Modification of crystal violet – sulfite ion equilibrium induced by SDS micelles.

E. Fernández[a], L. García-Río[a]*, J.R. Leis[a], J.C. Mejuto[b] and M. Pérez-Lorenzo[a]

[a]*Departamento de Química Física, Facultad de Química, Universidade de Santiago. Santiago, Spain*

[b]*Departamento de Química Física, Facultad de Ciencias, Universidade de Vigo, Ourense, Spain*

The presence of sodium dodecylsulfate micelles was found to displace the equilibrium between crystal violet and sulfite ion in the direction of the former and lead to complete recovery of the dye. The underlying mechanism for this anomalous behaviour was elucidated and the rate of the reversal process determined.

Keywords: micelles, crystal violet, kinetics

Micelles are self-assembled aggregates of surfactant molecules that exhibit two distinct regions of opposite hydrophobicity. One potential use of micellar media is for controlling chemical reactivity. Some reaction rates and equilibria in micellar media differ from those in conventional media as a result of the reactants being solubilised and their effective concentrations reduced through segregation into different "compartments" of the bulk medium (micelles included). These effects make micelles efficient catalysts or inhibitors for chemical reactions. The catalytic effect of micelles arises primarily from increased or decreased reactant concentrations in pseudophases of the medium.[1,2]

Predictions of reaction rates in micellar media are usually based on the *pseudophase* model,[3] which considers aqueous and surfactant components to form distinct phases where reactions occur and among which reactants and products distribute in accordance with applicable laws of kinetics and mass transfer. This model has enabled the qualitative and quantitative correlation of many experimental results,[4] often with no more than crude assumptions being made as to the distribution of reactants among *pseudophase*s.

Crystal violet (CV) is a carbonium ion that is stabilised by the presence of aromatic rings, with which it forms highly resonant structures that result in a deep blue–violet colour with an absorption maximum in the visible region.[5] The reactivity of this cation is of a high physico–chemical interest and was studied simultaneously with that of related cations with a view to establishing Ritchie's N_+ nucleophilic index.[6] Its chemistry has been examined under a variety of conditions in homogeneous[7] and microheterogeneous media.[8] In this work, we studied the effect of the presence of sodium dodecylsulphate (SDS) micelles on the reaction between CV and sulphite ion, as well as on its equilibrium. As can be tested by eye inspection the equilibrium is completely displaced to the reagents (deep blue) on addition of a crystal violet – sulphite (colourless) mixture to SDS micelles (Scheme 1).

Experimental

All chemicals used were of the highest commercially available purity, purchased from Merck or Sigma and used without further purification. CV has been supplied as chloride. The reaction medium was prepared *in situ* by using a large excess of sulfite ion, $[Na_2SO_3] = 0.5$ M, in order to ensure that all CV present would be in the form of CV–SO_3^-. Absorbance measurements were made on a Kontron Uvikon 930 spectrophotometer.

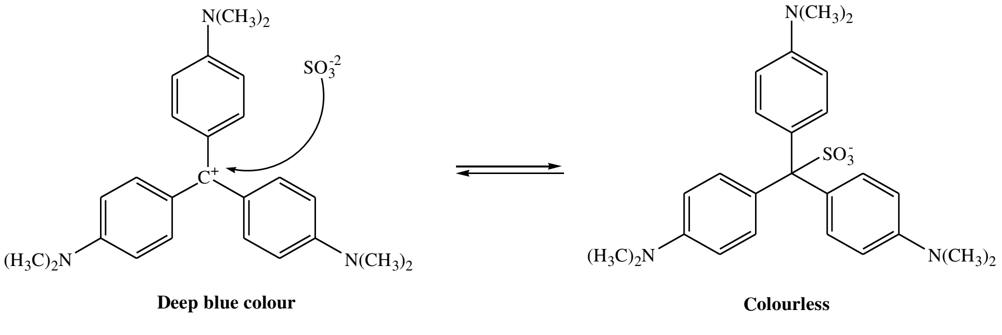
The crystal violet recovery kinetics from the equilibrium mixture between CV and SO_3^{2-} was monitored on an Applied Photophysics stopped-flow spectrophotometer by recording the increase in the absorbance at 590 nm resulting from the appearance of CV. The crystal violet – sulfite ion mixture was placed in one syringe and the SDS solution in the other one. For kinetic measurements three crystal violet concentrations were used: 5.00×10^{-6}M; 1.00×10^{-5}M and 2.50×10^{-5}M. No influence of crystal violet concentration on the observed rate constant was observed. All experiments were carried out at (25.0±.01)°C. The kinetic traces were fitted with one exponential equation using the software of the stopped-flow spectrophotometer apparatus. All the kinetic experiments could be reproduced within an error margin of 3%.

The surface tension, σ/mN m^{-1}, was measured using a Kruss tensiometer (K9) using the procedure of the Wilhelmy plates.[9] Data were the averages of 10 measurements and exhibited deviations less than 0.4% in all instances. All the measurements of surface tension had been carried out at (25.0±.01)°C.

Results and discussion

The reaction between CV and sulfite ion in the presence of sodium dodecylsulfate anionic micelles has been studied. The equilibrium constant for the reaction between CV and SO_3^{2-} in water was determined spectrophotometrically. On the assumption that the reaction product will not absorb at the working wavelength (590nm), the following equation can be obtained for the equilibrium constant between crystal violet and sulfite ion:

$$K^W = \frac{A_o - A}{\left[SO_3^{2-}\right]A} \qquad (1)$$



Scheme 1

---

* Correspondent. E-mail: qflgr3cn@usc.es

where A_0 is the absorbance of crystal violet in the absence of SO_3^{2-}, and A is the absorbance at t=∞ for different $[SO_3^{2-}]$. A plot of $(A_0–A)/A$ against sulfite ion concentration yields (not shown) a value of $K^W = (8.4 \pm 0.4) \times 10^3$ M^{-1} for the equilibrium constant in bulk water. This value is in good agreement with reported values.[7d]

The kinetic study of this reaction in bulk water allows us to obtain a value of the bimolecular rate constant, k_2=187 M^{-1} s^{-1} (at I=1.5 M). Judging by the reported value[7d] for k_2 at $I=1 \times 10^{-3}$ M (*viz.* k_2 = 470 M^{-1} s^{-1}), increasing the ionic strength has a markedly inhibitory effect on the reaction.

In the presence of SDS micelles no nucleophilic attack of sulfite ion on CV takes place. The observation that anionic surfaces make a total inhibition of the reaction is not unexpected. This behavior results from the dye associating to the micelle *pseudo*phase and SO_3^{2-} being completely excluded from it simply by electrostatic interactions. The association constant of CV to SDS micelles was determined by using a spectrophotometric procedure described elsewhere[10] and the following equation were established:

$$\frac{A - A_w}{A_m - A} = K_{CV}^m \left[D_n \right] \qquad (2)$$

where K_{CV}^m is the association constant of CV to the micelle pseudophase, A_w and A_m are its absorbances in the aqueous and micelle pseudophase, respectively. A is the absorbance at any surfactant concentration and $[D_n]$ is the concentration of micellised surfactant, defined as total surfactant concentration minus the critical micelle concentration (cmc). Where *cmc* is defined as the minimum surfactant concentration necessary for micellar aggregates to be formed. Fitting equation (2) to the experimental results (not shown) yield an association constant of crystal violet to SDS micelles of $K_{CV}^m = 25 \pm 2$ M^{-1}.

We have approached the reaction of Scheme 1 in the presence of SDS micelles along with CV-SO_3^- (colourless). When the reaction medium was supplied with SDS micelles, it regained the blue–violet colour of CV, which was completely recovered. This process was studied at variable SDS concentrations between 0 and 0.1 M, in the presence of excess sulfite ion ($[Na_2SO_3]$ = 0.5 M). Fig. 1 shows the influence of SDS concentration on the observed rate constant, k_{obs}, for CV recovery. As can be seen, k_{obs} was independent of the surfactant concentration and equal to 1.19 s^{-1}. However, below an SDS concentration of 2.5×10^{-5} M, the reaction mixture remained colourless indefinitely.

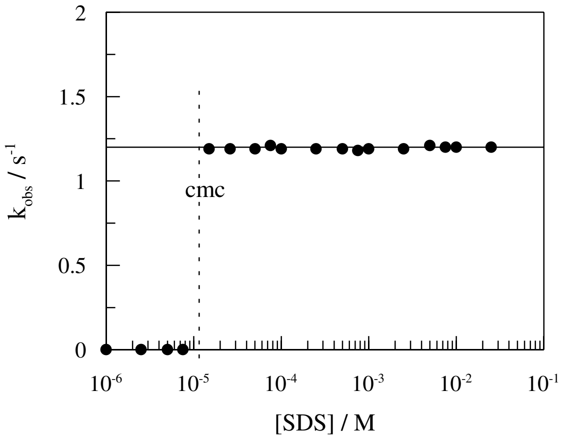


Fig. 1 Influence of SDS concentration on the observed rate constant, k_{obs}, for the crystal violet recovery from CD-SO_3^-. $[CV]=1.00 \times 10^{-5}$ M, $[SO_3^{2-}]$=0.5 M.

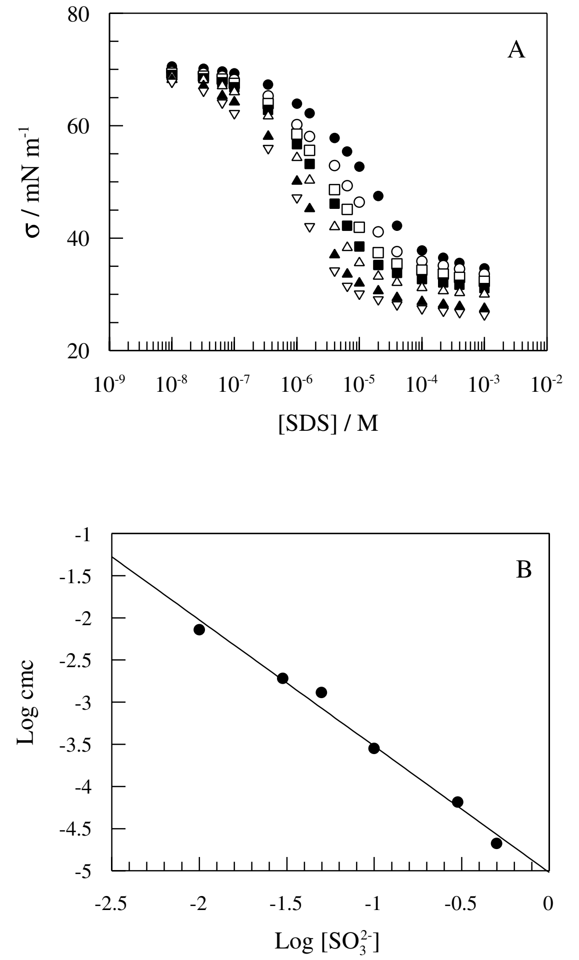


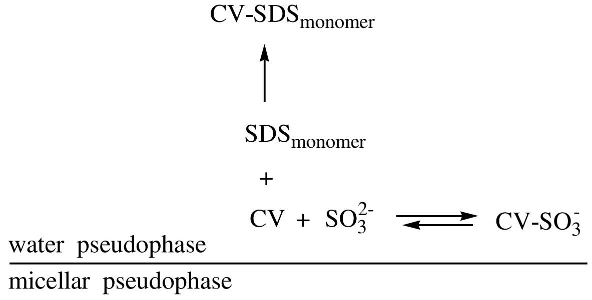
Fig. 2 (A) Influence of [SDS] upon surface tension of aqueous solutions of SDS + SO_3^{2-}. (B) Influence of $[SO_3^{2-}]$ upon *cmc* values of aqueous solutions of SDS + SO_3^{2-}.

The presence of electrolytes is known to significantly decrease the critical micelle concentration (*cmc*).[11] In order to determine the *cmc* for SDS in the presence of 0.5 M Na_2SO_3 (*i.e.* under the conditions used in our study), we made surface tension measurements of the solution at variable SDS concentrations between 0.1 and 10^{-7} M (Fig. 2). The *cmc* value thus obtained was 2.1×10^{-5} M.

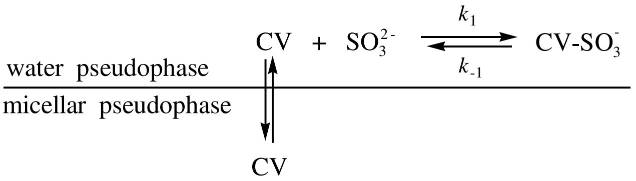
In order to understand the influence of SDS micelles on the equilibrium between CV and SO_3^{2-} we consider the following mechanisms.

Mechanism I

SDS may act as a nucleophile on CV[12], thereby altering its equilibrium with sulfite ion. In this mechanism SDS monomers should compete with SO_3^{2-} for CV as shown in Scheme 2.



Scheme 2



Scheme 3

Solid evidence against this mechanism, however, is provided by the fact that CV colour is not regained below the surfactant's *cmc*, where free monomers present could indeed act as nucleophiles. Moreover, the similarity between the surfactant concentration at which no further colour recovery is observed (see Fig. 1) and the *cmc* of SDS under our working conditions allows us to state that the origin of the colour recovery is the presence of SDS micelles rather than that of surfactant monomers in the reaction medium.

Mechanism II

Once the need for the presence of micelles has been admitted, one plausible mechanism for the experimental behaviour observed may be that which assumes that the fraction of CV in free form (about 1×10^{-8} M) associates to micelles and becomes unreactive by virtue of the inability of sulfite ion to attack micelle-associated CV. This would shift the equilibrium towards CV and hence towards colour recovery. The mechanism is depicted in Scheme 3.

From mechanistic Scheme 3 we can obtain the following rate equation:

$$k_{obs} = \frac{k_1\left[SO3^{2-}\right] + k_{-1} + k_{-1}K_{CV}^{m}\left[D_n\right]}{1 + K_{CV}^{m}\left[D_n\right]} \tag{3}$$

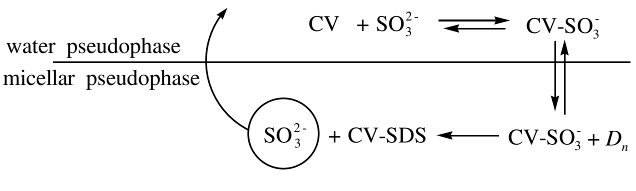
Equation 3 is not compatible with the experimental results showed in Fig. 1. In order of getting k_{obs} independent of SDS concentration we need to fit one of the following conditions: *(a)* $k_1[SO_3^{2-}] + k_{-1} \approx k_{-1}\ K_{CV}^m\ [D_n]$ and $K_{CV}^m\ [D_n] << 1$ so that $k_{obs} = k_1\ [SO_3^{2-}] + k_{-1}$ or *(b)* $k_{-1}\ [SO_3^{2-}] + k_{-1} \approx k_{-1}\ K_{CV}^m\ [D_n]$ and $K_{CV}^m\ [D_n] >> 1$ so that $k_{obs} = k_1$. By using previously obtained values of $k_1 = 187 M^{-1} s^{-1}$ and $K_{CV}^m = 25 M^{-1}$ we can see that condition *(a)* is not fitted because for $[SO_3^{2-}] = 0.50 M$ and using $k_{obs} = k_1\ [SO_3^{2-}] + k_{-1}$ we get $k_{obs} \approx 90 s^{-1}$. The possibility that condition (*b*) works also can be ruled out because the assumption $K_{CV}^m\ [D_n] >> 1$ by using $K_{CV}^m = 25 M^{-1}$ is only fitted for $[D_n] >> 0.05 M$. Because the experimental behaviour of Fig. 1 we can rule out the possibility shown in Scheme 3.

Mechanism III

Micellised SDS might act as a nucleophile and displace sulfite by attacking the central carbon atom in the $CV–SO_3^-$ system.

From Scheme 4, the following rate equation can be derived:

$$k_{obs} = k_m \frac{K\left[D_n\right]^2}{1 + K\left[D_n\right]} \tag{4}$$



Scheme 4

where K is $K_w K_s[SO_3^{2-}]$, K_s is the binding constant of $CV–SO_3^-$ to SDS micelles, K^W the equilibrium constant between crystal violet and sulphite ion, and k_m is the rate constant for nucleophilic attach of micellised SDS on $CV\text{-}SO_3^-$. Equation (4) predicts a quadratic dependence of k_{obs} on the surfactant concentration, which is not the case (see Fig. 1). Consequently, this potential mechanism can also be ruled out.

Mechanism IV

The reaction product may associate to micelles, thus cleaving the $CV–SO_3^-$ molecule and causing sulfite ion to be excluded from the micelle pseudophase by electrostatic repulsion from surfactant heads. As a result, CV would associate to the micelle pseudophase and sulfite ion would be repelled to the aqueous pseudophase (see Scheme 5).

From Scheme 5, and assuming that $V = K_{-1}^m[CVSO_3^-]_m$ we can obtain the following expression for the rate equation:

$$k_{obs} = \frac{k_{-1}^{m}\ K^{w}\ K_{CVSO_3^-}^{m}\left[SO_3^{2-}\right]_T\left[D_n\right]}{\left(1 + K^{w}\left[SO_3^{2-}\right]\right) + \left(K_{CV}^{m} + K^{w}\ K_{CVSO_3^-}^{m}\left[SO_3^{2-}\right]_T\right)\left[D_n\right]} \tag{4}$$

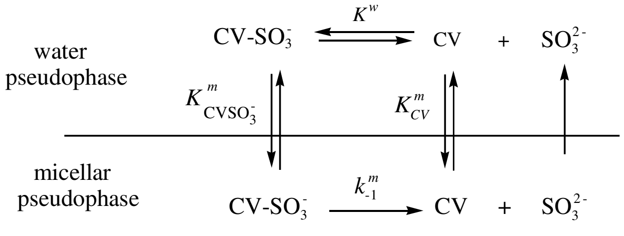
where $K_{CVSO\text{-}3}^m$ and K_{CV}^m are the binding constants of $CVSO_3^-$ and crystal violet to the SDS micelles. K^w is the equilibrium constant for the reaction in bulk water. Values of $K^w = (8.4 \pm 0.4) \times 10^3\ M^{-1}$ and $K_{CV}^m = 25 \pm 2\ M^{-1}$ were previously determined. By using these values and considering that $[SO_3^{2-}]_T = 0.50 M$, we can simplify equation (5) to $k_{ob} = k_{-1}^m$. This rate equation is consistent with experimental results showed in Fig. 1. This mechanism predicts a surfactant concentration-independent first-order rate constant, which is consistent with cleavage of the $CV–SO_3^-$ molecule ($k_{ob} = 1.19\ s^{-1}$).

Conclusions

The displacement of the equilibrium between crystal violet and sulfite ion in the direction of the former in the presence of SDS micelles has been demonstrated. The presence of SDS micelles implies a complete recovery of the dye. The mechanism for this behaviour was elucidated. The $CV–SO_3^-$ may associate to micelles, thus cleaving the $CV–SO_3^-$ molecule and causing sulfite ion to be excluded from the micelle pseudophase by electrostatic repulsion from surfactant heads. As a result, CV would associate to the micelle pseudophase and sulfite ion would be repelled to the aqueous pseudophase (Mechanism IV).

Financial support from the Xunta de Galicia (PGIDT03-PXIC20905PN and PGIDIT04TMT209003PR) and Ministerio de Ciencia y Tecnología (Project BQU2002-01184) is gratefully acknowledged.

Received 11 March 2005; accepted 11 July 2005
Paper 05/3127



Scheme 5

References

1 J.H. Fendler and E.J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York 1975.

2 C.A. Bunton and G. Sabelli, *Adv. Phys. Org. Chem.,* 1986, **22**, 213.

3 (a) L.S. Romsted, *Surfactants in Solution,* K.L. Mittal, B. Lidmann, Eds.; Plenum Press, New York 2, 1984; (b) E. Rodenas, F. Ortega, S. Vera, C. Otero and S. Maestro, *Surfactants in Solution,* K.L. Mital, B. Lidmann, Eds.; Plenum Press, New York 9, 1989; (c) L. García-Río, P. Herves, J.C. Mejuto, J. Perez-Juste and P. Rodriguez-Dafonte, *New J. Chem.*, 2003, **27**, 372.

4 (a) C.A. Bunton, F. Nome, F.H. Quina and L.S. Romsted, *Acc. Chem. Res.,* 1991, **24**, 357; (b) L. García-Río, E. Iglesias, J.R. Leis, M.E. Peña, *Langmuir,* 1993, **9**, 1263; (c) A. Fernández, E. Iglesias, L. García-Río, J.R. Leis, *Langmuir,* 1995, **11**, 1917; (d) L. García-Río, P. Hervés, J.R. Leis, J.C. Mejuto and J. Perez-Juste, *J. Phys. Org. Chem.,* 1998, **11**, 584.

5 G.N. Lewis, T.T. Magel, D. Lipkin, *J. Am. Chem. Soc.,* 1942, **64**, 1774.

6 C.D. Ritchie, *Can. J. Chem.,* 1986, **64**, 2239.

7 (a) C.D. Ritchie, D.J. Wright, H. Der-Sing and A.A. Kamego, *J. Am. Chem. Soc.*, 1975, **97**, 1163; (b) J.E. Dixon and T.C. Brucice, *J. Am. Chem. Soc.,* 1971, **93**, 6592; (c) L. García-Río, P. Hervés, J.R. Leis and J.C. Mejuto, *J. Chem. Res.,* 1997, 326; (d) C.D. Ritchie and P.O.I. Virtanen, *J. Am. Chem. Soc.,* 1973, **95**, 1882.

8 (a) L. Mukherjee, N. Mitra, P.K. Bhattacharya and S.P. Moulik, *Langmuir,* 1995, **11**, 2866; (b) J.R. Leis, J.C. Mejuto and M.E. Peña, *Langmuir,* 1993, **9** , 889; (c) L. García-Río, J.R. Leis, J.C. Mejuto, A. Navarro-Vazquez, J. Perez-Juste and P. Rodriguez-Dafonte, *Langmuir,* 2004, **20**, 606.

9 R. Van der Bogaert and P. Joos, *J. Phys. Chem.,* 1980, **84**, 190.

10 (a) P. Herves, J.R. Leis, J.C. Mejuto and J. Perez-Juste, *Langmuir,* 1997, **13**, 6633; (b) L. García-Río, P. Herves, J.C. Mejuto, M. Parajo and J. Perez-Juste, *J. Chem. Res.*, 1998, 716.

11 D. Stiger, *Electrostatic interactions in aqueous enviroments*, IUPAC Comission, La Joya, California, 1975.

12 J.C. Mejuto, unpublished results.