aqueous phase was removed and the thermal-lens signal from the organic phase was measured (P_e = 60 mW, λ_e = 514.5 m). The residual copper(II) concentration in the aqueous phase was determined by electrothermal atomic absorption spectroscopy.

Procedure 2: study of complex formation and extraction in the unagitated system. Distilled water (1.4 ml) and chloroform (1.4 ml) containing zinc diethyldithiocarbamate (4.6×10^{-5} mol/l) were placed in a quartz cell with an optical path length of 1 cm. The phases were not agitated. The laser beam was passed through the organic phase at a certain distance from the interface. The working solution of copper(II) (1×10^{-3} mol/l, 20–200 μl) was micropipetted into the aqueous phase. The thermal-lens signal from the organic phase was measured for 20 min at $\lambda_e = 514.5$ nm and an inducing radiation power of $P_e = 60$ mW.

Procedure 3: kinetic study of the diffusion transfer of copper(II) diethyldithiocarbamate in the organic phase. Distilled water (1.4 ml) and chloroform (1.4 ml) containing zinc diethyldithiocarbamate (4.6×10^{-5} mol/l) were placed in a quartz cell with an optical path length of 1 cm. The phases were not agitated. The laser beam was passed through the organic phase. The working solution of copper(II) (1×10^{-3} mol/l, 20 μl) was micropipetted into the aqueous phase. The thermal-lens signal from the organic phase was measured for 20 min while varying the beam–interface distance between 0 and 6 mm ($\lambda_e = 514.5$ nm, $P_e = 60$ mW).

Thermal-length signal evolution parameters. A single measurement taken from the sample is an apparatus signal (ϑ) defined as follows [11]:

$$\vartheta = \frac{I_p(0) - I_p(\infty)}{I_p(\infty)}, \tag{1}$$

where $I_p(0)$ is the intensity of probing radiation in the absence of a thermal lens (when the shutter of the modulator is closed) and $I_p(\infty)$ is the intensity of probing radiation when the thermal lens is fully developed (the

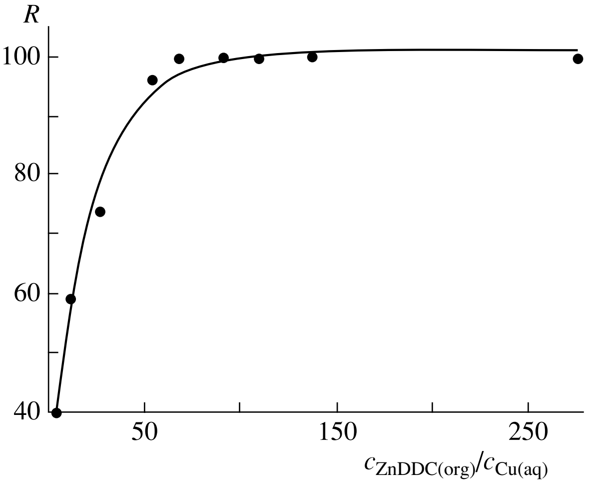

Fig. 1. Extent of copper(II) diethyldithiocarbamate extraction into the organic phase as a function of the reagent : metal ratio ($l_e = 514.5$ nm, $P_e = 60$ mW, $c_{Zn(DDC)_2} = 4.6 \times 10^{-5}$ mol/l).

shutter of the modulator is completely open). The following quantity was used as the analytical thermal-lens signal [11, 12]:

$$\theta = 2.303 E_0 P_e A, \tag{2}$$

where P_e is the power of the radiation inducing the thermal length (W), A is the absorbance of the sample (medium), and E_0 is the sensitivity enhancement factor as the ratio of the thermal-lens signal to the conventional spectrophotometric signal for inducing radiation of unit power. The factor E_0 is expressed as

$$E_0 = \frac{(-dn/dT)}{\lambda_e k}, \tag{3}$$

where λ_e is the wavelength of the inducing laser, dn/dT is the temperature gradient of the refractive index, and k is thermal conductivity. The analytical signal θ and the apparatus signal ϑ are interrelated by the equation

$$\vartheta = (1 - B\theta)^2 - 1, \tag{4}$$

where B is the geometric constant of the spectrometer,

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

which takes into account the distance between the waist of the probing beam and the cell (V, in units of the confocal length of the inducing laser), as well as the ratio of the cross-sectional areas of the probing and inducing beams in the sample m [11].

RESULTS AND DISCUSSION

In thermal-lens measurements in the organic phase, the signal evolution curve indicates convective oscillations with a constant period and a rather random amplitude. This causes severe difficulties in the measurements. Earlier, we demonstrated that the amplitude of convective oscillations depends strongly on thermal-lens signal measurement parameters [14]. In our experiments, we set the time-resolved measurement time at 300 ms (100 points) and the steady-state thermal-lens measurement time at 500 ms (900 points) for the reason that, at these measurement parameters, there are no significant oscillations of the thermooptical signal [14].

Thermal-lens study of the extraction of copper(II) with zinc diethyldithiocarbamate in an agitated system. Considering the high purity of the solvents and reagents, we did not further purify them prior to thermal-lens measurements. The magnitude of the thermal-lens signal in the blank run did not exceed 0.10 and was low as compared to the range in which the signal magnitude varied during the reaction ($\Delta\theta = 3.5$). The magnitude of the blank signal, which was determined by the purity of $Zn(DDC)_2$ in chloroform, decreased with time. For this reason, the working solution of this reagent was prepared immediately before measurements.

The metrological characteristics of the extraction–thermal-lens determination of copper(II) with zinc diethyldithiocarbamate (procedure 1) were evaluated using the calibration plot defined by the equation

$$\begin{gathered} \theta = (8.97 \pm 0.05) \times 10^5 c - (0.096 \pm 0.007), \\ n = 6, \quad P = 0.95, \quad r = 0.998, \end{gathered} \tag{6}$$

where c is the molar concentration of copper(II) in the organic phase. The detection limit is 8×10^{-9} mol/l, approximately six times lower than the detection limit in the extraction–thermal-lens determination of copper(II) with sodium diethyldithiocarbamate [16]. The range of determinable copper(II) concentrations is 3.0×10^{-8}–1.0×10^{-6} mol/l. For initial concentrations of 4×10^{-8} to 7×10^{-7} mol/l, it was demonstrated that the residual copper(II) concentration in the aqueous phase is negligible (the recovery factor is 100%). For the initial concentration 1×10^{-6} mol/l, the copper(II) concentration in the aqueous phase is no higher than 3×10^{-8} mol/l. The dependence of the amount of copper transferred to chloroform on the $c_{(ZnDDC)org}/c_{(Cu)aq}$ ratio is plotted in Fig. 1. The smallest reagent : metal ratio ensuring 100% recovery is 60 : 1.

Copper(II) mass transfer with zinc diethyldithiocarbamate. Extraction and complex formation were studied under conditions such that the metal (copper) ion is in the aqueous phase and the ligand (zinc diethyldithiocarbamate) is in the organic phase. The phases were not mixed mechanically. Complex formation at the interface and the diffusion of the complex into the organic phase were monitored by measuring the thermal-lens signal from the organic phase near the interface.

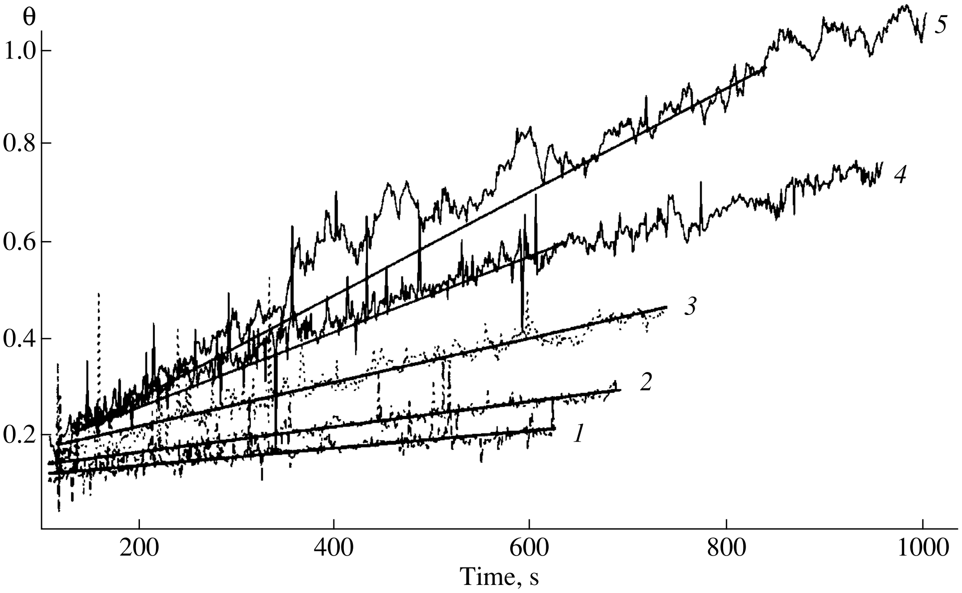

Fig. 2. Kinetics of copper(II) extraction with zinc diethyldithiocarbamate into the organic phase in the unagitated system. The copper(II) concentration in the aqueous phase is (*1*) 2.8×10^{-5}, (*2*) 4.3×10^{-5}, (*3*) 5.7×10^{-5}, (*4*) 7.1×10^{-5}, and (*5*) 1.4×10^{-4} mol/l. $c_{Zn(DDC)_2} = 4.6 \times 10^{-5}$ mol/l; $l_e = 514.5$ nm; $P_e = 60$ mW. Data processing is illustrated for curve *5*.

Figure 2 illustrates the evolution of the thermal-lens signal from the complex in the organic phase for various copper(II) concentrations in the aqueous phase. The increase in the signal magnitude is due to copper(II) transfer across the interface and the formation of copper diethyldithiocarbamate through the replacement of zinc in its complex. The amount of copper transferred in a certain time interval (10 min) is derived from the calibration plot for the thermal-lens signal (Eq. (1)). For all concentrations examined, the recovery factor did not exceed 3% (Fig. 3).

The copper(II) complex formation rate depends on two processes, namely, the diffusion of copper(II) ions across the interface and the substitution of copper(II) for zinc in zinc diethyldithiocarbamate. Which of the processes will dominate depends on the initial copper(II) concentration in the aqueous phase (Fig. 4). At a copper concentration below 4×10^{-5} mol/l in the aqueous phase, the complex formation rate is nearly constant. Evidently, copper(II) diffusion across the water–chloroform interface is the rate-limiting process and is most likely controlled by copper(II) diffusion in the aqueous medium toward the interface. At copper(II) concentrations of 4×10^{-5} to 1×10^{-4} mol/l in the aqueous phase, the complex formation rate is proportional to the copper concentration. Apparently, the rate-limiting process in this case is the formation of the copper(II) complex. This view is confirmed by the fact that, at high copper(II) concentrations, the signal magnitude grows less rapidly because of the decreased metal : reagent ratio.

Copper(II) diethyldithiocarbamate diffusion in the organic phase. Irrespective of the distance between the measurement point and the interface (l), the signal versus time curve runs like that shown in Fig. 5: the signal increases linearly up to some time point t_0, at which its buildup slows down. The higher-to-lower buildup

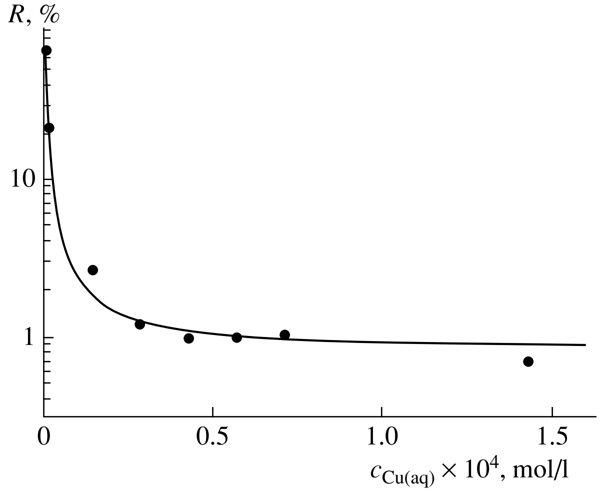

Fig. 3. Amount of copper(II) transferred into the organic phase in the unagitated system 10 min after the beginning of extraction as a function of the initial copper(II) concentration in the aqueous phase. $l_e = 514.5$ nm; $P_e = 60$ mW; $c_{Zn(DDC)_2} = 4.6 \times 10^{-5}$ mol/l.

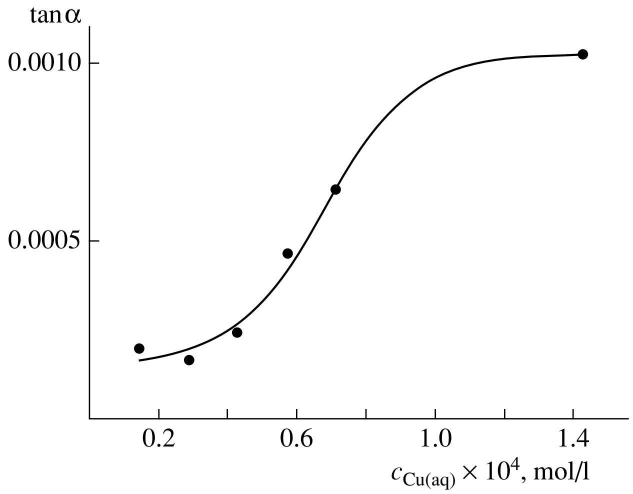

Fig. 4. Copper(II) diethyldithiocarbamate formation rate in chloroform as a function of copper(II) concentration in the aqueous phase. l_e = 514.5 nm; P_e = 60 mW; $c_{Zn(DDC)_2}$ = 4.6×10^{-5} mol/l.

rate transition occurs at the same time of $t_0 = 6.6 \pm 0.2$ s for l = 0.2–3.0 mm (Fig. 6). Since t_0 is independent of the measurement point, it is reasonable to assume that the run of the signal magnitude curve is governed by the copper diethyldithiocarbamate formation kinetics. In order to verify this assumption, we calculated the rate constant for copper diethyldithiocarbamate formation via the reaction between the copper ion and zinc diethyldithiocarbamate, using the following equation:

$$k_1 = \frac{\beta_{Cu(DDC)_2}}{\beta_{Zn(DDC)_2}} k_{-1}. \qquad (7)$$

Here, $\beta_{Cu(DDC)_2}$ and $\beta_{Zn(DDC)_2}$ are the stability constants of copper and zinc diethyldithiocarbamates ($\log\beta_{Cu(DDC)_2} = 12.6$ [16], and $\log\beta_{Zn(DDC)_2} = 11.4$ [17]) and k_{-1} is copper diethyldithiocarbamate decomposition rate constant ($k_{-1} = 0.03$ min^{-1} [16]). Equation (7) gives $k_1 = 0.6$ min^{-1}, implying that the degree of complexation of copper at the time t_0 is 95 ± 2%. Therefore, the run of the initial portion of the curve in Fig. 5 is explained by the fact that the process is controlled both by the formation of copper diethyldithiocarbamate and by the diffusion of this complex into the bulk of the organic phase. Starting at the time t_0, the process rate is determined only by the diffusion of the complex.

This inference is confirmed by the observed dependence of the copper(II) diethyldithiocarbamate signal buildup rate on the distance between the measurement point and the interface for both portions of the signal magnitude curve (Fig. 7). The slope of the second portion of the curve in Fig. 5 is in agreement with Fick's equation:

$$c(x, t) = \frac{c_0}{2}\left(1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right), \qquad (8)$$

where x is the coordinate along the diffusion mass transfer direction (normal to the interface), t is the diffusion time (s), c_0 is the substance concentration at the initial time point of diffusion (mol/l), and D is the diffusion coefficient (here, $D = 5 \times 10^{-6}$ cm^2/s).

Thus, the diffusion of the resulting complex in the organic phase is fairly rapid and does not affect the formation of copper(II) diethyldithiocarbamate. An analysis of the curve shown in Fig. 5 demonstrated that the

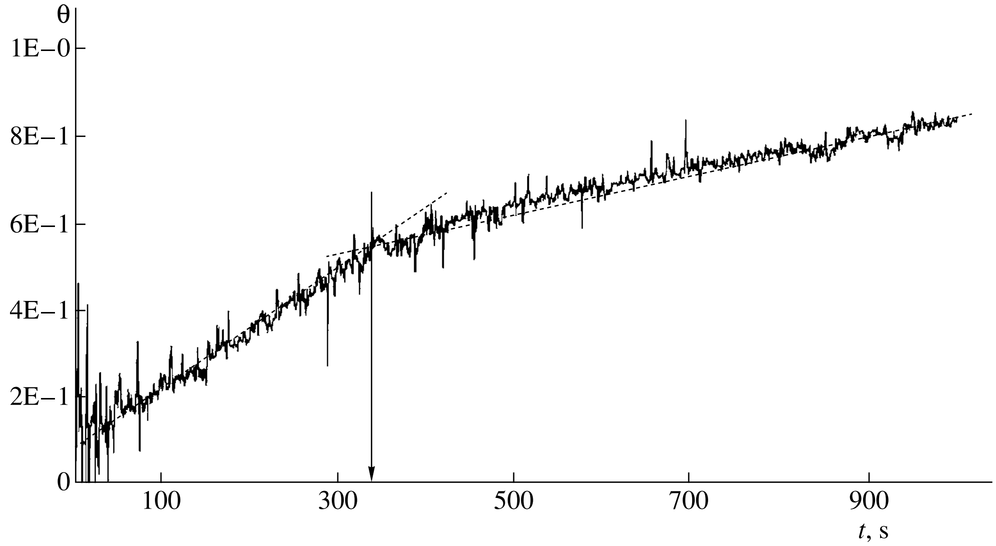

Fig. 5. Evolution of the thermal-lens signal from copper(II) diethyldithiocarbamate in chloroform. The distance between the measurement point and the interface is 620 μm; $c_{Cu(aq)} = 7 \times 10^{-5}$ mol/l; $c_{Zn(DDC)_2} = 4.6 \times 10^{-5}$ mol/l; l_e = 514.5 nm; P_e = 60 mW.

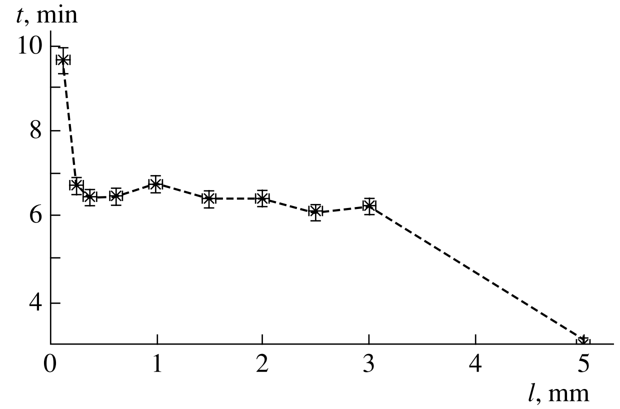

Fig. 6. Time point at which the thermal-lens signal changes its buildup rate versus the distance between the measurement point and the interface. $c_{\text{Cu(aq)}} = 7 \times 10^{-5}$ mol/l; $c_{\text{Zn(DDC)}_2} = 4.6 \times 10^{-5}$ mol/l; $l_e = 514.5$ nm; $P_e = 60$ mW.

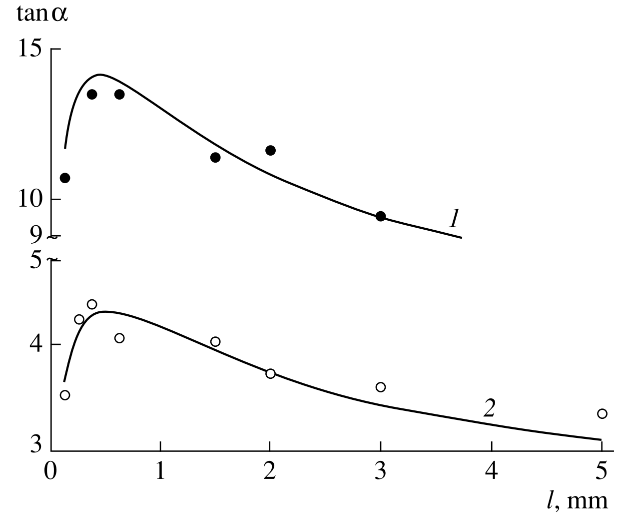

Fig. 7. Copper(II) diethyldithiocarbamate transfer rate in chloroform versus the distance between the measurement point and the interface for (*1*) the initial portion of the curve plotted in Fig. 5 and (*2*) the $t > t_0$ portion of the same curve. $c_{\text{Cu(aq)}} = 7 \times 10^{-5}$ mol/l; $c_{\text{Zn(DDC)}_2} = 4.6 \times 10^{-5}$ mol/l; $l_e = 514.5$ nm; $P_e = 60$ mW.

largest amount of copper(II) transferred into the organic phase under the conditions examined is 4%.

Metrological characteristics of copper determination. Under optimal measurement conditions, the calibration plots are given by the following equations:

$$\tan\alpha = (7.16 \pm 0.05)c + (0.00005 \pm 0.0001), \quad n = 10, \quad P = 0.95, \quad r = 0.978, \tag{9}$$

where c is the molar concentration of copper in the aqueous phase, and

$$\tan\alpha = (1.3 \pm 0.1) \times 10^3 c - (0.0003 \pm 0.001), \quad n = 10, \quad P = 0.95, \quad r = 0.997. \tag{10}$$

The copper detection limit is 2×10^{-7} mol/l (4×10^{-7} mol/l in the aqueous phase). The plots are linear in the copper(II) concentration range of 2.0×10^{-7} to 1.5×10^{-4} mol/l. The standard deviation in this concentration range does not exceed 0.03 ($n = 10$).

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