Thermodynamic characterization of the aggregation phenomena of SafranineT by spectral titration and chemometric analysis

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ABSTRACT

The dimerization constants of Safranine T have been determined by studying the dependence of its absorption spectra on the temperature in the range 30–70 $^{\circ}C$ at different total concentrations of Safranine T (1.03×10^{-5}, 1.44×10^{-5} and 1.73×10^{-5} M). The monomer–dimer equilibrium of Safranine T has been determined by applying MCR-ALS method on the absorption spectra. The quantitative analysis of the data of undefined mixtures, was carried out by simultaneous resolution of the overlapping spectral bands in the whole set of absorption spectra. In this work the dimerization constant of Safranine T has been determined by studying the dependence of absorption spectrum on temperature at different total concentrations of dye. The enthalpy and entropy of the dimerization reactions were determined from the dependence of the equilibrium constants on the temperature (van't Hoff equation). From these results it can be inferred that the driving force of the dimerization is of enthalpic origin.

Key words: Aggregation phenomena, Spectroscopic study, MCR-ALS, Equilibrium constant, Thermodynamic parameters

INTRODUCTION

Many dyes demonstrate ability for self-association which has applications in the photographic and dye industry (Miljanic et al, 2002). The self-association phenomenon plays an important role in biological processes. The photoprocesses of aggregated molecules play an important role for the photosynthesis in green plants and photosynthetic bacteria (Antonov et al, 1999). Dimers as the simplest aggregates are the subject of many studies concerned with the thermodynamics of monomer–dimer equilibrium and photo-physical properties, and therefore being of special interest (Chibisov et al, 1999). It is well known that the ionic dyes tend to aggregate in diluted solutions, leading to dimer formation, and sometimes even higher order aggregates. In such a case the molecular nature of dye is strongly affected by, and therefore related to such parameters as dye concentration, structure, ionic strengths, temperature and presence of organic solvents (Mchedloy-Petrossyan et al, 2003). Although dyes are very individualistic as structure and, of course behavior, certain broad rules are well established regarding the aggregation in general. It may increase with an increase of dye concentration or ionic strengths; it will decrease with temperature rising

or organic solvents adding; addition to the dye structure of ionic solubilizing groups will decrease aggregation, whereas the inclusion of long alkyl chains increase aggregation because of higher hydrophobic interaction in solution. Spectroscopic methods are in general highly sensitive and as such suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of the equilibrium constants is trivial. The absorption UV–vis spectroscopy is one of the most suitable methods for quantitative studying the aggregation phenomena of dyes as function of concentration (Micheau et al, 2004). In the commonly used concentration range (10^{-3} to 10^{-6} M) the main equilibrium is monomer–dimer reaction. In this work, we used physical constraints to determine the dimeric constants of ionic dyes (Scheme 1) in pure water.
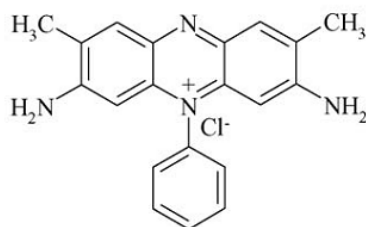
Safranine T

Scheme 1.

Aggregation is one of the features of dyes in solution (Miljanic et al, 2002; Micheau et al, 2004; Antonov et al, 1999; Ghasemi et al, 2004; Su et al, 2004; Chibisov et al, 1999), affecting their colouristic and photophysical properties and therefore being of special interest. It is famous that the ionic dyes tend to aggregate in diluted solutions, leading to dimer formation, and sometimes even higher order aggregates. In such a case the molecular nature of dye is strongly affected by, and therefore related to such parameters as dye structure, concentration, ionic strengths, presence of organic solvents and temperature. Although dyes are very individualistic as structure and, of course behavior, certain broad rules are well established regarding the aggregation in general. It may increase with an increase of ionic strengths or dye concentration; it will decrease with temperature rising or organic solvents adding; addition to the dye structure of ionic solubilizing groups will decrease aggregation, whereas the inclusion of long alkyl chains increase aggregation because of higher hydrophobic interaction in solution. Mchedlov-Petrossyan et al. recently reported several comprehensive studies on the rhodamine dyes (Mchedloy-Petrossyan et al, 1994; Mchedloy-Petrossyan et al, 2003; Mchedloy-Petrossyan et al, 2003). They studied the effects of the several experimental parameters and also the effect of the addition of some additives like crown ethers, β-cyclodextrin and inert salts as ionic strength modifiers. In spite of the presence of these interesting reports in one hand there are real vacancies on the thermodynamics parameters and on the other hand there are demands to determine the dimerization constants for the cited dyes in dilute solutions. The absorption UV–Vis spectroscopy is one of the most suitable methods for quantitative studying the aggregation phenomena of dyes as function of concentration. In the commonly used concentration range (10^{-3} to 10^{-6} M) the main reaction is monomer–dimer equilibrium. In this paper, the application of the multivariate curve resolution (MCR) method for the analysis of UV-Vis data is proposed. The goal is to calculation of the thermodynamic parameters and equilibrium constants of monomer-dimer equilibria of Safranine T.

EXPERIMENTAL

Material
All the chemicals used were of analytical reagent grade. Distilled water was used throughout of experiments. Safranine T was purchased from Fluka and were used without additional purification. A stock solution (2×10^{-4} M) was prepared by dissolving solid Safranine T in water. UV-Vis data were recorded for three concentration of Safranine solutions (1.03×10^{-5}M, 1.44×10^{-5}M, 1.73×10^{-5}M). In all experiments the ionic strengths were maintained constant by KCl (Fluka) at 1.0 mol l^{-1} solutions. The pH of the all solutions was kept constant at 7.10 using Tris buffer.

Apparatus
Absorption spectra were measured on CARY 100 UV–vis Spectrophotometer (Varian) equipped by temperature controller. Conventional quartz cell (10mm×10mm) were used throughout. The cuvettes were treated with repel-silane prior to measurements to avoid dye adsorption. The pH values were measured by a Metrohm 692 furnished with combined calomel Ag/AgCl electrode.
Computer hardware and software
All absorption spectra where digitized at five data points per nanometer in the wavelength 400–650 nm for Safranine T and transferred to a computer for subsequent analysis by MATLAB (Mathworks, Version 7.8).

Data treatment: Multivariate analysis
Multivariate UV-Vis data were analyzed with the softmodeling MCR procedure to evaluate pure spectra and concentration profiles of spectroscopically active components present in the system from decomposition of experimental data matrix D according to the equation:
$$D = CS^T + E \tag{1}$$

where C and S^T are data matrices containing concentration profiles and pure spectra for each one of these components or conformations present in the experiment, respectively. E contains residual noise not explained by the proposed components or conformations in C and S^T. The MCR procedure applied in this work consisted of the following steps (for a more extensive explanation, see references (Tauler et al, 1995).

Data arrangement
For an experiment monitored by UV-Vis, the recorded spectra were collected in a table or matrix D. The dimensions of this matrix were N_r rows×λ_m columns, where N_r represents the spectra recorded at successive temperature values and λ_m the number of wavelengths measured.

Determination of the number of conformations, N
The number of spectroscopically active conformations N was estimated by applying several methods, like singular value decomposition (SVD) or SIMPLISMA (Tauler et al, 1995).

ALS optimization
The ALS optimization procedure is an iterative method used to solve Eq. (1) for the proposed number of conformations N. This iterative process is started with an initial estimation of the pure spectra S_T for each one of the N components or conformations proposed (Tauler et al, 1995). Concentration profiles C and pure spectra S_T resolved for each conformation in the analysis of individual data matrices may differ from the true ones because of possible unresolved underlying factor analysis ambiguities (Tauler et al, 1995).

This means that concentration profiles and pure spectra may be only one solution within a band of feasible solutions that are bounded by the constraints applied in the calculation. Some of these ambiguities are more easily solved by means of the simultaneous MCR analysis of multiple experiments under different conditions. The model used for MCR simultaneous analysis of several dimerization systems at different total concentrations is described by Eq. (2):

$$
\begin{bmatrix} D_{5.15x10^{-5}M} \\ D_{5.75x10^{-5}M} \\ D_{6.35x10^{-5}M} \end{bmatrix} = \begin{bmatrix} C_{5.15x10^{-5}M} \\ C_{5.75x10^{-5}M} \\ C_{6.35x10^{-5}M} \end{bmatrix} S^T + \begin{bmatrix} E_{5.15x10^{-5}M} \\ E_{5.75x10^{-5}M} \\ E_{6.35x10^{-5}M} \end{bmatrix} \tag{2}
$$

This simultaneous analysis of several matrices has already been shown to be more powerful than the separate individual analysis, and allows improvement of the resolution of complex experimental data structures. MCR analysis of column-wise augmented data matrices has been shown to give more reliable solutions, eventually removing rotational ambiguities and rank deficiency problems (Tauler et al, 1995). All MCR calculations were performed using in MATLAB (version 7.8, The Mathworks Inc., Natick, MA, USA) routines, which can be downloaded from the MCR webpage (ASCII files).

RESULTS AND DISCUSSION

The absorption spectra of Safranine T, at different total dye concentrations, were recorded in the wavelength 400–650 nm and temperature 30–70 $^{\circ C}$ at 5 $^{\circ C}$ intervals and pH 7.10. The sample absorption spectra are shown in Fig. 1. As it is expected, by increasing the temperature and decreasing the concentration, the monomer form would be predominant over the dimer form. So it is wise to choose the spectrum of the dye at the highest temperature and at lowest concentration as an initial estimate for the monomer in the subsequent calculations. The experiments were carried out at three concentrations $(1.03x10^{-5}M, 1.44x10^{-5}M, 1.73x10^{-5}M)$.
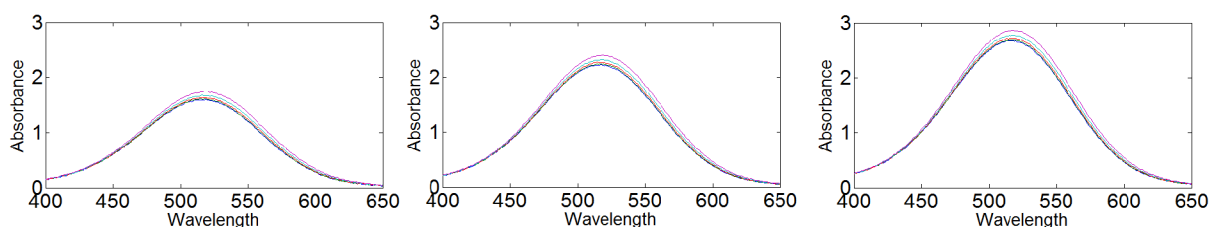

Figure 1. Absorption spectra of Safranine T: a) $1.03x10^{-5}M$, b) $1.44x10^{-5}M$ and c) $1.73x10^{-5}M$ in5 $^{\circ}$C intervals between 30 and 70 $^{\circ}$C at pH 7.10.

The MCR analysis was repeated with three and four components, and with several combinations of constraints, i.e. non-negativity, equality, unimodality and closure. The best (chemically meaningful) results were obtained when only two components were considered, all of them included in the closure constraint, and when the non-negativity constraint was applied to both spectral and concentration profiles. The lack of fit was 3.55% of the experimental data matrix D, which was considered good taking into account the instrumental technique and the large number of matrices simultaneously analyzed, recorded

in independent experimental conditions. The dependence of the concentrations of the monomer and dimer of Safranine T on the temperature in different concentrations are shown diagrammatically in (Fig. 2) and spectra profiles (Fig. 3) show the presence of two components (monomer and dimer). The spectrum of the monomer has maximum intensity at 537 nm. It is very similar to the spectrum measured in dilute solution at high temperature that was used as initial constraint. The dimer spectrum has maximum at 521 nm.
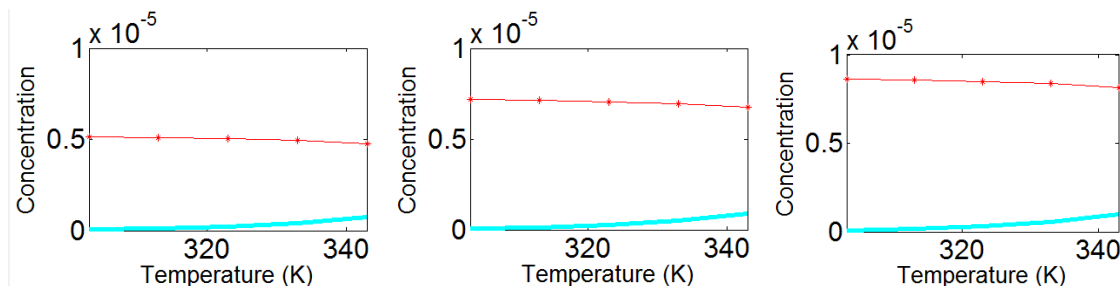

Figure 2. Concentration profiles of monomer (—) and dimer (-*-): a) 1.03×10^{-5}M, b) 1.44×10^{-5}M and c) 1.73×10^{-5}M in 5 $^{\circ}$C intervals between 30 and 70 $^{\circ}$C.
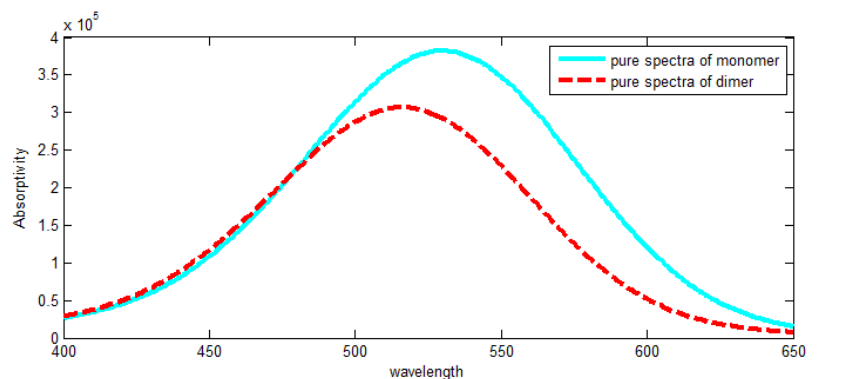

Figure 3. Spectra profiles of monomer (—) and dimer (---).

In the present paper, by utilizing the Vant-Hoff relation (Ghasemi et al, 2004), which describes the dependence of equilibrium constant on temperature, thermodynamic parameters of dimerization equilibrium have been determined:

$$lnK = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (3)$$

where H◦ is the molar enthalpy change, S is the molar entropy change , R = 8.31 Jmol^{-1} K^{-1} the universal gas constant, and T the Kelvin temperature. A linear regression of equilibrium constants with respect to 1/T is then performed, which determines enthalpy and entropy change of the reaction. The dimerization constants at 30 $^{\circ}$C and at different concentrations and thermodynamic parameters of the dimerization reactions of the Safranine T dye are listed in Table 1. We can affirm that dimerization is driven by enthalpic factors traceable to strong attractive van der Waals interaction between the two large and highly polarizable dye molecules.

Table 1: Dimeric constant (K$_D$) and thermodynamic parameters values of Safranine T dye at different concentrations

Concentration		1.03×10^{-5} mol l^{-1}	1.44×10^{-5} mol l^{-1}	1.73×10^{-5} mol l^{-1}
Log K$_D$ (30$^{\circ C}$)		4.42	4.41	4.50
ΔH° (kJ mol^{-1})		-111.2	-110.6	-110.9
ΔS° (J mol^{-1} K^{-1})		-194.1	-194.4	-192.1

The dimerization constants (K$_D$) were calculated at different temperatures and dye concentrations in pure water. As expected K$_D$ decreased with increasing temperature, while it is virtually independent of total dye concentration.

CONCLUSION

Multivariate analysis has been shown to be a useful tool for the analysis of UV-Vis data recorded during thermal change of monomer-dimer equilibria. The application of MCR improved the results obtained by classical univariate analysis of UV-Vis data. The simultaneous analysis of several data matrices, corresponding to different experimental conditions, has allowed the resolution of several systems which are difficult to solve by individual analysis.

REFERENCES

Toptygin, D., Packard, B. Z., and Brand, L. (1997). Resolution of absorption spectra of rhodamine 6G aggregates in aqueous solution using the law of mass action. *Chemical Physics letter*. 277: 430-435.

Miljanic, S., Cimerman, Z., Frkanec, L., and Zinic, M. (2002). Lipophilic derivative of rhodamine 19: Characterization and spectroscopic properties. *Analytica chimica acta*. 468: 13-25.

Micheau, J. C., Zakharova, G. V., and Chibisov, A. K. (2004). Reversible aggregation, precipitation and re-dissolution of rhodamine 6G in aqueous sodium dodecyl sulfate. *Physical Chemistry Chemical Physics*. 6: 2420-2425.

Antonov, L., gergov, G., Petrov, V., Kubista, M., and Nygren, J. (1999). UV-Vis spectroscopic and chemometric study on the aggregation of ionic dyes in water. *Talanta*. 49: 99-106.

Ghasemi, J., Niazi, A., Westman, G., and Kubista, M. (2004). Thermodynamic characterization of the dimerization equilibrium of an asymmetric dye by spectral titration and chemometric analysis. *Talanta*. 62: 835- 841.

Su, G. J., Yin, S. X., Wan, L. J., Zhao, J. C., and Bia, C. L. (2004) Dimerization of three xantene dyes on Au(1 1 1) surface. *Surface Science*. 551: 204-212.

Visser, A. J. W. G., Vos, K., van Hoek, A., and Santema, J. S. (1988). Time-resolved fluorescence depolarization of rhodamine B and (octadecyl) rhodamine B in triton X-100 micelles and aerosol OT reversed micelles. *Journal of Physical Chemistry*. 92: 759-765.

Chibisov, A. K., Prokhorenko, V. I., and Gorner, H. (1999) Effects of surfactants on the aggregation behavior of thiacarbocianine dyes. *Chemical Physic*. 250: 47-60.

Mchedloy-Petrossyan, N. O., Kukhtik, V. I., and Alekseeva, V. I., (1994). Ionization and tautomerism of fluorceine, rhodamine B, N, N-diethylirodole and related dyes in mixed and nonaqueous solvents. *Dyes and pigments*. 24: 11-35.

Mchedloy-Petrossyan, N. O., Kukhtik, V. I., and Bezugliyz, V. D. (2003). Dissociation, tautomerism and electroreduction of xantene and sulfonephetalein dyes in N, N-dimethylformamide and other solvents. *Journal of Physical Organic Chemistry.* 16: 380-397.

Mchedloy-Petrossyan, N. O., Vodolazkaya, N. A., and Doroshenko, A. O. (2003). Microenvironment on protolytic and photophysical properties of rhodamine B. *Journal of Fluorescence*. 13: 235-248.

Tauler, R., Smilde, A., and Kowalski, B. (1995). Selectivity, local rank, three-way data analysis and ambiguity in multivariate curve rsolution. *Journal of Chemometrics.* 9: 31-58.