

# Catalysis of Cationic Surfactants in Organic Solvent: Hydrolysis of 2-Nitro-4-Carboxyphenyl Acetate

ANTONIO CIPICIANI\* and STEFANIA PRIMIERI

*Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy.*

and

ANTONIO ARCELLI

*Dipartimento di Chimica 'G. Ciamician', Università di Bologna, 40126 Bologna, Italy.*

(Received: 7 February 1992; in final form: 19 May 1993)

**Abstract.** The hydrolysis reaction of 2-nitro-4-carboxyphenyl acetate was studied in dichloromethane in the presence of an added electrolyte (NaOH) and cationic surfactants systems with varying quantities of added water at 25°C. The kinetic and conductivity data were correlated.

**Key words:** 2-Nitro-4-carboxyphenyl acetate, catalysis, hydrolysis, dichloromethane, reverse micelles.

## 1. Introduction

Amphiphilic molecules, when dissolved in organic solvents, are capable of self-organization. These aggregates of surfactant molecules solubilise readily, in apolar solvents, water and several other polar solvents, e.g. glycerol and formamide.

Solubilised water differs from bulk water in its physicochemical properties [1]. However, when water volume increases in the system, the differences in solubilised and bulk water properties become less pronounced.

Many techniques [2] have been used to study the state and influence of water solubilised in apolar solvents by different surfactants (cationic, anionic and zwitterionic) on the aggregation of amphiphilic molecules in apolar solvents.

Both the size and shape of the surfactant aggregates in organic solvents are critically dependent on the number of water molecules available per polar head of the surfactant, that is on the ratio  $R = [\text{H}_2\text{O}]/[\text{surfactant}]$ .

Therefore the structures of surfactant systems in apolar solvents also depend upon the relative amounts of surfactant and water.

In dry solvents these systems may exist as ion assemblies rather than as micelles. The anomalous water entrapped in surfactant aggregates in organic solvents will obviously influence the chemical behaviour of guest molecules and, on the other hand, the presence of guest chemical species can considerably modify the physicochemical properties of the water.

---

\* Author for correspondence.

Another reason for interest in the study of the nature of the water of such systems is that, according to several authors, the entrapped water resembles the water adjacent to biological membranes [3]. To date, no general theory exists which quantitatively describes the solubilised water properties and which can predict its behavior in different situations.

Therefore we undertook the study of the hydrolysis reaction of 2-nitro-4-carboxyphenyl acetate (**1**) in dichloromethane at 25°C in the presence of cationic surfactants and an electrolyte (NaOH) with various amounts of water.

## 2. Experimental

The surfactants and the substrate (**1**) were prepared and purified according to standard methods [4–7]. Dichloromethane was distilled over P<sub>2</sub>O<sub>5</sub>. Solutions of NaOH were prepared at different pH values such that the surfactant solutions with the different water concentrations had the same analytical pH.

### 2.1 RATE MEASUREMENTS

The hydrolysis reaction of (**1**) in dichloromethane was followed at 25°C using a Perkin-Elmer 551S spectrophotometer at 420 nm under pseudo-first order kinetic conditions. The substrate concentration was  $6 \times 10^{-5}$  M.

### 2.2 SPECIFIC CONDUCTIVITY MEASUREMENTS

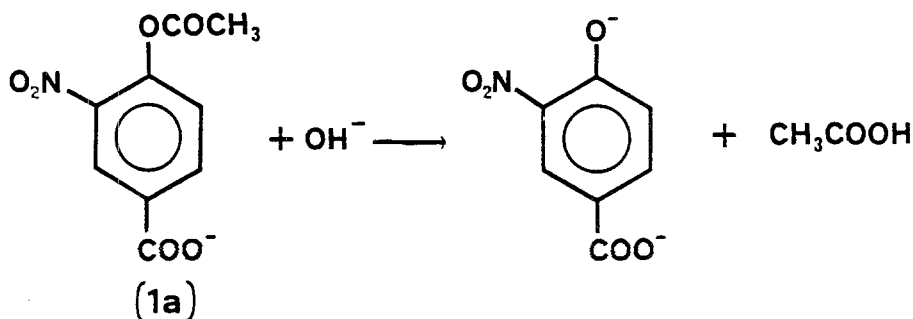
The conductivity of the surfactant solutions was measured at 25°C with an Amel Model 133 Conductivity meter equipped with a Philips PW 9512/01 closed dipping cell (1 cm).

## 3. Results and Discussion

The hydrolysis reaction of (**1**) in dichloromethane in the presence of cationic surfactants such as dodecyltrimethylammonium bromide (DTABr), cetyltrimethylammonium bromide and chloride (CTABr and CTACl), was investigated in various concentrations of water, adding NaOH to the system at a concentration of  $2.7 \times 10^{-3}$  M. This concentration is that of the single surfactant solutions at the various water concentrations and not necessarily of the reaction site.

The specific conductivities of the single surfactant solutions were also determined.

Under the experimental conditions, (1) is present as an anion (**1a**):



The anion, compared with (1), guarantees greater affinity towards the aqueous phase than towards the continuing apolar phase. The partition coefficient between the two phases was determined:

$$[(1)](\text{H}_2\text{O})/[(1)](\text{dichloromethane}) = 1.8.$$

It can therefore be hypothesised that the reaction center of (**1a**) is not in the continuing apolar phase, dichloromethane, but rather in the polar microenvironment resulting from the self-organization of the surfactant in dichloromethane and in which the hydroxide ions are mainly present.

There is no hydrolysis of (1) in the [dichloromethane–water–surfactant] system without NaOH. The rate of hydrolysis of (1) in the [dichloromethane–water–surfactant–NaOH] system obviously depends on the NaOH concentration: an increased NaOH concentration increases the rate of the reaction. In an aqueous NaOH solution at the concentration of  $2.7 \times 10^{-3}$  M, the pseudo-first order rate constant,  $k_{\text{obs}}$ , is  $1.8 \times 10^{-2} \text{ s}^{-1}$ , while in aqueous solution at pH 8 (potassium dihydrogen phosphate–sodium hydroxide) the  $k_{\text{obs}}$  value is  $2 \times 10^{-5} \text{ s}^{-1}$ .

The possibility that (**1a**) can act as a nucleophile on another substrate molecule was experimentally excluded: the rate of hydrolysis of (1) is independent of the substrate concentration in both an aqueous solution of NaOH at a concentration of  $2.7 \times 10^{-3}$  M and in the [0.1M CTABr – dichloromethane – 0.7M H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] system.

The spectrophotometric comparison of the hydrolysis product with an authentic sample of 4-hydroxy-3-nitrobenzoic acid, excluded the hypothesis that the substrate can decarboxylate.

The kinetic and conductivity data show that our experimental evidence is consistent with ‘continuous equilibrium’ models of aggregates in apolar solvents [8].

The kinetic data of (1) are a response to the evolution of the aggregation process of surfactant systems as a function of the quantity of water added.

The solubilised water from different surfactant systems for a NaOH concentration of  $2.7 \times 10^{-3}$  M in dichloromethane is such that:

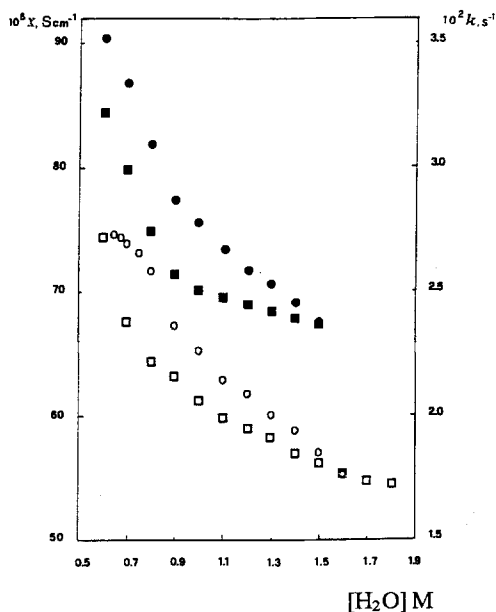


Fig. 1. [0.1M DTABr – dichloromethane – H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] system: ●  $k_{\text{obs}}$  values with increased water concentration; ■  $X$  values with increased water concentration. [0.1M CTABr – dichloromethane – H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] system: ○  $k_{\text{obs}}$  values with increased water concentration; □  $X$  values with increased water concentration.



In both 0.1M DTABr and 0.1M CTABr, the hydrolysis reaction of (1) in dichloromethane-NaOH slows down with increased water concentration (Figure 1). The minimum quantity of solubilised water from CTABr and DTABr is 0.6–0.7M. At this water concentration the slight plateau of the kinetic profile, for both surfactants, suggests a situation of maximum reactivity. The inhibition of the reactivity with increased water concentration corresponding to an evolution of the surfactant at the water-pool (see the specific conductivity profiles shown in Figure 1), is related primarily to a dilution effect of the nucleophile.

The  $k_{\text{obs}}$  values related to the 0.1M DTABr surfactant system are slightly greater than those of the 0.1M CTAB system; this probably suggests that the nucleophilic activity and/or the stabilization of intermediate are different in CTABr than in DTABr.

The hydrolysis reaction of (1) in [0.1M CTACl – dichloromethane – H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] first shows catalysis for small quantities of added water (up to [H<sub>2</sub>O] = 0.3M) and then inhibition occurs with increased water concentration (Figure 2).

The [CTABr – dichloromethane – 0.7M H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] and [CTABr – dichloromethane – 1.6M H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] systems have a decreased reactivity and increased conductivity with increased surfactant con-

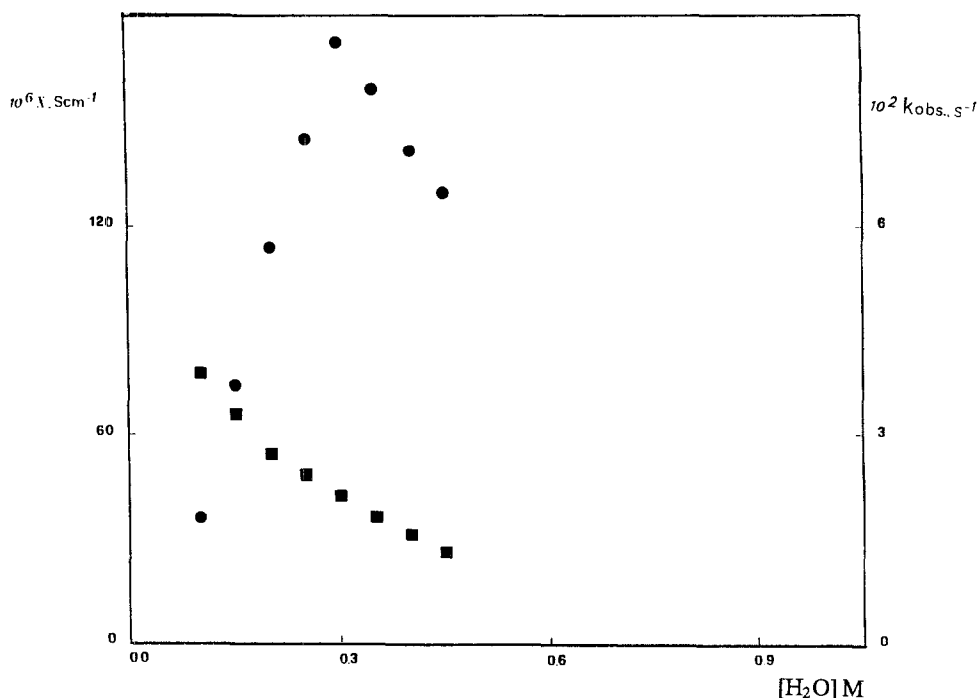


Fig. 2. [0.1M CTACl – dichloromethane – H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] system: ●  $k_{\text{obs}}$  values with increased water concentration; ■  $X$  values with increased water concentration.

centration (Figure 3). The conductivity profiles reflect the change, with decreased surfactant concentration, from small-sized aggregates or clusters to larger but fewer aggregates.

Therefore, lowering the surfactant concentration causes a change from a colloidal system type of organization in which the nucleophile is more structured, 'more bound', and therefore probably less reactive, to more hydrated aggregates with a more active nucleophile.

The [CTACl – dichloromethane – 0.2M H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] system shows increased conductivity and decreased reactivity with increased surfactant concentration as shown for CTABr (Figure 4). However, for [H<sub>2</sub>O] = 0.4M, increases in both conductivity and reactivity can be seen with increased surfactant concentration. This can be related to the evolution of the surfactant system from large aggregates which probably are affected by the dilution of the reagents to smaller but more numerous aggregates which obviously represent a better condition for the reactivity of (1). When the two surfactant systems CTABr and CTACl are compared, the different roles of the counterions in the reactive process must be considered; Cl<sup>-</sup>, more hydrated than Br<sup>-</sup>, determines a nucleophilic activity in the reaction site which is probably different from Br<sup>-</sup>.

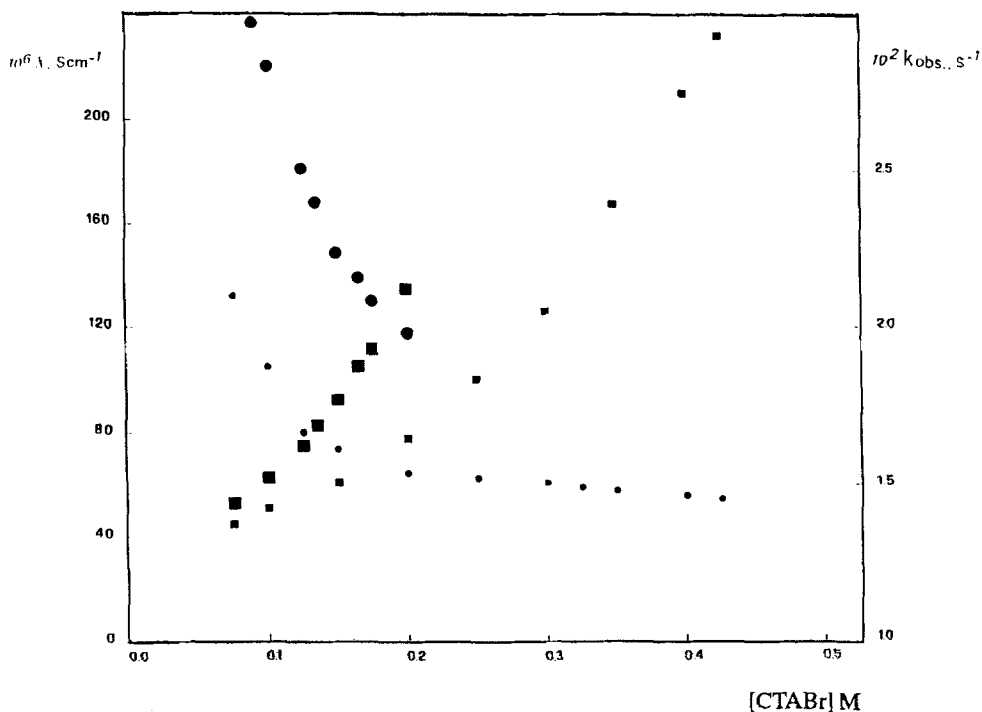


Fig. 3. [CTABr – dichloromethane – H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$  M] system: ●  $k_{obs}$ . values with increased surfactant concentration for [H<sub>2</sub>O] = 0.7M; ■  $X$  values with increased surfactant concentration for [H<sub>2</sub>O] = 0.7M; ●  $k_{obs}$ . values with increased surfactant concentration for [H<sub>2</sub>O] = 1.6M; ■  $X$  values with increased surfactant concentration for [H<sub>2</sub>O] = 1.6M.

At this point it can be reasonably hypothesised that the kinetic profile of catalysis and inhibition shown by the [0.1M CTACl – dichloromethane – H<sub>2</sub>O – NaOH  $2.7 \times 10^{-3}$ ] system (Figure 2) reflects the whole evolution of the surfactant in the aggregation process in organic solvent with increased water added. The ion pairs or small clusters in dry dichloromethane hydrate with added water and form small aggregates. As the water increases, the aggregates become larger and the nucleophile is 'freer' for the reactive process and then a reduced conductivity and increased reactivity is observed. However, beyond [H<sub>2</sub>O] = 0.3M, the aggregates become larger to the point that the dilution effect of the reagents on the reactive process begins to be important causing a decreased reactivity and further reduced conductivity.

Therefore with 0.1M CTACl, we can follow the evolution of the aggregation process from small ion clusters while with 0.1M CTABr this process begins from an advanced stage of surfactant aggregation in so far as the system is homogeneous from [H<sub>2</sub>O] = 0.6–0.7M. Then the nature of the counterion seems to play an important role in the organization of the surfactant system in organic solvent.

The observed  $k_{obs}$ . values in the three surfactant systems studied under the same

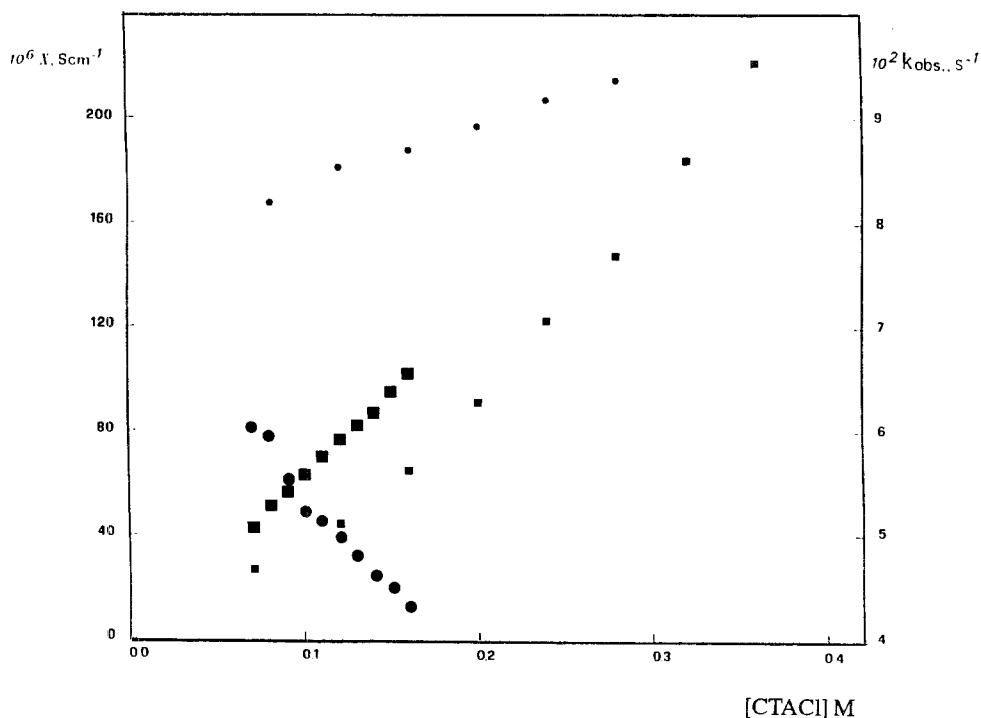


Fig. 4. [CTACl – dichloromethane –  $\text{H}_2\text{O}$  –  $\text{NaOH } 2.7 \times 10^{-3} \text{ M}$ ] system: ●  $k_{\text{obs.}}$  values with increased surfactant concentration for  $[\text{H}_2\text{O}] = 0.2\text{M}$ ; ■  $X$  values with increased surfactant concentration for  $[\text{H}_2\text{O}] = 0.2\text{M}$ ; ●  $k_{\text{obs.}}$  values with increased surfactant concentration for  $[\text{H}_2\text{O}] = 0.4\text{M}$ ; ■  $X$  values with increased surfactant concentration for  $[\text{H}_2\text{O}] = 0.4\text{M}$ .

experimental conditions are such that:

$$k_{\text{obs.}} (\text{CTACl}) > k_{\text{obs.}} (\text{DTABr}) > k_{\text{obs.}} (\text{CTABr})$$

It is interesting to note that the  $k_{\text{obs.}}$  values in the [CTABr 0.1M –  $\text{H}_2\text{O}$  – dichloromethane –  $\text{NaOH } 2.7 \times 10^{-3} \text{ M}$ ] system are similar to those in an aqueous solution of  $\text{NaOH}$  at the concentration of  $2.7 \times 10^{-3} \text{ M}$  ( $k_{\text{obs.}} = 1.8 \times 10^{-2} \text{ s}^{-1}$ ).

This suggests that CTABr in dichloromethane forms microdroplets in which the physico-chemical properties of the water-pool are similar to those of the bulk water and that the substrate probably has the reaction center immersed in the water-pool.

Therefore passing from CTABr to DTABr to CTACl, the physico-chemical properties of the water pools become steadily more distant from those of the bulk water. Therefore, both the head group and the counterion of the amphiphilic molecules, play an important role in the organization of colloidal systems in organic solvents and consequently in the reactivity of eventual probes studied in them.

## References

1. K. Martinek, A.V. Levashov, N.L. Klyachko, Yu.L. Khmel'nitski, and I.V. Berezin: *Eur. J.*

- Biochem.* **155**, 453 (1986).
2. P.L. Luisi, and B. Straub: *Reverse Micelles*, Plenum Press, New York (1984).
  3. C.A. Boicelli, F. Conti, M. Giomini, and A.M. Giuliani: *Physical Methods on Biological Membranes and Their Model Systems*, Plenum, New York (1985).
  4. A. Cipiciani, R. Germani, G. Savelli, C.A. Bunton, M. Mhala, and J.R. Moffatt: *J. Chem. Soc., Perkin Trans. 2*, 541 (1987).
  5. C.A. Bunton, L.H. Gan, J.R. Moffatt, L.S. Romsted, and G. Savelli: *J. Phys. Chem.* **85**, 4118 (1981).
  6. A. Cipiciani, R. Germani, G. Savelli, and C.A. Bunton: *J. Chem. Soc., Perkin Trans. 2*, 527 (1985).
  7. C.G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky: *J. Am. Chem. Soc.* **87**, 296 (1965).
  8. E. Geladè, A. Verbeeck, and F.C. De Schryver: *Surfactant in Solution* (Vol. 5, Eds. K.L. Mittal and P. Bothorel), p. 565, Plenum, New York (1986).