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Crystallization monitoring by thermal-lens spectrometry

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Abstract. This work considers the application of thermal-lens spectrometry to the monitoring of the crystallization processes in aqueous solutions. Formation of a crystalline germ in a previously homogeneous medium drastically changes the heat and mass transfer along the laser beam path; thus, affecting both equilibrium and time-resolved thermal-lens phenomena. It is shown that long-term oscillations of the steady-state thermal-lens signal could be associated with the formation and growth of the crystal germ. The preliminary estimation of the minimal germ size detectable from this data gives the limit at the level of 300 nm.

1. Introduction

The methods of thermal-lens spectrometry (TLS) proved to be a sensitive and accurate [1, 2] tool for determination of light absorption in various samples: gases, solids, water, and non-aqueous solutions, detection in flow etc. Thermal lensing successfully determines light absorption in the case of inhomogeneous systems: colloid or micellar solutions, solutions of gold nanoparticles [2, 3]. Presence of salts, micelles, or polymers in solution could change some thermo-optical parameters of the sample like density, thermal conductivity, or the temperature gradient of the refraction index [1]. These effects affecting the thermo-optical parameters of the system were reported to be used in determination of non-absorbing sample components by the change in the thermal-lens effect observed in their presence [3]. One of the most well known applications of these effects is the alcohol determination in the aqueous solutions by the change of temperature refraction gradient resulting in the change of the steady state thermal-lens signal of the light absorbing solution [2].

In this work, we propose the application of thermal lensing to the monitoring of the early stages of the crystallization processes by consideration of the system response on the increasing sample inhomogeneity due to the formation of the crystalline germ. Some of the system parameters determining the thermal lens signal like the Soret effect or mass and heat convection processes, thermal conductivity and others are expected to be very sensitive to the formation of even uncolored crystalline germs in the solution [3]. At the moment, there are no techniques to detect the very moment of the crystalline germ formation in the solution that could be used to optimize the crystal quality. Given the tool to detect a germ formation it could be possible to change the conditions of the crystallization process without the need to wait for the crystal to grow up to the micrometer size to be detectable by optical microscopy. For the estimation of the thermal lensing in this field two different types of crystalline germs were considered: uncolored crystals forming in a colored solution (calcium oxalate) and colored crystals formed in a nonabsorbing solution (nickel dimethylglyoximate).

2. Experimental

2.1. Thermal-lens spectrometer

The thermal-lens spectrometers used in the work to monitor the changes in the solution properties upon formation of the crystalline germ was developed on the base of the spectrometer optimized for the determination of solutions with a light absorption down to 1×10^{-6} a.u. The scheme is given at Fig. 1. The key parameters are summarized in Table 1. The optimization of the spectrometer geometry for accounting convection processes or the Soret effect was out of the scope of this work. Quartz cells with optical path lengths of 10 mm were used. A Shimadzu UVmini 1240 spectrophotometer was used to control absorbance of samples. An Olympus BX51 microscope coupled with an E 330 digital camera was used to determine the shape and the size of the crystalline germs formed in the solution.

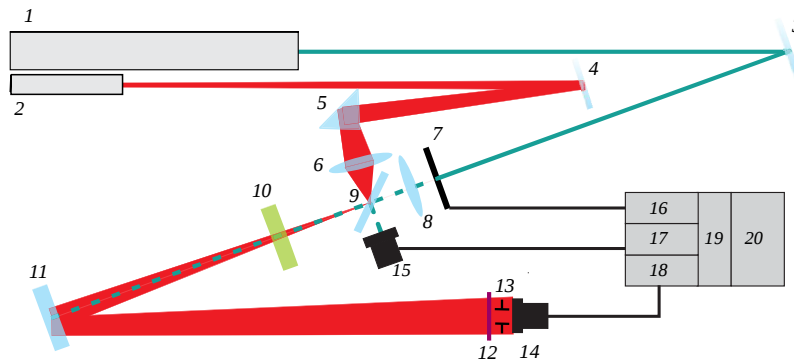


Fig. 1. Principal schematics of the thermal-lens spectrometer. 1, excitation laser; 2, probe laser; 3, 4, 9, and 11, diachronic mirrors; 5, quartz prism; 6 and 8, focusing lenses; 7, chopper; 10, sample; 12 and 13, filter and a pinhole; 14 and 15, photodiodes; 16, 17, and 18, analog amplifiers; 19, DAC-ADC board; 20, PC.

Table 1. The key parameters of the thermal lens spectrometer

Excitation laser Ar ⁺ Innova 90-6 (Coherent, USA)	The main wavelengths, λ_e Max power (TEM ₀₀ mode), P_e Waist in the sample, ω_{0e}	514.5nm and 488.0 nm 1.5 W 61.2 μ m
Probe laser He-Ne HRP020 (ThorLabs, USA)	Wavelength, λ_p Power (TEM ₀₀ mode), P_p	632.8 nm 2 mW
Chopper repetition rate	φ , Hz	0.1–10

2.2. Thermal lens signal processing

The thermal-lens phenomenon and the definition of the thermal-lens signal are thoughtfully considered in a number of works [1–3]. Here, we will specify the dependencies used to describe convection in the sample. In general, the thermal-lens signal, ϑ , is proportional to the solution absorbance, A , (i.e. analyte concentration), power of the excitation beam, P_e , and spectrometer geometry through the spectrometer sensitivity parameter, B , and is proportional to the sensitivity parameter for a given medium, E_0 for the wavelength λ_p of the probe beam

$$E_0 = (-dn/dT)/\lambda_p k \quad (1)$$

Here, dn/dT is temperature gradient of the refraction index and k is medium thermal conductivity. In the case if convection occurs in sample, this is reflected in the sensitivity parameter, B , and characteristic convection parameter, K_c [4]:

$$1/B = 1/B + 4K_c/\kappa\omega_{0e}, \text{ and } K_c = P_e/\tau q = P_e/2\varphi q. \quad (2), (3)$$

Here, κ is the relaxation constant of the excited states, φ is chopper repetition rate, q is the convection flow determined by the Newton law of cooling [5],

$$q = h\Delta T = Nu \cdot k\Delta T / L, \quad (4)$$

Here, h is convective heat transfer coefficient, Nu is the Nusselt number, L is the characteristic dimension of the thermal lens, ΔT is the increase in the temperature due to absorption of laser irradiation. Two latter values were estimated as given in [4]. The Nusselt number for Eq. (4) was determined according to [5] by an empiric formula for a horizontal cylinder.

2.3. Crystallization techniques

To provide the control over crystallization processes in the solution the method of emerging reagents was selected. Crystallization techniques were optimized both for water and 6% water-polyethyleneglycol (PEG) mixtures.

2.3.1. Nickel dimethylglyoximate. The initial 0.45 M solution of nickel sulfate was mixed with equal volumes of 0.50 M hydroxylamine (pH 7.5 ± 0.1) and 0.14 M diacetyl (volume in the range from 20 to 180 μ l that corresponds to the final concentration of nickel 1.8 – 16.2 mM). The final solution was adjusted to 5 ml by water or 6% water-PEG solution. The emerging of dimethylglyoxime (dgmH) in solution according to the reaction: $\text{CH}_3\text{COCOCH}_3 + 2\text{H}_2\text{NOH} \rightarrow \text{dgmH} + 2\text{H}_2\text{O}$ provides a slow formation of the crystalline germ.

2.3.2. Calcium oxalate. Initial calcium carbonate solution was prepared by dissolving 0.017 g of CaCO_3 , 1ml of HCl and 1 g of NH_4Cl in 50 ml of water (or water – 6% PEG mixture). Then 7.5 ml of this solution were mixed with 1 ml of 5% ammonium oxalate solution and 1 μ ml of 8.4 mM methyl-orange solution. The mixture was heated up to 80-90 °C during 3 min, then 0.25 grams of carbamide were added. The resulting hydrolysis of the carbamide $\text{NH}_2\text{CONH}_2 + 2\text{H}_2\text{O} \leftrightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-}$ provide slow increase of solution pH leading to the slow formation of the calcium oxalate crystalline germs.

3. Results and discussion

3.1. Light absorbing crystalline germs in the clear solution

Thermal lensing and spectrophotometric monitoring was made for aqueous solutions during the formation of the nickel dimethylglyoximate germs. The crystallization conditions (section 2.3.1) were selected to provide a slow rate of crystallization in the solution. In the case of the highest nickel concentration used (16.2 mM), the absorbance of the water solution at $\lambda = 540$ nm increases from 0.05 a.u. to 0.35 a.u. in 40 minutes. In a 6% PEG solution, the crystallization rate is decreased compared to aqueous medium from 0.05 to 0.13 a.u. in 40 min. Light scattering significantly starts to affect the results of measurements after this time.

As it was expected, the thermal-lens signal from these samples linearly increases in time reflecting the formation of light-absorbing germs of nickel dimethylglyoximate in the solution. With the use of linear crystal growth model suitable in this case [6], we estimated the size of the corresponding germs and extrapolated these values below the level unattainable for microscope germ size measurements to estimate sensitivity of the method, Fig. 2. The estimated minimum size of the germ for which the TLS signal differs significantly is 300 nm, the corresponding amount of nickel is 200 ng/ml (0.001 ppm). For lower concentrations of nickel in solution, the development of the thermal-lens effect is characterized by lower rate and a presence of signal growth retardation period.

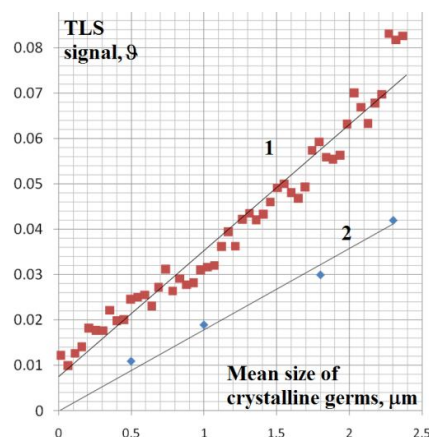


Fig. 2. TLS signal upon formation of the $\text{Ni}(\text{dmgH})_2$ crystalline germs (14.8 mM of Ni in solution): 1, crystallization in solution, 2, molecular solution of $\text{Ni}(\text{dmgH})_2$ with the same amount of nickel.

3.2. Uncolored crystal formation in a light-absorbing solution

The formation of the clear crystals in solution is of the high interest as soon as the circle of uncolored crystals or crystalline proteins is much higher. The slow crystallization of calcium oxalate was performed (section 2.3.2) in the presence of Methyl Orange dye. In this case at the beginning of the crystallization we can hardly expect formation of the stationary heat and mass flows as soon as the dye concentration and the change in the temperature, Eqs. (2) and (3) are low, Fig. 3.

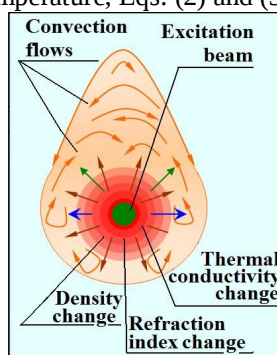


Fig. 3. Heat and mass flows in thermal lensing.

The spectrophotometric monitoring of calcium oxalate crystallization shows no change in the spectrum, but the presence of light scattering at the late stages of crystal growth (after 20–30 min). On the contrary, TLS signal is significantly affected by the crystal formation. In Fig. 4, the curve of the TLS signal development during the experiment is presented.

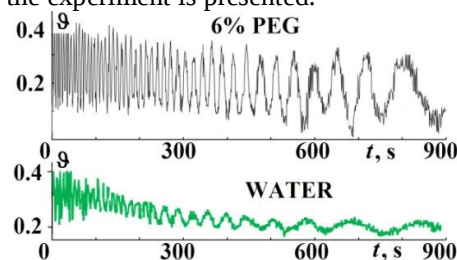


Fig. 4. TLS signals, $\mathcal{S}$, in the 6% PEG and water solutions for $\text{Ca}(\text{COO})_2$.

The period of the signal oscillations increases proportionally to t^3 (t is the experiment duration in s). The observed decrease in the thermal lens signal could be associated with the change in the thermal conductivity of the sample due to formation of an organized medium, Eq. (1) (at this stage the influence of the excitation beam scattering by the crystals is negligible). With the use of optical

microscope we verified the size of the crystalline germs. The period of these oscillations, τ (s) and the mean size of the germs, d (μm), could be described by the following calibration functions:

$$\begin{aligned}\tau &= 3.0d + 0.6, r = 0.996 (n = 11, P = 0.95, \text{PEG}); \\ \tau &= 1.6d + 0.6, r = 0.990 (n = 10, P = 0.95, \text{water}).\end{aligned}$$

Based on these results, the minimum size of the germ at which the signal is significantly affected was determined. It is 200 nm, the corresponding amount of calcium in solution is 500 ng/ml, that is close to the data obtained for $\text{Ni}(\text{dmgH})_2$ germs.

Another interesting issue is the shape of the crystals. It was found out that the shape of the crystals in the case of thermal-lens monitoring slightly differs from the control experiment. While the volume of the crystals seems to be the same, the crystalline germs in the control experiments are longer than in the case of thermal lensing. Probably, the influence of the external source of energy in the crystallization process is very important. It will be considered in our future studies, as soon as it could provide a tool not only to monitor but to control the crystallization.

4. Conclusions

The successful application of thermal-lens spectrometry method to monitoring of the crystallization processes was demonstrated. The minimal size of the crystals detectable from a characteristic change of the signal both for the light-absorbing or uncoloured crystals was below the optical diffraction limit.

Acknowledgements

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