Effect of Electrolytes on the Sensitivity of Thermal-Lens Measurements in Aqueous Media

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Abstract—The thermooptical properties of aqueous solutions of strong electrolytes (H_2SO_4, HCl, NaCl, Na_2SO_4, and NaOH) are considered. The thermal lens signal depends on the nature of the electrolyte. The effect of an electrolyte is not the sum of the effects of the constituent ions. The largest gain in the sensitivity of thermal-lens measurements is achieved with sulfuric acid (sensitivity enhancement factor of 2 for 0.6 M H_2SO_4 versus water) and sodium chloride (sensitivity enhancement factor of 1.5 for 3 M NaCl), while the effect of hydrochloric acid is negligible.

Thermal-lens spectrometry (TLS) is a modern molecular absorption spectroscopic technique [1]. It is based on the fact that the refractive index of a medium absorbing laser radiation is proportional to the concentration of the absorbing substance. This technique is 2–3 orders of magnitude more sensitive than spectrophotometry and can, therefore, be used in trace analysis. The analytical signal in TLS depends strongly on the properties of the medium, primarily thermal conductivity and heat capacity. While the thermooptical properties of water and some common organic solvents are well known [1, 2], those of electrolyte solutions have not been adequately studied as yet, even though these solutions are widely employed in chemical analysis.

Here, we report our study of the thermooptical properties of some common aqueous electrolytes. This study, aimed at enhancing the sensitivity of thermal-lens measurements, is based on theoretical calculations of thermooptical properties and on checking the calculated data against experimental data for model systems.

CALCULATIONS

The matter in the laser-irradiated space is locally heated owing to the nonradiative relaxation of electronically excited molecules. The resulting refractive index profile is determined by the spatial distribution of energy in the incident light beam and acts as an optical element [1]. The assumptions made in the calculation of the properties of this optical element and the derivation of the equation describing the refractive index profile due to the temperature field in the medium are known from the literature:

$$n(r, t) = n_0 + \frac{dn}{dT}\Delta T(r, t), \qquad (1)$$

where n_0 is the refractive index of the sample before irradiation.

The phase shift introduced by this optical element into the probe beam is

$$\Phi = \frac{\theta}{t_c}\int_0^t \frac{1}{1 + 2t'/t_c}\left[1 - \exp\left(\frac{-2r^2/\omega_e^2}{1 + 2t'/t_c}\right)\right]dt', \qquad (2)$$

where t_c is the characteristic thermal-lens development time and ω_e is the beam waist radius, and

$$\theta = 2.303\frac{P_e A dn/dT}{k\lambda_p}. \qquad (3)$$

Here, A is the absorbance of the sample, k is thermal conductivity, λ_p is the wavelength of the beam probing the thermal lens, and P_e is the power of the excitation beam [1].

The optical element acts like a diverging lens because, far from strong absorption bands, the refractive index of most substances (except highly aggregated liquids near a phase transition point) decreases with increasing temperature [1]. Formula (3) expresses the analytical signal of TLS. It can be rewritten as

$$\theta = 2.303 A E_0 P_e, \qquad (4)$$

where

$$E_0 = -\frac{dn/dT}{k\lambda_p} \qquad (5)$$

is the sensitivity enhancement factor determined only by the properties of the medium.

The optical heterogeneity appearing in the laser-irradiated portion of the medium is due to the local

heating caused by the nonradiative relaxation of electronically excited molecules and the heat-induced change in the refractive index. The refractive index is among the fundamental properties of a substance. According to the Maxwell equations, the refractive index of a substance far from absorption bands is determined by the dielectric constant and the permeability of the substance ($n = \sqrt{\varepsilon\mu}$).

The relationship between the refractive index and the electromagnetic polarizability of a substance is given by the Lorentz–Lorenz equation:

$$R_m = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}, \qquad (6)$$

where R_m is molar refractivity.

Refractive index values measured under normal conditions (20°C) are generally used. The refractive index depends on many parameters in a complicated way and cannot be directly expressed in terms of the functions of state of the system. In TLS, of principal significance is the temperature dependence of the refractive index since this dependence, along with thermal conductivity, determines the sensitivity enhancement factor of the method.

For small temperature changes, the contributions from the temperature and density of the medium to the change in the refractive index (Eq. (1)) may be considered separately:

$$\partial n(T, \rho) = \left(\frac{\partial n}{\partial T}\right)_P \partial T + \left(\frac{\partial n}{\partial \rho}\right)_T \partial\rho. \qquad (7)$$

The first term on the right-hand side of this equation accounts for the contribution from the temperature dependence of the molar refractivity of the molecules of the sample. This contribution is usually small as compared to the contribution from the variation of the refractive index with density, which is described by the Lorentz–Lorenz equation and is accounted for by the second term on the right-hand side of Eq. (7). This latter term is expressed in terms of the volumetric thermal expansion coefficient β. Thus, the temperature dependence of the refractive index (Eq. (1)) can be represented as the sum of two terms:

$$\partial n(T, \rho) = \left(\frac{\partial n}{\partial T}\right)_P \partial T + \left(\frac{\partial n}{\partial \rho}\right)_T \partial\rho. \qquad (8)$$

Using the Lorentz–Lorenz equation (6), we obtain

$$\left(\frac{\partial n}{\partial \rho}\right)_T = \frac{(n_0^2 + 2)^2}{6n_0}\frac{R_m}{M} = \frac{(n_0^2 + 2)(n_0^2 - 1)}{6n_0\rho_0}, \qquad (9)$$

where n_0 and ρ_0 are the refractive index and density, respectively, at an intermediate temperature value. The density of the medium is linearly related to temperature through equilibrium thermodynamic functions. The

second term of the relationship between the refractive index and temperature can be represented as follows:

$$\left(\frac{\partial n}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial T}\right)_P = -\rho_0\beta\left(\frac{\partial n}{\partial \rho}\right)_T = -\beta\frac{(n_0^2 + 2)(n_0^2 - 1)}{6n_0}. \quad (10)$$

For a gas at a pressure of a few atmospheres, the refractive index inside the optical element can be directly related to the refractive index outside the optical element (outside the heated space) using gas laws. This is possible owing to the fact that the refractive index of a gas at a low pressure is very close to unity. Therefore, for a gas sample in an ordinary pressure range,

$$\left(\frac{\partial n}{\partial T}\right)_{T_0} \approx -\frac{1}{2}\beta(n_0^2 - 1) = -\frac{n_0^2 - 1}{2T_0}, \qquad (11)$$

where T_0 is the equilibrium temperature of the sample. At a constant density, the temperature dependence of the refractive index is determined by the temperature dependence of the molar refractivity:

$$\left(\frac{\partial n}{\partial T}\right)_\rho = \frac{\rho}{M}\frac{(n_0^2 + 2)^2}{6n_0}\left(\frac{\partial R_m}{\partial T}\right). \qquad (12)$$

The main parameter determining the sensitivity enhancement factor (5) is the temperature derivative of the refractive index of the substance, dn/dT. For the great majority of aqueous solutions, including electrolyte solutions, direct refractive index data available from the literature refer only to room temperature. The only way of estimating and calculating the temperature dependence of the refractive index in this situation is by using the Lorentz–Lorenz equation and density tables, which are usually available from the reference or specialized literature for common solutions. However, the data obtained in this way should be judged critically because of the limited applicability of the Lorentz–Lorenz equation to condensed phases. In particular, the calculation of dn/dT for water using this method leads to a positive error over 50%. For the other media, which are less polar than water, one should expect a better agreement between calculated and observed data. The following equation derived from Eqs. (11) and (12) is used in these calculations:

$$\frac{\partial n}{\partial T} \cong \left(\frac{dn}{dT}\right)_P = \left(\frac{d\rho}{dT}\right)_P\frac{(n^2 - 1)(n^2 + 2)}{6n_0\rho_0}. \qquad (13)$$

No correlation equations suitable for the thermal conductivity of such solutions have been reported. However, the thermal conductivity of many commercially important solutions has been accurately determined at several temperatures [3–5], so it is possible to calculate the sensitivity enhancement factor for TLS measurements in some systems. Table 1 lists thermooptical data calculated for sulfuric acid, hydrochloric acid, and sodium chloride solutions.

Table 1. Calculated thermooptical properties of electrolytes [3–5]

Modifies, c, mol/l	ρ, kg/dm³	$-d\rho/dT$, kg/m³	n_D	$-dn/dT \times 10^4$, K⁻¹	k, W/(m K)	$E_0/E_{0,\,water}$
Sulfuric acid*						
0	0.9982	3.58	1.33319	0.91	0.5994	1
0.204	1.0131	6.31	1.33572	2.31	0.5969	1.76
0.408	1.0252	6.80	1.33801	2.47	0.5916	1.90
0.612	1.0372	7.28	1.34023	2.64	0.5864	2.04
0.816	1.0492	7.76	1.34245	2.79	0.5813	2.19
1.020	1.0612	8.24	1.34465	2.96	0.5762	2.34
1.531	1.0912	9.45	1.34999	3.36	0.5641	2.71
2.041	1.1212	10.07	1.35513	3.74	0.5526	3.08
Hydrochloric acid**						
0	0.9986	3.58	1.33319	0.91	0.5988	1
0.548	1.0092	4.49	1.33779	1.66	0.5774	1.89
1.096	1.0183	4.78	1.34227	1.78	0.5558	2.10
1.644	1.0273	5.07	1.34669	1.90	0.5345	2.33
2.192	1.0364	5.36	1.35102	2.01	0.5137	2.58
2.740	1.0455	5.65	1.35528	2.13	0.4932	2.85
Sodium chloride**						
0	0.9982	3.58	1.33299	0.91	0.5988	1
0.342	1.0134	4.10	1.33667	1.5	0.5784	1.66
0.684	1.0262	4.61	1.34002	1.69	0.5579	1.86
1.025	1.0390	5.12	1.34332	1.87	0.5375	2.07
1.368	1.0518	5.63	1.34651	2.05	0.5170	2.28
1.709	1.0646	6.13	1.34963	2.23	0.4966	2.49
2.564	1.0966	7.41	1.35721	2.68	0.4455	3.02
3.418	1.1286	8.68	1.36446	3.13	0.3944	3.54

Notes: * 17.5°C.
     ** 20°C.

EXPERIMENTAL

Instruments

All preliminary measurements at the spectrophotometric examination stage were made on a Shimadzu UVmini 1240CE spectrophotometer (Japan) in the wavelength range of 400–700 nm. In thermal-lens measurements, we used a laser thermal-lens spectrometer described in [6]. The thermal lens was excited in a quartz cell (l = 1 cm) using an Innova 90-6 argon ion laser (Coherent, United States) with λ = 488.0 and 514.5 nm (TEM$_{00}$ mode, input power of 100 mW). The probe laser was an SP-106-1 He–Ne laser (Spectra Physics, United States) with λ = 632.8 nm (TEM$_{00}$ mode, 10 mW). The signal from a photodiode (proportional to the light intensity at the center of the probe beam) was directed to an ADC/DAC device connected to a PC-compatible computer. Measurements were computer-synchronized using a special-purpose program. The relative standard deviation in TLS measurements was 0.01–0.02. Prior to the TLS experiment, in order to verify the constancy of ε_{488}, we measured the absorbance of all colored samples in various media on a Shimadzu UVmini 1240CE spectrophotometer using the same quartz cell (l = 1 cm) as was intended for TLS measurements.

Solvents and Chemicals

The solvents were distilled water (pH 5.8, for spectrophotometry) and twice distilled deionized water (resistivity of 18 MΩ cm, pH 6.5, purified on a Milli-Q system (Millipore, France)). The following chemicals were used: ferroin sulfate (aqueous solution, 0.1 wt %, analytical grade), ammonium dichromate (analytical grade), sodium chloride (reagent grade), sodium sulfate (reagent grade), sulfuric acid (reagent grade), hydrochloric acid (reagent grade), and sodium hydroxide (analytical grade). All solutions were prepared immedi-

ately before measurements. The base solutions of colored compounds (ferroin sulfate and ammonium dichromate) were prepared by dissolving precisely weighed samples in water. The solutions were stored in test tubes and flasks with ground-glass stoppers. Laboratory glassware was kept in a dichromate solution and in nitric acid and was then thoroughly washed with distilled water. All weighings were done on an analytical balance with an accuracy of 0.1 mg. Volumes were measured with graduated pipettes with an accuracy of ±0.01 ml. Sodium sulfate was dissolved in an ultrasonic bath (Branson) for 30–60 min.

Several series of aqueous solutions containing a certain amount of a colored compound were prepared. Variable amounts of a modifier were added to the solutions of each series, and the solutions were adjusted to 50 ml with deionized water. Thermal-lens measurements were taken at $\lambda = 488.0$ and 514.5 nm for 3–5 min. In order to obtain more correct analytical data and to increase the accuracy of the determination of sensitivity enhancement factor for water, calibration relationships for modifier solutions were obtained on the same day and under the same conditions as the calibration relationships for pure aqueous solutions.

Selection of Indicator Compounds

Iron(II) tris-(1,10-phenanthrolinate) was chosen to be the colored indicator in the study of the thermooptical properties of the salts for the reason that it has a large molar absorptivity (>11 000) at the working wavelength of the argon ion laser. The independence of the ferroin extinction coefficient of the ionic strength of the solution was verified spectrophotometrically.

Iron(II) tris-(1,10-phenanthrolinate) is unstable in reactive media; for this reason, the dichromate ion was used as the colored indicator in the study of the thermooptical properties of strong acids and bases. The extinction coefficient of the dichromate ion in aqueous solution depends only on pH. Preliminary spectrophotometric experiments demonstrated that, between pH 6 and pH 0.2, the absorption spectrum is essentially invariable for $\lambda = 480$–520 nm.

In highly alkaline media, the dichromate–chromate equilibrium is shifted to the chromate ion, thus changing the absorption spectrum. This effect was taken into account by normalizing the ratio of the slopes of the calibration plots to the ratio of the absorbances of the aqueous and alkali solutions at the TLS wavelength.

TLS Data Processing

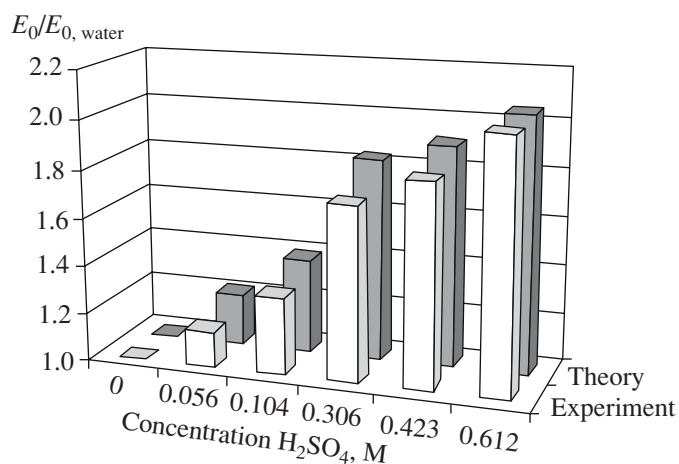The thermal-lens signal θ is determined by the lens-induced relative change in the light intensity in the central part of the laser beam that has passed through the sample at thermodynamic equilibrium [1]:

$$\theta = \frac{1}{B}\left(1 + \sqrt{\frac{I_{\text{off}} - I_{\text{on}}}{I_{\text{on}}}}\right), \qquad (14)$$

where I_{on} and I_{off} are the light intensities at the center of the probe beam in the presence of a developed thermal lens (when the excitation laser is on) and in the absence of a thermal lens (when the laser is off), respectively. The geometric factor B is defined as

$$B = 0.5\arctan\left(\frac{2mV}{1 + 2m + V^2}\right), \qquad (15)$$

where V is the distance between the waist of the probe beam and the sample and m is the ratio of the cross-sectional areas of the probe and excitation beams in the sample. The analytical thermal-lens signal θ is converted to absorbance using Eq. (4).

RESULTS AND DISCUSSION
Comparing the Modifying Properties of Electrolyte Solutions

For sulfuric acid solutions, the observed sensitivity enhancement factor is in good agreement with the factor calculated using Eq. (13) (Fig. 1): the deviation does not exceed 5%. This is usually the case only for low-polarity unassociated liquids [7]. It can be assumed that, in moderately concentrated (0.01–1.0 M) sulfuric acid solutions, the association of molecules due to dipole–dipole interactions is suppressed because of the ion–dipole interactions of water molecules with hydronium and sulfate ions. Thus, sulfuric acid is a perfect structure-breaking modifier. It is demonstrated by the data presented in Table 2 that the deviation from the Lorentz–Lorenz equation decreases as the sulfuric acid

Fig. 1. Observed and calculated sensitivity enhancement factors for thermal-lens measurements in sulfuric acid solutions.

Table 2. Observed and calculated sensitivity enhancement factors and dichromate ion (*) and ferroin (**) detections limits for electrolyte solutions ($n = 10$, $P = 0.95$) at excitation wavelengths of 488.0 nm (*) and 514.5 nm (**) and an excitation power of 100 mW

Modifier, c, mol/l	$E_0/E_{0,\,water}$ (observed)	$E_0/E_{0,\,water}$ (calculated)	Deviation from Eq. (13), %	Detection limit, mol/l $\times 10^8$	RSD in the middle of the calibration plot
Sulfuric acid*					
0	1	1	–	50	0.03
0.056	1.147	1.21	–5.1	15	The same
0.104	1.320	1.39	–4.9	20	The same
0.306	1.483	1.83	–5.2	25	The same
0.423	1.835	1.91	–3.9	25	The same
0.612	2.034	2.05	–0.6	50	The same
Hydrochloric acid*					
0	1	1	–	50	0.03
0.548	1.017	1.873	–48.3	20	The same
1.096	1.092	2.112	–45.7	20	The same
Sodium chloride**					
0	1	1	–	2	0.03
0.3	–	1.75	–41.7	1.5	The same
1.0	1.204	2.06	–41.5	3	The same
3.0	1.534	3.30	–53.3	3	The same
Sodium hydroxide*					
0	1	1	–	50	0.03
0.5	1.149	1.841	–37.6	20	The same
1.0	1.587	1.807	–12.2	20	The same
Sodium sulfate**					
0	1	Not calculated		5.0	0.03
0.423	1.110			1.0	0.05

concentration in the solution is raised and almost vanishes at an acid concentration of 0.6 mol/l. This trend is likely due to the fact that, as the hydronium and sulfate ion concentrations are raised, the proportion of ion–dipole interactions increases, the proportion of dipole–dipole interactions decreases, and, accordingly, the association of molecules is progressively suppressed.

This can be explained by the fact that an ion in solution binds several water molecules into its solvation shell by ion–dipole interactions. This breaks part of the association species formed by water molecules through dipole–dipole interactions. If the number of water molecules in the solvation shell is larger than the number of molecules in the association species broken because of ion solvation, more extensive structure formation will take place in water. If the number of molecules is smaller in the resulting solvation shell than in the broken association species, the extent of molecular association will decrease.

However, it is difficult to distinguish the effects of individual ions on water association because at least two different types of ions are always present in a solution. In view of this, we examined sodium sulfate solutions.

The observed sensitivity enhancement factor is much smaller in a sodium sulfate solution than in a sul-

furic acid solution of the same molarity (Table 2). Therefore, the sodium ion is a much weaker structure-breaking modifier than the hydronium ion. Apparently, the latter has a larger charge-to-surface area ratio. As a consequence, the solvation shell of the hydronium ion is smaller than that of the sodium ion and, accordingly, association due to ion–dipole interactions is less pronounced in the case of the hydronium ion. This inference is confirmed by the fact that the capacity of ions to suppress water association decreases in the order K > Na > Li; moreover, lithium is a structure-forming modifier [8]. This conception provides an explanation for the great difference between the thermooptical properties of sulfuric acid and sodium sulfate solutions.

As compared to sulfuric acid and sodium chloride, hydrochloric acid affords a much smaller gain in TLS sensitivity relative to the sensitivity in water (Table 2). Therefore, the chloride ion is a structure-forming modifier partly neutralizing the structure-breaking effect of the hydronium ion. However, a marked enhancement of sensitivity is observed for sodium chloride solutions. This finding is in conflict with the view that the hydronium ion is a stronger structure-breaking modifier than the sodium ion. A comparison between the sensitivity enhancement factors for the sodium sulfate and chloride solutions with equal molar concentrations of the
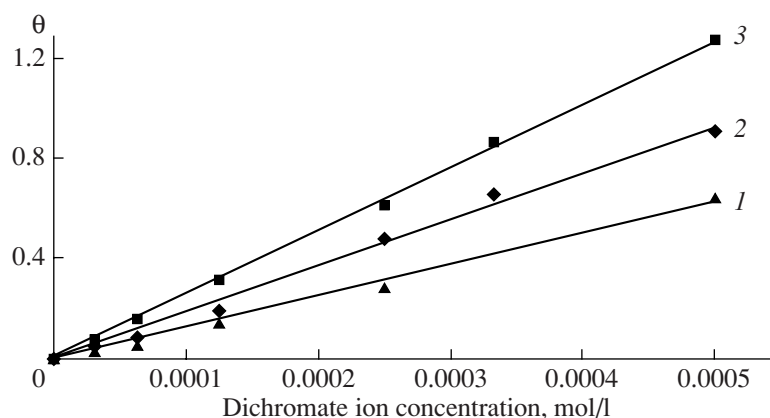
Fig. 2. Thermal-lens signal magnitude (θ) versus the dichromate concentration at various sulfuric acid concentrations: (*1*) water ($r = 0.997$), (*2*) 30 g/l of H_2SO_4 ($r = 0.997$), and (*3*) 60 g/l of H_2SO_4 ($r = 0.999$); $T = 298$ K; $\lambda = 488.0$ nm.

sodium ion shows that the sensitivity enhancement factor for the chloride solution is 8% larger (Table 2).

It is clear from the above that the effect of a substance on the sensitivity of TLS measurements in aqueous solutions cannot be predicted without making experiments, because it is impossible to precisely predict the effect of each particular ion on the structure of water. Furthermore, the effect of electrolytes on the thermooptical properties of the medium should necessarily be taken into account. At equal pH values, sulfuric acid and hydrochloric acid solutions have quite different thermooptical parameters. While the effect of hydrochloric acid on the thermal-lens signal is negligible, the effect of sulfuric acid is fairly strong. Therefore, in precision measurements (such as stability constant determination), acidity should be created with hydrochloric acid. When it is necessary to enhance the sensitivity of measurements (e.g., in the case of a weak analytical signal), it is better to use sulfuric acid.

The above examples demonstrate that the thermal-lens signal depends not only on pH and ionic strength, but also on the nature of the ions in the solution. The thermooptical data obtained for the salt solutions indicate that the nature and concentration of the ionic strength modifier must be taken into account in order to avoid large determination errors.

CONCLUSIONS

The metrological characteristics of thermal-lens measurements in aqueous solutions depend strongly on the composition of the medium. By using various modifiers, it is possible to significantly enhance the sensitivity and to lower the detection limit of the method. For example, thermal-lens measurements in 0.5 M H_2SO_4 are nearly 2 times more sensitive than the same measurements in water containing no significant amounts of electrolytes (Fig. 2) and, therefore, have better metrological characteristics. As is demonstrated in Table 2, the same is true for >1 M NaCl and >1 M NaOH solu-

tions. Since these media are widely used in the photometric determination of elements and organic compounds, the results presented here are essential for enhancement of analytical sensitivity. In our opinion, optimizing the determination conditions for various compounds in aqueous acids and bases is a promising way of developing sensitive thermal-lens determination procedures.

Thermal-lens spectrometry is a promising method for investigation of the thermooptical properties of electrolyte solutions. Significant interfering factors in this investigation may be thermal diffusion and the Soret effect (concentration gradient formation) due to the local laser heating of the medium. This is particularly true for highly viscous media, such as sulfuric acid solutions. These effects are beyond the scope of this study. However, they deserve rapt attention not only as interfering factors, but also as physical phenomena and optimization parameters in the development of thermal-lens determination procedures.

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