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Investigation of ionene adsorption on quartz surfaces by thermal-lens spectrometry

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Abstract

Thermal-lens spectrometry was used for the investigation of the adsorption of ionene to quartz surfaces. The thermooptical analysis of the surface makes it possible to distinguish the modified surface from a clean quartz surface and to provide sensitive direct concentration measurements of the light absorbing co-adsorbed substance. The co-adsorption of chromate ions and 2,10-ionene from aqueous solutions to quartz surfaces was investigated and the desorption procedure proposed.

Keywords: Thermal-lens spectrometry; Surface study; Ionene; Adsorption on quartz; Ion-exchange capacity; Desorption; Capillary electrophoresis

1. Introduction

Analytical applications of cationic surfactants in the field of capillary electrophoresis (CE) are well-known [1–5]. Their use as additives to carrier electrolytes in CE of low-molecular weight anions provides the reversal the electroosmotic flow and even changes in the separation selectivity by an ion-pairing mechanism. The modification of ion-exchange materials in capillary electrochromatography (CEC) also provides the solution retention control by changing the nature of the modifier [6,7].

The use of ionenes (polymers with quaternary nitrogen atoms in the backbone) as capillary-conditioning reagents [2–5] and ion-exchange phase modifiers [6,7] seems very promising both for CE and CEC. In both cases, the adsorption of the polyelectrolyte is very high due to the formation of the so-called “polyelectrolyte complexes” on the surface with charged groups [8–11]. However, the data on the ion-exchange capacity of ionene layers on silica is lacking due to the paucity of methods for the direct determination of absorbed ions in the polyelectrolyte layer on silica surfaces [8,10,12]. At the same time, the irreversible adsorption of chromate ions and other colourants on polyelectrolyte-covered capillary surfaces in indirect detection in CE and CEC is known and provides a baseline growth [1,3,5,7]. In this paper, we discuss the use of thermal-lens spectrometry as a tool for investigating the ionene adsorption on flat quartz surfaces and estimating ion-exchange capacity of the resulting layer.

2. Experimental

2.1. Instrumentation

Two types of the thermooptical detectors were used for characterizing light-absorbing substances on quartz surfaces. These are (1) a co-axial dual-beam mode-mismatched far-field thermal-lens spectrometer and (2) a dual-beam near-field crossed-beam thermal-lens detector designed for CE. Block diagrams of the signal generation for both cases of thermal-lens detection are presented in Fig. 1.

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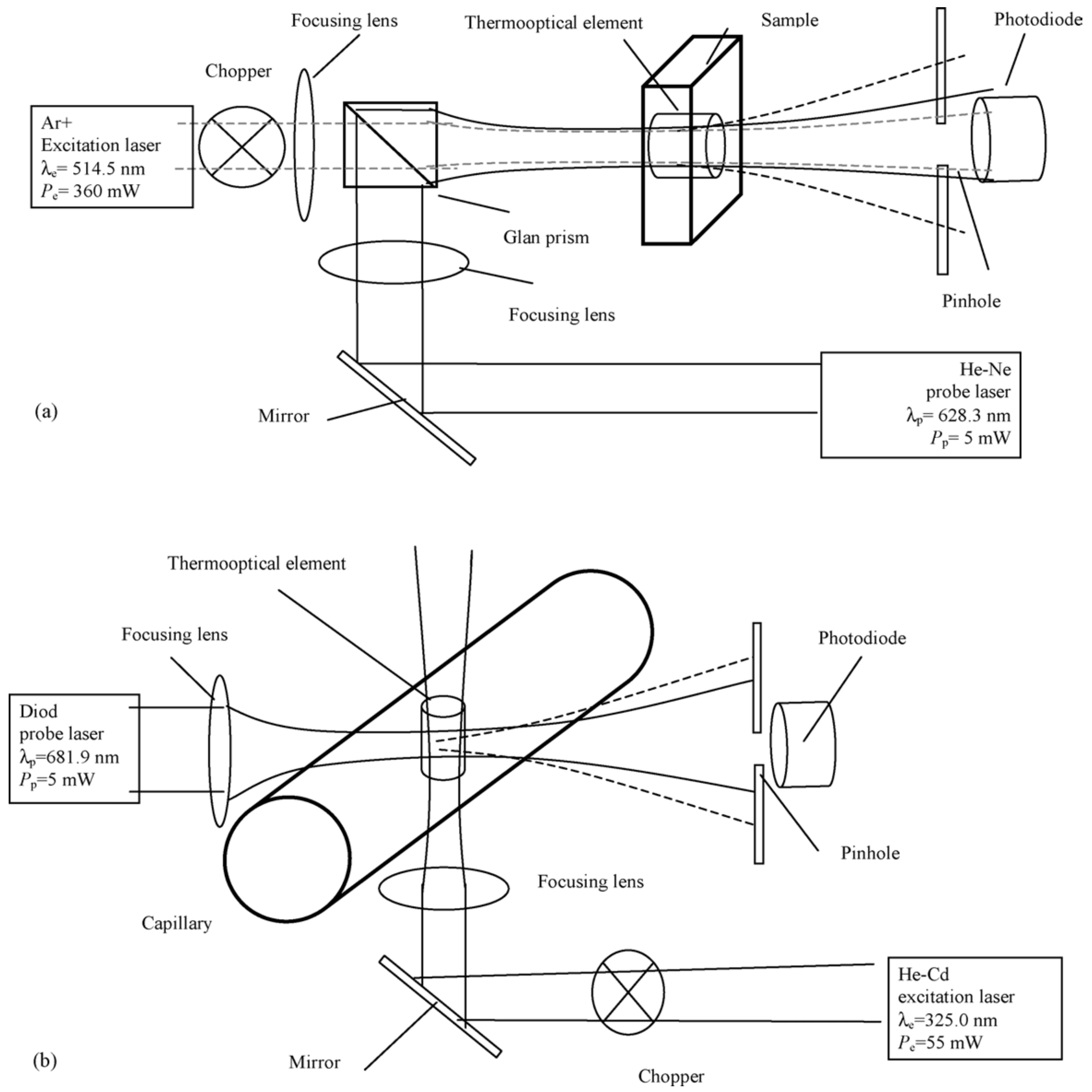


Fig. 1. Block diagrams of the TLS signal generation in (a) coaxial dual-beam far-field thermal-lens detector and (b) crossed-beams thermal-lens detector designed for capillary electrophoresis.

The details of the far-field thermal-lens spectrometer (Fig. 1a) are given elsewhere [13]. The set-up comprises an excitation Ar^+ laser (Innova 90–6, Coherent, Palo Alto, CA, USA) operated at 514.5 (350 mW in the sample) and 488.0 nm (390 mW in the sample) and a He–Ne probe laser (SP 106–1, Spectra-Physics, Eugene, OR, USA; 632.8 nm, 5 mW in the sample). Beams were adjusted co-axially using a Glan prism. Other relevant parameters are summarised in Table 1. The data are gathered and processed by a Pentium I (166 MHz) computer using the software written in-house [14]. The chopping frequency was low (4 Hz) to ensure the complete dissipation of the thermal-lens at the end of each steady-state excitation–cooling cycle. The quartz-glass samples were inserted directly into the optical path of the spectrometer at the waist of the excitation beam. The thermal-lens signal of the sample was calculated as an average of ten measurements at different sites of the sample.

The crossed-beam thermal-lens detector (Fig. 1b) used for the investigations of the quartz capillaries was designed for the detection in capillary electrophoresis [15]. It comprised an excitation laser (He–Cd, IK3552R-G KIMMON Electronic Co., Ltd. Tokyo, Japan) operated at 325.0 nm (50 mW in the capillary) and a probe laser diode (Toshiba TOLD 1050, Chaeffer&Kirchhoff, Germany) operated at 681.9 nm, 5 mW in the sample (Table 1). In this configuration, the capillary, the excitation beam, and the probe beam intersect at right angles. The signal from the photodetector (intensity of the probe beam in the centre) is translated to a home-made lock-in amplifier and then to a PC by ADC-DAC. The synchronisation of the measurements is implemented by the specially designed software.

Table 1
Thermal-lens spectrometers parameters

Parameter	Far-field spectrometer		Near-field spectrometer
Excitation laser			
λ_e (nm)	488.0	514.5	325.0
Spot size at the waist ω_{e0} (μm)	61.3	64.6	7.7
Laser power at the sample P_e (mW)	385	360	50
Probe laser			
λ_p (nm)	623.8		681.9
Laser power at the sample P_p (mW)	5		30
Spot size in the sample ω_2 (μm)	108.8		75
Other constants			
Optical path in the sample (μm)	1000		75
Spectrometer time resolution (ms)	36		–
Chopper frequency (Hz)	4		40–95

2.2. Thermal-lens experiment in the coloured polyelectrolyte surface layer

Both in far-field and in near-field thermal-lens experiments, the dimensionless instrumental signal is calculated as a relative change of the probe beam intensity after the absorption of the excitation laser irradiation.

$$\vartheta(t)=\frac{I_0-I(t)}{I_0}=1-(1-B\theta)^2=1-(1-2.303E_0P_eAB)^2, \quad (1)$$

where $\theta=2.303E_0AP_e$ is the analytical signal; B the spectrometer geometry parameter [16]; I_0 the initial intensity of the probe beam and $I(t)$ the intensity at the moment t; P_e the excitation power (W); A the absorbance of the sample (medium); E_0 is the enhancement factor of thermal lensing for unit pump power in the case of homogeneous sample [16]:

$$E_0=\frac{-\mathrm{d}n/\mathrm{d}T}{\lambda_p k}. \quad (2)$$

At low θ values, all θ^2 terms in Eq. (1) can be neglected simplifying it to a linear dependence $\vartheta(t)=2B\theta=4.606BE_0P_eA$ [16]. The main task in the theoretical description of the thermooptical element in the sample is the calculation of the temperature profile in the medium.

2.2.1. Far-field thermal-lens experiments

The detailed theoretical model describing the far-field thermal-lens experiment in the surface-absorbing solids is given elsewhere [17]. The thermooptical element in the sample emerges due to the formation of a Gaussian temperature profile in the surface layers and in the transparent support itself due to the surface absorption of the laser TEM_{00} irradiation and subsequent thermal diffusion processes [12,17]. As the main part of the resulting temperature profile due to a heat transfer is located in the support, it is almost impossible to estimate the thickness of the surface layer. In general, the sample can be represented as an assemblage of N light-absorbing layers with laser-induced heat dissipation in each described by a complementary error function:

$$\Delta T(z,t)_{r=0}=\int_0^t\sum_{i=1}^{N}\frac{8D}{\sqrt{\pi}k(\omega_e^2+4Dt)}(\alpha_i I_{i-1})\times\left[e^{\alpha_i(z+z_{i-1})}e^{\alpha_i^2Dt}\left[\operatorname{erfc}\left\{\frac{z+z_{i-1}}{\sqrt{4Dt}}+\alpha_i\sqrt{Dt}\right\}-\operatorname{erfc}\left\{\frac{z+z_i}{\sqrt{4Dt}}+\alpha_i\sqrt{Dt}\right\}\right]\right]\mathrm{d}t. \quad (3)$$

Here, k is the thermal conductivity of a sample (W m^{-1} K^{-1}); D the thermal diffusion coefficient (m^2 s^{-1}); ω_e^2 the waist of the excitation laser; α_j and z_i are the linear absorption coefficient and position of the ith layer, respectively. I_{i-1} is the intensity of the excitation laser radiation at the ith layer after passing through all the previous levels. Generally, the maximum temperature rise ΔT in the coloured quartz sample is not higher than 0.5 K; thus, further it will be considered that no thermal decomposition takes place.

Interpretation of the thermal-lens experiment is based on the theoretical calculations of the dependence of the thermooptical signal (calculated from the temperature profile data) on the absorbance of a sample. It should be noted that this data should be used only for the estimation of the colourant concentration because the thermooptical parameters of the support are sometimes scarce and unreliable [17]. Thus, for a quartz plate with both sides modified with the use of the given spectrometer parameters (Table 1), the following calibration plot was achieved [17]:

$$A=\frac{\vartheta-\vartheta_0}{8.7}, \quad (4)$$

Here, A is the total absorbance of all the surface light-absorbing layers; ϑ the thermal-lens signal from the experiment; ϑ_0 the thermal-lens signal of the unmodified plate (for 1 mm thick quartz plate ϑ_0 equals to 3×10^{-5}).

2.2.2. Near-field thermal-lens experiment

In the case of the thermal-lens experiment in the capillary, the spatial distribution of the temperature increase in the capillary against the environment can be calculated as [12]:

$$\Delta T(r)=\frac{P_e\alpha}{2\pi k}\int_0^{\frac{1}{2\varphi t_c}}\frac{\exp\left(\frac{-2r^2}{1+2x}\right)}{1+2x}\,\mathrm{d}x, \quad (5)$$

where r is the distance from the pump laser beam centre in units of the pump laser beams radius; φ the chopper frequency (Hz); t_c is the characteristic time of the thermal-lens:

$$t_c=\frac{\omega_{0e}^2}{4D}, \quad (6)$$

where ω_{0e} is the radius of the excitation beam waist.

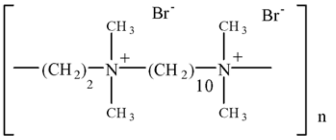
The difference in the signals from an unmodified capillary and a capillary after adsorption can be used for the estimation of the substance concentration on the capillary surface with the use of the experimental spectrometer calibration with standard solutions (e.g., the thermal-lens signal of the capillary filled with 25 μM chromate/5 mM Tris solutions equals to 4000 spectrometer units and water signal change after ionene adsorption is 800 spectrometer units).

2.3. Reagents

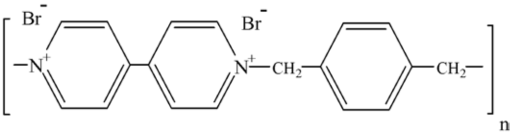
Deionised high-purity water (Milli-Q plus 185 (18.0 MΩ), Millipore, Bedford, MA, USA) was used to prepare all the solutions. Chemically pure potassium permanganate, analytical-grade sulfuric acid, analytical-grade nitric acid and analytical-grade hydrogen peroxide solution (30%) were used throughout. Potassium chromate and *tris*-(hydroxymethyl)aminomethane (Tris) for the preparation of buffer solutions were obtained from Merck (Darmstadt, Germany). All other reagents were from Reakhim (Moscow, Russia), at least of cp grade, and no extra purification was performed. The walls of a quartz-glass photometric cell (Specord, Germany) were sliced to pieces and used as flat plates for adsorption studies. Fused-silica capillaries used for adsorption study were from Polymicro Technologies, USA (i.d. 75 μm, o.d. 360 μm).

The synthesis of 2,10-ionene and DpyX-ionene was described in the previous paper [7], the average molecular weight values were 10.4 ± 0.5 and 4 ± 0.5 kDa, respectively (determined by viscosity measurements).

2,10-ionene



DpyX-ionene



2.4. Procedures

All the chemical glassware in contact with the ionene was pre-treated with the working solution of the test ionene (1%) to prevent polyelectrolyte waste from adsorption on the glassware during the experiment. The adsorption was studied under batch conditions with a quartz plate placed in a modifier solution; thus, both sides of the plate were modified in order to maximise the signal of the thermal-lens experiment [17] and in the water-filled capillary in a stopped-flow mode.

2.4.1. Ionene adsorption on quartz surfaces

Initial quartz plate surfaces were cleaned with 50% nitric acid and washed with water. Further, plates were placed into solutions of ionene for 10 min, water-washed and air-dried. Thermooptical signals of the plates were measured and calculated against the signal from a clean plate.

2.4.2. Chromate adsorption in the surface ionene layer

Flat quartz plates were treated with a 0.15% solution of 2,10-ionene for 10 min, water-rinsed, air-dried (in order to estimate the blank signal of the modified surface), and immersed into a 0.1–30 mM chromate solution for 10 min and after the measurement for another 72 h. The pH of the solution was adjusted to 8.55 with a 4% Tris solution. The resulting surface was air-dried and studied by thermal lensing. Thermooptical signals from the plates with a layer of the modifier and potassium chromate were compared to the signals of the plates treated with ionene only.

2.4.3. Chromate adsorption from mixtures with 2.10-ionene

Quartz plates were treated with a 0.1 M NaOH solution for 10 min and placed into a 0.65% solution (pH 8.55 was established with the use of Tris) of 2,10-ionene containing 15 mM potassium chromate. Thermal-lens signals were measured after 20 and 200 h.

2.4.4. Desorption of ionene from the quartz plate surface

Blank thermal-lens signals of the clean quartz plates were measured, and plates were treated with a 2,10-ionene solution (Section 2.4.2) for 72 h, water-rinsed and air-dried. Thermal-lens signal of the surface was measured at the wavelength of the excitation laser of 488.0 nm for several surface points on the plate. Next, plates were placed into a solution of cleaning agents for 72 h, rinsed, dried, and measured.

2.4.5. Ionene–chromate adsorption in the quartz capillary

New capillaries were flushed twice with a 0.1 M NaOH solution for 45 min and water-washed for 30 min. Thermal-lens signals from a clean capillary surface and the one after the ionene–chromate adsorption (capillary flushed with 0.65% 2,10-ionene solution containing 15 mM potassium chromate for 60 min and water wash for 30 min) were measured in water-filled capillary in a stopped-flow mode. The scan of the capillary profile was conducted at a shift of the excitation beam transversely to the capillary direction with a spatial resolution of 5 μm.

2.4.6. Capillary cleaning

The capillary treated with ionene–chromate mixture (Section 2.4.5) were flushed with cleaning-agent solutions then with water, and the washing was repeated twice (total time 4 h). Thermal-lens signals of the cleaned capillary surface were compared to the previously measured (after the new capillary flush with the running buffer). In order to prove the desorption of the ionene layer, the capillary was flushed with a chromate solution for 20 min and the thermal-lens signal at the centre of the capillary was measured.

Table 2
Thermal-lens signal of adsorbed polymer on the quartz surface with different excitation laser modes

Quartz treatment	514.5 nm, 360 Mw	488.0 nm, 385 mW
	Average signal, $\bar{\vartheta}_n$, ($n = 8$, $P = 0.95$)	Average signal, $\bar{\vartheta}_n$, ($n = 5$, $P = 0.95$)
2,10-Ionene, 1% solution (without NaOH treatment)	$(-1 \pm 3) \times 10^{-3}$	$(-1 \pm 2) \times 10^{-3}$
2,10-Ionene, 1% solution	$(-4 \pm 2) \times 10^{-3}$	$(-1 \pm 1) \times 10^{-3}$
2,10-Ionene, 15% solution	$(-4 \pm 2) \times 10^{-3}$	–
DpyX-ionene, 3.5% solution (without NaOH treatment)	$(-1 \pm 1) \times 10^{-3}$	–
DpyX-ionene, 3.5% solution	$(-4 \pm 1) \times 10^{-3}$	$(-2 \pm 1) \times 10^{-3}$

3. Results and discussion

In CE indirect-detection mode, the separation buffers may contain up to 5–15 mM of chromate and 0.1–0.5% of ionene. Experiments made with these buffers in CE indicate that even after several runs, the baseline rises significantly due to the adsorption of chromate in the polyelectrolyte layer. The use of the far-field thermal-lens spectrometer in the study of chromate adsorption in the 2,10-ionene layer under batch conditions provides the necessary information concerning specific features of the adsorption processes due to a possibility for directly measuring chromate concentration in the layer bulk.

3.1. Polyelectrolyte adsorption

The study of polyelectrolyte adsorption laws was not the main objective of this work but some possibilities of the thermal lensing in this field should be discussed. Adsorption of the polyelectrolyte on the silica surface is due to the polyelectrolyte complexes arrangement on the surface with charged Si–O^{-} groups [8–11]. As expected, the thermal-lens signal from a quartz surface without pre-treatment by an alkali solution (Section 2.4.1) contacted with an ionene solution differs very little from a clean surface [7]. Thus, in all further experiments, the quartz surface pre-treatment with 0.1 M NaOH for 5 min was used. This procedure produced a significant increase in the thermal-lens signal over the signal from a clean surface, thereby proving the appearance of a surface modifier layer. Average thermal-lens signals are summed up in Table 2.

The investigation of polyelectrolyte adsorption by thermal lensing can be based on the signal change due to a change of thermooptical properties of the surface with a layer of the modifier even if the layer does not significantly absorb the excitation radiation. Also, it is reasonable to expect that a low-light absorptivity of 2,10-ionene would lead to an increase in the contribution of the solvent absorptivity to the total signal. Thermal lensing is generally nonselective and cannot be used for directly calculating the concentrations of adsorbed substances in the case of similar values of light absorptivity of colourants. However, calculations based on signals obtained at two different wavelengths of the excitation laser can be very worthy. The excitation Ar^{+} laser used in our work provides cw laser irradiation with 488.0 and 514.5 nm wavelengths. In order to find out the role of the solvent in the generation of the signal, a quartz plate was placed into a DpyX-ionene (selected because of higher light absorptivity at the wavelength of the spectrometer) solution and the thermal-lens signal was measured at 488.0 and 514.5 nm. The extrapolation of the DpyX-ionene absorption spectrum gives corresponding linear absorption coefficients $\alpha_{488} = 6 \times 10^{-1}\,\mathrm{m}^{-1}$ and $\alpha_{514} = 4.7 \times 10^{-1}\,\mathrm{m}^{-1}$, and water absorptivity is $\alpha_{488} = 1.5 \times 10^{-2}\,\mathrm{m}^{-1}$ and $\alpha_{514} = 3.9 \times 10^{-2}\,\mathrm{m}^{-1}$ [18]. Thus, if the signal generally depends on the light absorptivity of ionene, the $\vartheta_{514}/\vartheta_{488}$ ratio is 0.8, for water it is 2.6 and experimentally measured $\vartheta_{514}/\vartheta_{488}$ ratio is 2.0. This data prove that the surface layer of DpyX-ionene captures water in its structure. Close levels of thermal-lens signals from DpyX-ionene and 2,10-ionene layers can be explained by taking into consideration the difference in the molecular weight resulting in a layer of 2,10-ionene thicker than the level difference in light absorptivity of the polymers. However, this observation cannot be proved without additional experimental information on the parameters of adsorbed layers such as layer thickness (which cannot be obtained by thermal lensing alone). A more detailed study of the ionene adsorption laws by means of thermal lensing seems very promising provided UV-excitation lasers are used; this would better fit the absorption spectra of the selected ionenes.

3.2. Co-adsorption of 2,10-ionene and chromate ions

Chromate adsorption in the surface ionene layers was monitored at the wavelength of the excitation laser of 488.0 nm. Thus, a minimum contribution from the ionene layer was achieved to increase the accuracy of the measurement of chromate.

At the first stage, the influence of chromate concentration on the level of adsorption on the surface of a pre-treated plate was studied. As expected, the thermal-lens signal from a plate untreated with 2,10-ionene (the blank experiment) immersed into a solution of potassium chromate (Section 2.4.2) does not differ from the signal from a clean surface (due to an insignificant adsorption ratio). Adsorption of the polyelectrolyte and co-adsorption of chromate as a counter ion considerably change the thermal-lens signal of the sample, but in the selected range of chromate concentrations, the thermal-lens signal does not depend on it significantly (Fig. 2). Thus, it can be expected that in the range of chromate concentrations used for indirect CE analysis, the conditions for surface saturation were reached. However, a change in this signal with time proves that the development of the light-absorbing layer is not an instantaneous process and takes time.

At the second stage, a study of surface modification from mixtures of 2,10-ionene and potassium chromate (Section

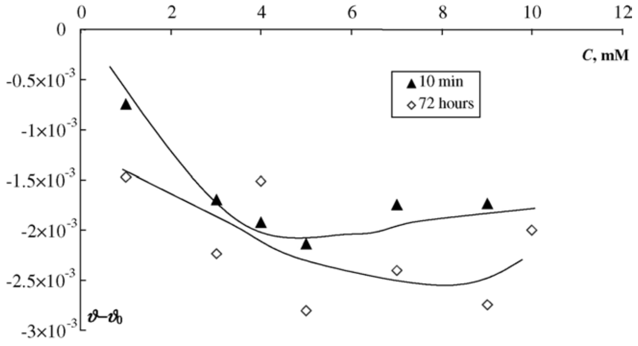


Fig. 2. Dependence of thermooptical signal of the adsorbed ionene layer on the chromate concentration in the solution (see text for details).

2.4.3) was made and the outcome compared to a step-by-step surface modification. In the case of step-by-step modification (Section 2.4.2), surfaces were pre-treated with a 0.65% solution of 2,10-ionene and after that it was immersed into a solution containing potassium chromate only (concentration range 1–30 mM).

Analytical signals of all the surfaces obtained by step-by-step modification and by the modification from mixtures do not significantly depend on the concentration of chromate in solution. Thus, all the experimental data for different chromate concentrations was summarised in Table 3. The data on the adsorption of 2,10-ionene and chromate ions from mixtures cannot reveal the origin of the time-changing signal, because it can result from either (1) a slow formation of the polyelectrolyte layer on the surface with the already organised ion-aggregates or (2) slow adsorption of chromate into the bulk of a quickly arranged ionene layer. A quick formation of the polyelectrolyte layer in this system followed by a slow diffusion of coloured chromate ions into surface layers seems more reasonable. A close co-incidence of the measured TLS signals for surfaces pre-treated with 2,10-ionene (step-by-step modification) and for surfaces treated with a mixture can be considered as an evidence of this viewpoint.

Table 3
Thermal-lens signal of adsorbed polymer on the quartz surface

	Time of contact and corresponding signal, $P = 0.95$	
Adsorption of chromate and 2,10-ionene from mixture on the quartz plate	22 h ($n = 7$)	200 h ($n = 9$)
	$(-1.3 \pm 0.5) \times 10^{-3}$	$(-2.3 \pm 0.5) \times 10^{-3}$
Adsorption of chromate on the quartz plate previously treated with 2,10-ionene 0.65% solution	22 h ($n = 7$)	200 h ($n = 7$)
	$(-1.5 \pm 0.3) \times 10^{-3}$	$(-2.1 \pm 0.5) \times 10^{-3}$

Calculations based on the theoretical model of thermooptical experiments in the layered solid [17] made it possible to estimate chromate concentration in the layer and corresponding ion-exchange capacity of the 2,10-ionene layer from the thermal-lens signal value, Eq. (4). The surface concentration of chromate was estimated as 3×10^{-9} mol/cm^2. Thus, the resulting 2,10-ionene layers can adsorb about 15 chromate ions/nm^2. This data are in a good agreement with the CE data concerning the amount of free counter ions (1.7×10^{-9} mol/cm^2 of bromide) in the 2,10-ionene molecule adsorbed on the inner surface of capillary [7].

3.3. Polyelectrolyte desorption

Baseline growth in CE after the adsorption of the 2,10-ionene on the quartz surface is accounted for by the irreversible absorption of chromate (or other colurant used for indirect detection) in the surface layer. One of the tasks of this work was to clean the surface and remove the colourant from the layer or to remove the polyelectrolyte itself.

Several agents were tested for surface cleaning: concentrated sulfuric acid in a mixture with concentrated nitric acid (I), a solution of $K_2Cr_2O_7$ in concentrated sulfuric acid (II),

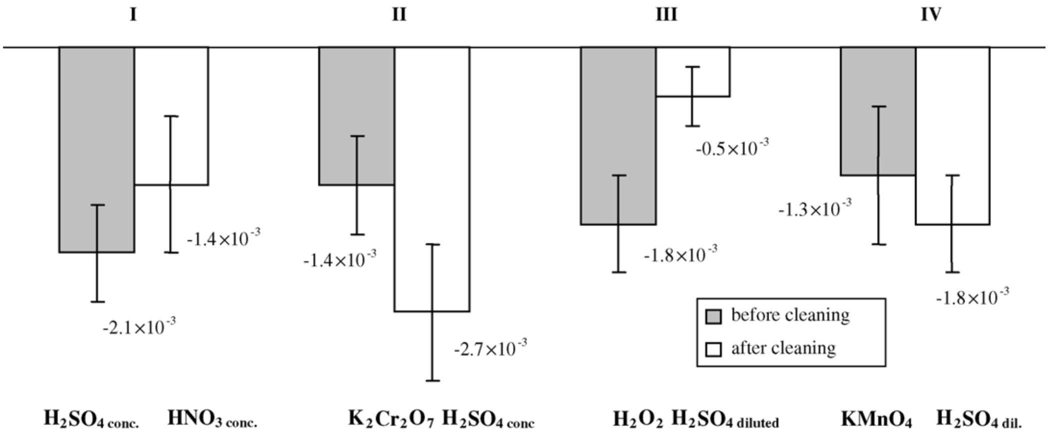


Fig. 3. Far-field thermal-lens signals of the quartz surfaces before and after the desorption of ionene from the surface.

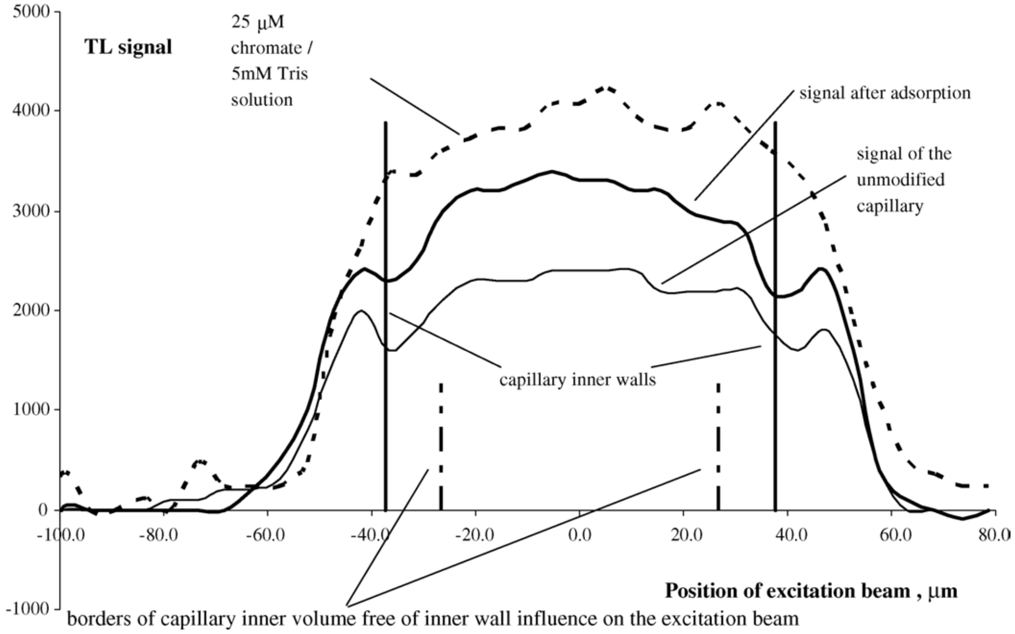


Fig. 4. Capillary profile screening with TLS near-field detector before and after running buffer (chromate 5 mM/2,10-ionene 0.01%/Tris 5 mM) flush through the capillary with i.d. of 75 µm for 30 min. Excitation laser step 5.2 µm.

a 15% H_2O_2 solution in 30% sulfuric acid (III), and a solution of $KMnO_4$ in concentrated nitric acid (IV). Plates were placed into solutions of cleaning agents for 72 h in order to obtain the maximum efficiency of polyelectrolyte desorption. As expected, coloured cleaning agents (II and IV) were unable to remove 2,10-ionene layers and the light adsorption of the samples surface increases (Fig. 3). In order to prove the presence of polyelectrolyte coating after the treatment with agents II and IV, the investigation of hydrophobic properties of the surface was conducted by means of the air-bubble breaking-off method [19]. It was found that the surface is slightly hydrophobic compared to a clean quartz surface. However, no data for the estimation of polyelectrolyte concentration can be obtained in this manner. A mixture of acids (I) only reduced light absorption of the sample, while the subsequent treatment with potassium chromate solution did increase light absorption of the sample. Thus, it can be concluded that only chromate ions were washed out. The best results were obtained with the use of a hydrogen-peroxide solution in diluted sulfuric acid (III). The thermal-lens signal of the surface after cleaning was the lowest and further treatment with a 15 mM potassium chromate solution did not increase light absorption of the sample.

3.4. In-capillary thermal-lens measurements

The experimental verification of the batch-mode results was provided by in-capillary studies using a crossed-beam near-field thermal-lens detector designed for CE. Near-field TLS detector provides highly sensitive measurements of absorbance in the capillary. Thus, the measurement of the water background signal before and after capillary flush with the ionene/chromate containing separation buffer (Section 2.4.5) may provide the necessary information on the efficiency of polyelectrolyte absorption/desorption/cleaning agents.

In order to prove the adsorption nature of the signal growth, the capillary light-absorption profile was made by shifting the excitation laser beam across the capillary. It was found that there is a significant difference in the profile shape for an absorbing solution of chromate in the capillary and for a capillary filled with water after the adsorption of polyelectrolyte–chromate aggregates on the walls (Fig. 4). From our point of view, the difference in the profile shape near the capillary wall region can result from the disposition of the light-absorbing 2,10-ionene only at the capillary walls.

As expected, the signal change for this zone is minimal and can be accounted for by the change of the diffraction picture at the detector pinhole with a shift in the excitation beam only. The significant thermal-lens signal rise in the central part of the capillary after ionene–chromate flush (Fig. 4) was observed. The resulting capillary absorbance rise calculated from the corresponding thermal-lens signals (2300 ± 20 before and 3100 ± 20 after modification) corresponds to the filling of the capillary with a chromate solution with absorbance of 5×10^{-5} abs. units.

Also, the efficiency of tested cleaning agents for ionene desorption was investigated. A combination of the capillary rinsing followed by a chromate treatment (Section 2.4.6) proved the batch-mode results obtained with the use of the far-field thermal-lens spectrometer. As expected, the use of the hydrogen peroxide in sulfuric acid (III) provided the most efficient capillary surface cleaning and no re-adsorption of chromate from solution after capillary washing takes place.

4. Conclusions

As a whole, it was shown that thermal lensing both in far-field and in near-field designs is suitable for the investigation of surface adsorbed polymer layers. The major advantage of these methods is the possibility to estimate dye concentrations in the adsorbed layer. It was possible to distinguish a layer of polyelectrolyte modifier on the surface both with and without co-adsorbed substances. The calculated ion-exchange capacity of ionene layer (the example of chromate adsorption) is in a good agreement with that for previously obtained by CE [7]. The study of desorption of ionene from the quartz surface showed that 15% H_2O_2 solution in 30% sulfuric acid provides the most efficient cleaning of the surface.

Acknowledgments

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