



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Reaction kinetics of molecular aggregation of rhodamine 123 in colloids with synthetic saponite nanoparticles

Tímea Baranyaiová^a, Juraj Bujdák^{a,b,*}

^a Comenius University in Bratislava, Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, 842 15 Bratislava, Slovakia

^b Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

ARTICLE INFO

Article history:

Received 12 October 2015

Received in revised form 8 January 2016

Accepted 25 January 2016

Available online xxxx

Keywords:

Smectite

Rhodamine 123

Molecular aggregates

Stopped-flow

UV–Vis spectroscopy

Chemometry

ABSTRACT

The reaction kinetics of the molecular aggregation of rhodamine 123 in the colloids of synthetic saponite (Sumecton, Kunimine, Japan) was measured using a UV–Vis spectrophotometer equipped with a diode array detector with fast sampling and combined with a thermostatic stopped-flow device. The colloids exhibited a very small tendency to produce dye molecular aggregates, which can be explained by the low layer charge of saponite. Nevertheless chemometric methods, including principal component analysis and multivariate curve resolution, were able to sensitively identify spectral components. The reaction kinetics of dye aggregation followed the model, which was mathematically described by two-phase exponential functions, which indicated the presence of two parallel first-order reactions. Oblique aggregates were formed, characterized by approximate right angles between interacting transition moments. Another reaction, which was assigned to the structural changes of the aggregates, was detected after longer reaction times. The total span of the reaction was relatively low (~5%). The reaction was relatively fast, giving half-lives in the range 8–10 s. Reaction kinetics parameters can be useful for the characterization of similar reactions occurring in dye/clay mineral colloidal systems.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Metachromasy is an interesting phenomenon observed as a colour change of some organic dyes (Kugel, 1993). Before the physical principles of this phenomenon were understood, it had been used in clinical biology to characterize or identify cells, biopolymers or tissues. Metachromasy is interpreted in terms of the formation of dye molecular aggregates with variable spectral properties. In general, this phenomenon represents an extremely sensitive but affordable tool for the characterization of various substances with biological and inorganic origins. Dye molecular aggregation frequently occurs in the colloids of some clay minerals (Bergmann and O'Konski, 1963; Bujdák, 2006). The majority of the studies reported metachromatic behaviour of cationic dyes in smectite dispersions. The phenomenon does not directly relate to the type of mineral, but is mainly influenced by layer charge density (Bujdák, 2006). Qualitative estimations or detection of the changes in the layer charge have been investigated by measuring dye spectral properties.

Dye molecular aggregation occurring at the interface of clay mineral particles is a very complex process (Lofaj et al., 2013). Its mechanism consists of at least two steps (Murakami, 2002): The first step is a

rapid adsorption (Gemeay, 2002), often accompanied by the formation of unstable molecular aggregates. The initial aggregation may occur in the zones of the electric double layer surrounding the particles, before diffusing dye molecules reach the particle surface (Bujdák and Iyi, 2006; Bujdák et al., 2004). The second step consists of the rearrangement of the initially formed species, which is a much slower process taking several hours. The species formed over the course of dye molecular aggregation are specific for the type of dye cations (Bujdák, 2006). For example, methylene blue initially forms H-aggregates, which slowly decompose over time to J-aggregates and monomers (Bujdák et al., 2002; Bujdák and Komadel, 1997), but an opposite trend has been found for some rhodamine dyes (Lofaj et al., 2013).

Reaction kinetics and the mechanism of the dye rearrangement process are strongly related to the clay mineral's properties (Bujdák and Iyi, 2006). In order to analyse the reaction kinetics appropriately, a sufficiently precise and universal method must be developed. Simplified models which have been applied for similar systems are straightforward solutions (Chibisov et al., 2004; Görner et al., 2006). The reaction kinetics of dye molecular aggregation in clay mineral colloids is interesting from several viewpoints:

1. Measuring the reaction kinetics of dye aggregation could be useful for the quantitative characterization of some surface parameters of clay minerals. It is highly likely that some surface properties sensitively affect the activation energy of molecular aggregation. For clay minerals, the influence of the layer charge has been often observed

* Corresponding author at: Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia.
E-mail address: bujdak@fns.uniba.sk (J. Bujdák).

- (Bujdák, 2006). Mechanism and reaction kinetics seem to reflect the layer charge more sensitively than static measurements of the spectra (Bujdák and Iyi, 2006; Bujdák et al., 2004).
- There is no unique theory built on basic physicochemical laws which could explain the effects of substrate properties on dye molecular aggregation; neither in terms of thermodynamics (equilibrium) nor reaction kinetics. If a theory describing molecular aggregation in relation to the clay's surface parameters is developed, it could be applied for the characterization of other substances. Systems of poly-electrolytes (Moreno-Villoslada et al., 2009), including biopolymers (Maj et al., 2013), other substances of biological origin, and last but not least, the surface properties of nanomaterials (Liu and Kamat, 1996; Wiederrecht et al., 2003) have attracted great attention. Since some clay minerals are natural nanomaterials, the dye molecular aggregation method could be used for the sensitive detection of pollution of the environment with nanopollutants. This might help to identify the ecological impacts of the release of some nanoproducts into the environment.
 - Thanks to the high sensitivity of spectroscopic methods to detect molecular aggregates, it is possible to deeply characterize the adsorption of dye molecules at interfaces. It is impossible to obtain similar information for other organic compounds, which do not bear chromophoric groups and cannot be probed so sensitively. The basic principles of adsorption and molecular aggregation are universal, and therefore knowledge obtained from dye metachromatic behaviour can be very valuable for understanding the adsorption processes of other organic compounds.

The objective of this work was the implementation of reliable methodologies based on molecular spectroscopy in the visible region and chemometric methods, which could be used to find the mechanism of dye molecular aggregation in the colloids of clay minerals. The dispersions of rhodamine 123 (R123) and saponite (Sap) were chosen deliberately to analyse the systems which exhibit only minor spectral changes and slight tendencies to form dye molecular aggregates. The strategy was based on an appropriate processing of the spectral data by chemometry and using the results for the calculation of reaction kinetics parameters. The developed methodology is sensitive enough to be widely and efficiently applied for similar reaction systems.

2. Materials and methods

The synthetic saponite Sumecton (Sap), a product from Kunimine Ind. (Japan), was used as received without any treatment. Its structural formula has been published elsewhere (Utracki et al., 2007):



R123 was purchased in laser-grade purity from Sigma-Aldrich. Aqueous colloids and solutions were prepared in deionized water. The colloids were always prepared fresh before their use in the experiments. The solutions were always standardized using absorption spectroscopy taking into account the dye molar absorption coefficient $\varepsilon_{512} = 8.52 \cdot 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ (Du et al., 1998). For the reaction kinetics experiment, the concentrations of the dye (c_{R123}) and saponite (c_{Sap}) were $8.32 \cdot 10^{-6} \text{ mol dm}^{-3}$ and $9.02 \cdot 10^{-2} \text{ g dm}^{-3}$, respectively. The dye loading was $9.22 \cdot 10^{-5} \text{ mol g}^{-1}$. The temperature of the reactants was adjusted to 25 °C before the reaction and kinetics measurements were carried out. A UV–Vis spectrophotometer (Agilent 8453) was used to sample the spectra. It was equipped with inverted optics and a diode array detector. The measurement of each spectrum over the full spectral range was completed in less than 1 s. The quartz cell was attached to an RX2000 Rapid Mixing Stopped-Flow Unit (Applied Photophysics Ltd.), controlled with the software of the spectrophotometer, Agilent UV–Vis ChemStation, and its temperature kept constant using an 89054A Thermostatted Cell Holder (Agilent). Two runs were

carried out, the one for a longer and the other for a shorter reaction time taking 10,800 and 60 s, respectively.

Chemometric analysis applying principal component analysis (PCA) and multivariate curve resolution – alternating least squares (MCR) was performed using the software packages R and Unscrambler (Lofaj et al., 2013). They were performed for both the long and short runs. Each run was analysed for a full range of spectra, including an ultraviolet (UV) part, and for the reduced spectral range covering the main spectral band in the visible (Vis) region. The identities of the bands were only interpreted in the Vis region. Non-linear fits of the reaction kinetics models were performed using the software OriginPro 8 (OriginLab Corp.) using the concentration profiles of spectral components obtained by the MCR method. Two-phase exponential decay or growth (Vujačić et al., 2012) was applied using Eq. (1):

$$c' = c_{\infty}' + A_1'e^{-k_1t} + A_2'e^{-k_2t} \quad (1)$$

where c_{∞}' represents the plateau, which is the concentration achieved at infinite time, k_1 and k_2 represent the rate constants for the fast and slow processes, respectively. A_1' and A_2' are the spans of the reaction for the fast and slow processes. Their signs determine whether growth or decay applies. (The symbols for non-real concentrations and related parameters obtained by the MCR method or by kinetic fits from MCR data have a quotation mark, e.g. c' , A_1' , etc.). c_0' , representing the concentration value at time zero, is the sum of the parameters c_{∞}' , A_1' , A_2' obtained from the fits using Eq. (1). It can be determined from Eq. (2):

$$c_0' = c_{\infty}' + A_1' + A_2'. \quad (2)$$

Real concentrations (c) were obtained from the MCR concentrations (c') by multiple linear regression using OriginPro 8. The sum of dye concentrations c_{R123} was fitted with the concentrations obtained by MCR:

$$c_{\text{R123}} = c_{\text{aggr}} + c_{\text{mon}} = F_{\text{aggr}}c'_{\text{aggr}} + F_{\text{mon}}c'_{\text{mon}} \quad (3)$$

The F parameters denote the ratios between the real concentrations (c_{aggr} , c_{mon}) and the concentrations determined by the MCR method (c'_{aggr} , c'_{mon}). The intercept was fixed to zero during the regression.

3. Results and discussion

3.1. Absorption spectra

The aqueous solution of R123 had a maximal absorption at 500 nm (Fig. 1, dashed line). The dye adsorption on Sap particles was instantaneous, and the reaction kinetics of this process could not be followed by a stopped-flow technique. The dye adsorption was reflected in a slight shift of the main spectral band to longer wavelengths (508 nm), which was detected after the first measurement (1 s) after mixing the components. The spectral shift represented an energy difference equal to 315 cm^{-1} . Second-derivative spectroscopy confirmed this trend, although yielding partially higher wavelength values, 502 and 510 nm, respectively (see Supplementary data 1, SD1). After R123 had been adsorbed, slow, partial changes in the spectra were detected which were hardly observable (indicated by arrows in Fig. 1). The changes can be ascribed to a slight decrease in the absorbance values of the main spectral band over time, and an absorbance increase at the longer wavelengths. The spectral changes over time indicate the formation of dye molecular aggregates. The very low amount of the molecular aggregates can be explained by the low layer charge of Sap. Derivative spectroscopy was unable to detect any spectral shifts (SD2). The analysis of such minor spectral variation was challenged by chemometric analysis.

Download English Version:

<https://daneshyari.com/en/article/5469126>

Download Persian Version:

<https://daneshyari.com/article/5469126>

[Daneshyari.com](https://daneshyari.com)