Development of a heat-sensor for the measurement of reaction enthalpy based on laser deflection

Thomas Schneider, Mário J. Politi, Mauricio S. Baptista[*]

*Departamento de Bioquímica, Instituto de Química, Universidade de São Paulo, C.P. 26077,
C.E.P. 05599-970 São Paulo, SP, Brazil*

Abstract

A new method for the measurements of reaction enthalpies based on a laser deflection heat-sensor was developed. The heat released or absorbed from a chemical reaction in an aqueous phase causes the formation of thermally driven refractive index gradients in an adjacent organic phase. This effect is monitored by the change in the deflection angle of a laser light in the organic phase. The instrument was tested in the complexation reaction of EDTA with magnesium (endothermic) and calcium (exothermic). It is shown that the direction of the deflection angle is indicative of the sign of the enthalpy change. The magnitude of this enthalpy change can be calculated using the intensity of the maximum deflection and a calibration slope obtained using the reaction enthalpy of the NaOH/HCl neutralization. The heat limit of detection (HLOD) was calculated to be 60 mJ. Possible improvements in the HLOD are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Microcalorimetric techniques are of major importance to almost every field of science [1,2]. Nowadays, isothermal, reaction and temperature scanning calorimeters reach detection limits lower than microjoule, allowing sensitive investigations of protein denaturation processes, phase diagram determinations and study of adsorption phenomena at interfaces [3,4]. Although providing good sensitivity these instruments are yet expensive, and are invasive in nature [5].

Laser techniques have revolutionized several fields of science specially physical-chemistry [6]. The interaction of laser light with heat-induced temperature gradients has allowed the characterization of thermo-optical properties of materials (solids, liquids and gases), as well as photophysical properties of excited states [7]. The so-called photothermal techniques are generally very sensitive, i.e. detection limits of pico-joules and single molecule determinations have been reported [8,9]. However the application of laser techniques for the study of thermo-properties of chemical reactions has not yet been properly explored.

Wu and coworkers were the first to demonstrate that the heat released in chemical reactions causes the deflection in a laser beam positioned in an adjacent medium. This phenomenon was used in several analytical applications including acid base titration, the analytical determinations based in enzymatic reactions in tandem with flow injection devices, and gas diffusion measurements [10–13]. We have recently shown its application for the quantitative determination of singlet oxygen [14].

* Corresponding author. Fax: +55-11-8155579.
E-mail address: baptista@iq.usp.br (M.S. Baptista).

Given the fact that analytical determinations, i.e. to find out analyte concentrations, are just an indirect application of this essentially calorimetric method, our goal in this work is to demonstrate the application of this laser deflection heat-sensor for the determination of enthalpy changes of chemical reactions. It will be shown that by using a low-cost, non-contact detector, it is possible to perform the determination of exothermic and endothermic enthalpies of complexation reactions.

2. Experimental

2.1. Materials

Carbon tetrachloride was spectroscopic grade (Merck). $CdCl_2$, $MgCl_2$, were obtained from Merck and were dried for 5 h at $100°C$. Ethylenediaminetetraacetic acid disodium salt dihydrate ($\geq 99\%$, Aldrich) (EDTA) was used without further treatment. Water was doubly distilled in an all glass apparatus, and further deionized and ultra-filtrated (Milli-Q).

2.2. Instrumentation

The heat-sensor based on laser deflection is schematically depicted in Fig. 1. The beam from a 1.4 mW
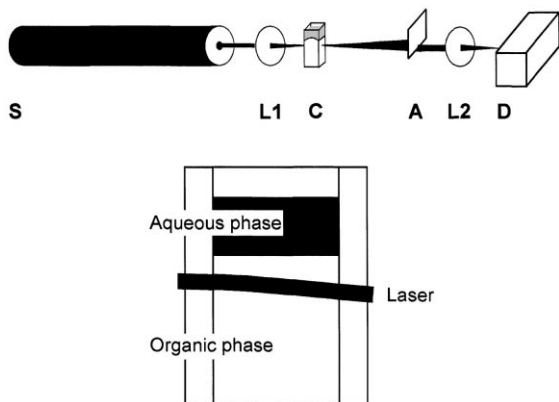

Fig. 1. Scheme of the laser deflection heat-sensor, where S is He–Ne laser, L1 is a verging lens ($f_0 = 11$ cm), C is a 1×1 quartz cuvette, A is a knife-edge, L2 is verging lens ($f_0 = 5$ cm), D is a photodiode. The lower panel represents an amplification of the cuvette where the aqueous phase is black, the organic phase is clear and the laser beam is passing in the organic phase below the aqueous/CCl_4 interface.

cw He–Ne laser (Oriel-79309) is focused in the sample cuvette (1 cm quartz) in the CCl_4 phase (~ 3 mm below the interface with water). A knife-edge blocks around 50% of the beam and a converging lens is used to refocus the beam in the photodiode (OPT101-DIP, Burr–Brown). The signal is digitized by a 12 bit A/D board (CIO-AD08, Computer Boards) installed in a 386 PC computer (TRI). The total volumes of the aqueous and organic phases are 0.2 and 1.0 ml, respectively. The CCl_4 is chosen because of its large dn/dT value, which maximizes the refractive index gradient generated [10,11]. The experiments are run at $T \sim 20°C$.

2.3. Methods

Chemical reactions (HCl/NaOH neutralization and Ca^{2+}/Mg^{2+} complexation with EDTA) are initiated by adding a small volume (few microliters) of a solution that has one of the reactants to the aqueous phase containing the other reactant. The solutions are prepared with a large molar excess of one of the reactants. Considering the concentration excess and that the equilibrium constants of these chemical reactions are $10^{11}\,M^{-1}$ or higher [15], the forward chemical reaction is completed in a pseudo-first order regime.

The heat liberated or absorbed by the chemical reaction in the aqueous phase (depending on the sign of the enthalpy change) propagates to the organic phase causing a temperature gradient, which ultimately causes a refraction index gradient. The laser beam passing through the organic phase senses this refraction index gradient, which acts as a thermal prism and causes the deflection of the laser beam (Fig. 1). Depending on the intensity of deflection, the laser beam is more or less blocked by the knife-edge. The laser light intensity is monitored by a photodiode (Fig. 1). Therefore, this laser based detection method differs fundamentally from the ones present in commercially available calorimeters, which are usually based in thermistors' responses.

The amplitude of the deflection signal is calibrated with a chemical reaction whose enthalpy value is known (neutralization of NaOH by HCl, $\Delta H^0 = -56.5$ kJ/mol) [15], i.e. a calibration curve with Volts per Joule (V/J) units is obtained. This calibration curve, which is obtained just before or after the actual experiment is performed, to keep the same laser and

detector alignments, is used to the enthalpy determination of other chemical reactions as expressed by Eq. (1).

$$\Delta H = \frac{\Delta I}{\text{Slo} \times N} \quad (1)$$

where ΔH is the enthalpy change calculated for the reaction, ΔI the maximum deflection signal, Slo the calibration curve slope obtained with the acid/base neutralization, and N the number of mols of the limiting reactant.

3. Results and discussion

In Fig. 2, typical laser deflection signals measured after the addition of X µmol of HCl to a NaOH solution, are shown. These signals are composed of the following features: at $\sim$25 s after the addition of HCl the voltage measured in the photodiode starts to decrease, indicating that a higher percentage of the beam is being blocked and, therefore, that the beam is being deflected. The signal change reaches its maximum value at around $\sim$35 s and then starts to return to the original value leveling off at $\sim$150 s.

For fast reactions like the ones investigated in this work, the heat liberated from the reaction works as an instantaneous heat source and the temporal signal behavior can be explained based only on heat con-

duction between the two phases. For slower chemical reactions (rate in the order of min^{-1}) kinetic information can also be obtained [10–14]. Different ways of injecting the sample at different velocities, at different positions of the sample surface and by using different sample volumes (keeping number of mols constant) were tested and the results turn out the same within the experimental error, suggesting that mixing did not affect substantially the deflection signal.

By increasing the number of mols of HCl and consequently the amount of heat released there is a proportional increase in the ΔI (initial voltage minus voltage at 35 s) (Fig. 2). This result is in agreement with the acid/base titration performed in a similar apparatus by Wu and coworkers [10,11]. The heat detection limit calculated as three times the blank standard deviation divided by the calibration curve slope was $\sim$60 mJ.

In order to test whether this instrument can measure the enthalpy change related with other chemical processes, the complexation reactions between $MgCl_2$ and $CdCl_2$ with EDTA were investigated. It is shown in Fig. 3 that the deflection signals measured after the addition of 15 µmols of $MgCl_2$ and of 15 µmol of $CdCl_2$ in a 1 M EDTA solution. It is clearly seen that a positive and a negative ΔI were measured for the EDTA/Mg and EDTA/Cd complexation, respectively. This can be understood considering that the enthalpy change related with these processes have opposite
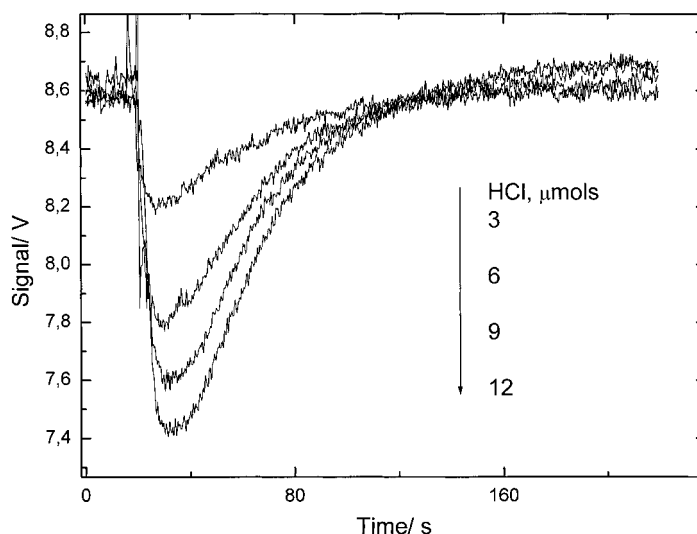

Fig. 2. Deflection signal obtained after the reaction of 3, 6, 9 and 12 µmol of HCl with a 1 M NaOH aqueous solution.

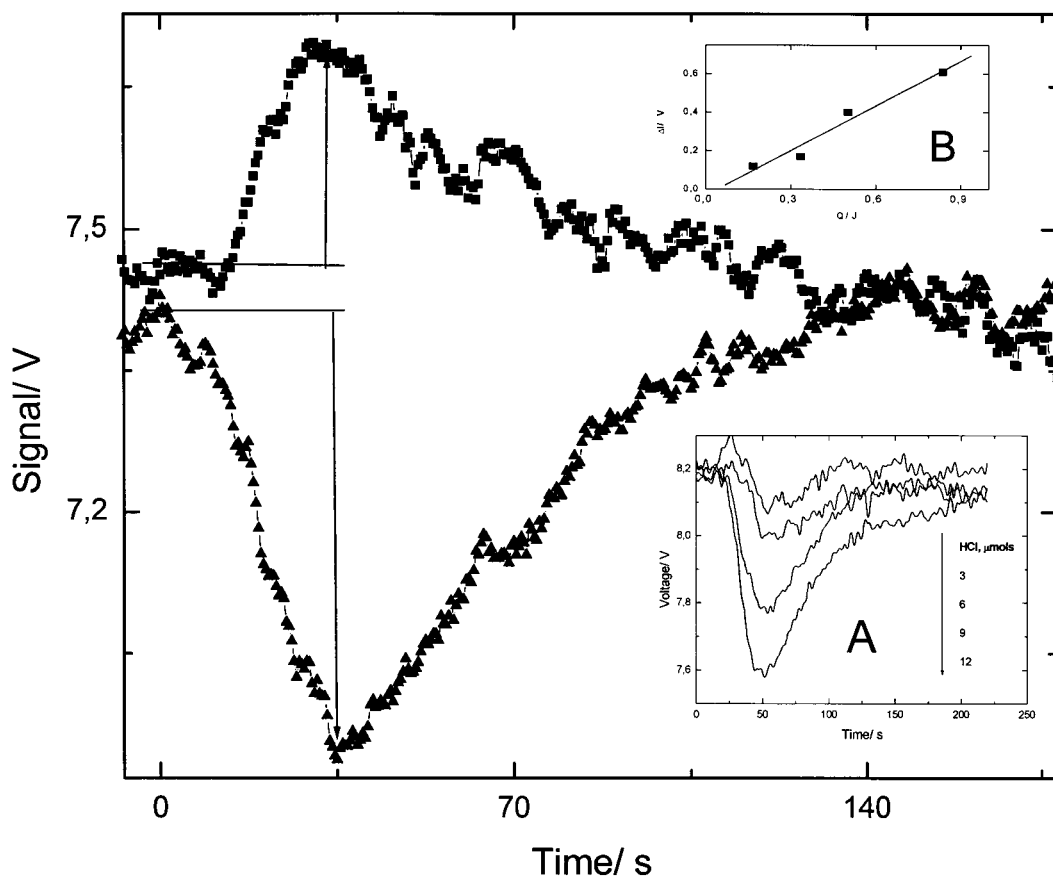Fig. 3. Deflection signals obtained after the reaction of 15 µmol of $CdCl_2$ (▲) and $MgCl_2$ (■) with a 1 M EDTA solution. The figure inserts show the laser deflection signals of HCl/NaOH neutralization reactions (A) used to construct the calibration curve (B).

signs, i.e. −38 and 23 kJ/mol for EDTA/Cd and EDTA/Mg, respectively [16]. Therefore, in the case of the EDTA/Cd reaction a negative refractive index gradient is created, deflecting the laser beam to the same direction as observed for the HCl/NaOH neutralization reaction. It is important to emphasize that the dn/dT value of CCl_4 is $−6.1 \times 10^{−4}\ K^{−1}$, consequently with the increase in the temperature there is a decrease in the refractive index [7]. In the case of the EDTA/Mg reaction, the aqueous phase removes heat from its boundaries creating a negative heat and a positive refractive index gradients in the organic phase, which deflect the laser beam to an opposite direction.

In order to calculate the enthalpy changes related with these reactions, the measured ΔI values were compared with the calibration curve slope of an HCl/ NaOH reaction series (Fig. 3 insets — slope = 0.775 V/J) and the heat changes were calculated (Q). The reaction enthalpies were obtained by dividing the Q values by the number of mols of $CdCl_2$ and $MgCl_2$ added to the EDTA solution (Eq. (1)).

It is shown in Table 1 that the reaction enthalpy values calculated agree, within the experimental error, with the literature values of these reaction enthalpies, obtained by Jordan and Aleman using titrimetric enthalpy determinations [15]. The chelation of EDTA with magnesium has also been studied by other authors and conflicting results were found. Charles reported an endothermic ΔH^0 of $\sim$3 kJ/mol [16], while Carini and Martel obtained an exothermic ΔH^0 of approx. $−12$ kJ/mol [17]. Our result is in quantitative agreement with the ΔH^0 reported by Jordan and Alleman [15].

Table 1
ΔH for the $CdCl_2$ and $MgCl_2$ complexation with EDTA

	ΔI (V)	Q (kJ)	ΔH (experimental) (kJ/mol)	ΔH (literature)[a] (kJ/mol)
$CdCl_2$	−0.41	−0.53	−35 ± 5	−38
$MgCl_2$	0.26	0.34	23 ± 3	23

[a] Values were obtained from [15].

The reproducibility of thermometric titrations is characteristically good, usually around 1% or better. Linde et al. reported reproducibility lower than 1% for several kinds of reactions including, neutralization titrations, complex formation and precipitation [18]. Similar results were obtained by Jordan and Alleman [15]. High sensitivity calorimeters in development stage, that use smaller sample volumes tend to have reproducibility worse than the ones cited above (around 5%) [19]. In our case, the final uncertainty obtained in the ΔH calculation was around 15% (Table 1). The high final uncertainty values observed in the ΔH calculation are the result of several errors along the procedure, including sample volume delivery in the microliter range and problems with the interface of the two liquids (meniscus position is a factor that contribute for the scattering of values around the average). We are confident that these difficulties can be worked out by designing a better sample compartment and sample delivery device.

The high HLOD values obtained (60 mJ) can be explained by the fact that in our sample compartment the heat is diffused to all spatial directions and only a minor fraction is felt by the probe laser and also by the fact that there is a large magnitude difference between the size of the reaction compartment (0.2 cm × 1 cm of the sample cell and 0.2 cm of the liquid phase height) and the diameter of the probe laser (∼50 μm). In this context, micromechanical technology can improve our instrument as has been shown to other newly devised integrated circuit calorimeters [19]. In fact, a micrometer sample compartment is being built for us by the Engineering School of our University. In this sample compartment, the size differences between the laser beam and the sample compartment is minimized and the heat generated in the aqueous phase will be driven to the laser beam compartment by the differences in thermal conductivities of the materials used. We have also been working to improve the sensitivity of this detection scheme by measuring the heat wave using an interferometer in the laser beam pathlength.

4. Conclusion

It has been shown that the laser deflection sensor is capable of measuring enthalpy changes related with endothermic and exothermic processes. Depending upon the sign of the enthalpy change of the chemical reaction, refractive index gradients of opposite signs will be generated in the adjacent medium, deflecting the laser beam to opposite directions. This instrument can be calibrated to obtain the value of the enthalpy change. The HLOD and the final uncertainty in ΔH (∼60 mJ and 15%, respectively) are still too high compared with the ones obtained using detection schemes available in nowadays microcalorimeters. It should be mentioned, however, that the absolute value of these parameters are dependent on cuvette design and size and other instrumental variables that can be improved. These modifications would allow us to adapt this detector in the sample compartment of a differential scanning microcalorimeter to test its performance in temperature scanning thermograms.

Acknowledgements

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