

Effects of temperature on micellar-assisted bimolecular reaction of methylnaphthalene-2-sulphonate with bromide and chloride ions

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Dedicated to the late Professor Giuseppe Onori, our friend and colleague suddenly died in 2012.

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ABSTRACT

Reactivity of methyl naphthalene-2-sulphonate, MeONs, with H₂O, Br⁻ and Cl⁻ in water and in cationic micelles of cetyltrialkylammonium surfactants, *n*-C₁₆H₃₃N⁺R₃X⁻, R = Me (CTA⁺), *n*-Pr (CTPA⁺), X = Br, Cl, CH₃SO₃, has been investigated in the temperature range 25–45 °C. Micellar rate effects were analysed by using the pseudophase treatment, and the second-order rate constants in the micellar pseudophase were evaluated at the various temperatures. Values of these rate constants increase with temperature, and the effect is less important in micelles than in water and more important for chloride than for bromide ions. Micelles lead to an ion behaviour discrimination, whose extent depends on surfactant type and on temperature, with maximum effect in CTPA⁺ at 25 °C and with bromide being always more reactive than chloride.

Quantitative analysis of the temperature effect by the Eyring equation showed that micelles speed up reaction of MeONs with halide ions by decreasing the activation enthalpies, which is partially offset by decreases in the activation entropies. The rate acceleration by increase in surfactant head group size has only enthalpic origin for bromide and only entropic origin for chloride: this different behaviour was rationalised taking into account both solvation of anions and the hydrophobic effect.

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1. Introduction

The study of chemical reactions in presence of aqueous association colloids has been traditionally related by many researchers to the understanding of membrane mediated processes in living cells [1,2]; nevertheless, the vast majority of the experimental investigations have been carried out at 25 °C, sometimes at 30 °C and rarely at different temperatures [1,3–6]. Moreover, there is currently an increasing use of surfactants in biological systems: they have been used to bind DNA molecules for, e.g., transfection into living cells [7,8], in antibacterial formulations [9], or in pharmaceutical formulations as dissolving vehicle and as protecting agent (from degradation of the drug) [10,11]. A deeper understanding of such complex systems is required in order to be able to design new surfactants and their supramolecular aggregates for specific applications, and we think that the study of processes occurring in the presence of association colloids around physiological temperatures (37 °C) and the systematic investigations of the temperature effects upon processes are important steps in this direction. Furthermore, investigations of temperature effects upon chemical

processes in aqueous association colloids are useful also to have an approach more “structure–property relationship based” rather than empirical in relatively new, practical, applications of surfactants such as Enhanced Oil Recovery [12] or as nonconventional reaction media at temperature up to 100 °C for industrial uses [13].

Actually, in the literature, there are investigations of structural properties of surfactant systems at various temperatures, for instance studies of the thermodynamic of micellisation process [1,14–16]. However, to the best of our knowledge, there is limited investigation on the temperature effects upon reactivity of micellar-associated substrates. Furthermore, most of them have been devoted to monomolecular reactions, because of the simpler treatment of reactivity data. In fact, micellar effects upon spontaneous reactions can be treated quantitatively in terms of an equilibrium distribution of substrate, *S*, between water and micelles, which are treated as a distinct reaction regions, as shown in Scheme 1.

In this Scheme, *S* is substrate and subscripts *W* and *M* denote aqueous and micellar pseudophase respectively, *k*'_W and *k*'_M are first-order rate constants, and *K*_S is the association constant of substrate, *S*, with micellized surfactant (detergent), Dn, whose concentration is the total less that of monomer, given by the cmc [1,4–6]. The overall first-order rate constant, *k*_{obs}, is therefore given by the following equation:

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Nomenclature

| | | | |
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| α | degree of micellar ionisation | k_2^m | second-order rate constant in the micellar pseudophase ($M^{-1} s^{-1}$): $k_2^m = k_M V_M$ |
| cmc | critical micellar concentration | S | reactive substrate |
| Dt | stoichiometric concentration of surfactant (detergent) | V_M | molar volume element of reaction in the micelle |
| Dn | concentration of micellized surfactant: generally $[Dn] = [Dt] - cmc$ | CTA ⁺ | cetyltrimethylammonium |
| K_S | binding constant* of solute based on concentration of micellized surfactant | CTPA ⁺ | cetyltripropylammonium |
| K'_{Nu} | mass action binding constant* of ionic species Nu | CTABr | cetyltrimethylammonium bromide |
| k'_W | first-order rate constant (s^{-1}) in the aqueous pseudophase | CTACl | cetyltrimethylammonium chloride |
| k_W | second-order rate constant ($M^{-1} s^{-1}$) in the micellar pseudophase | CTAOMs | cetyltrimethylammonium methanesulphonate |
| k'_M | first-order rate constant (s^{-1}) in the micellar pseudophase | CTPABr | cetyltripropylammonium bromide |
| k_M | second-order rate constant (s^{-1}) in the micellar pseudophase, with concentration expressed as mole ratio | CTPACl | cetyltripropylammonium chloride |
| | | CTPAOMs | cetyltripropylammonium methanesulphonate |
| | | MeONs | methyl naphthalene-2-sulphonate |

*We use the word constants as usual in the literature, but we have to indicate that they are not thermodynamic constants.

$$k_{obs} = \frac{k'_W + k'_M K_S [Dn]}{1 + K_S [Dn]} \quad (1)$$

This equation predicts that for fully bound substrate (i.e. $K_S [Dn] \gg 1$ and $K_S [Dn] k'_M \gg k'_W$), values of k_{obs} reach a constant value, and k_{obs} equals k'_M :

$$k_{obs} = k'_M \quad (2)$$

Following this treatment, activation parameters for monomolecular reactions in the micellar pseudophase have been calculated unambiguously from temperature effects on k'_M and compared with values for reaction in water [17–19].

The situation is more complicated for bimolecular reactions. In fact, for these, overall second-order rate constants depend upon the distributions of both reactants between the aqueous and the micellar pseudophases, and the second-order rate constants in each pseudophase [1,4–6]; therefore, the temperature affects both these distributions and the rate constants. It is difficult to measure the temperature effect on distributions and therefore to rationalise the overall observed effect on the kinetics; moreover, most kinetic analyses have been based on data at only one temperature [1,4–6]. Notwithstanding these difficulties, there have been attempts (also quite recently) to study temperature effects upon reactivity of reactions more complex than simple monomolecular ones, and values of “apparent” activation parameters were obtained from treatment of temperature effects upon overall rate constants [3,20–22]; although these parameters are of some utility, the authors themselves stated that these are often of ambiguous interpretation [21]. Other recent studies concerned the kinetic study of certain reactions at temperatures higher than 25 °C, such as investigations at physiological temperatures of ca. 35–37 °C, [23,24] but also up to 80 °C [25]; anyway, quantitative analyses of rate data were based on several (three-four) adjustable parameters evaluated

from fittings, and for this reason, the interpretation can be ambiguous.

In this paper, we studied the temperature effect upon the S_N2 reaction of methylnaphthalene-2-sulphonate (MeONs) with nucleophiles, as shown in Scheme 2.

Reactivity of MeONs with water had already been investigated in cationic surfactant cetyltrimethylammonium methanesulphonate (CTAOMs) [26,27], and reactivity with bromide and chloride had already been investigated in cationic surfactants of increasing head group bulk, i.e. in cetyltrimethylammonium halides (CTABr and CTACl) and cetyltripropylammonium halides (CTPABr and CTPACl) [28–30]. Here, we extended the investigation, using a temperature range of 20 °C (from 25 to 45 °C) around the physiological temperature. This reaction has been (and still is) extensively investigated in a variety of colloidal assemblies and quantitative treatments have been applied to it, so that various parameters to fit kinetic data at 25 °C are available in the literature, which is of great help in analysing the kinetic data [28–36]. Moreover, a recent systematic investigation of temperature effect upon structural parameters of these four surfactants was essential for our current work, helping in the evaluation of consistent parameters to be used in fitting kinetic data at the different temperatures [16].

The effect of temperature upon ion behaviours and reactivities for different halides such as bromide and chloride could be thus analysed, and also, the effect of increasing head group size could be studied.

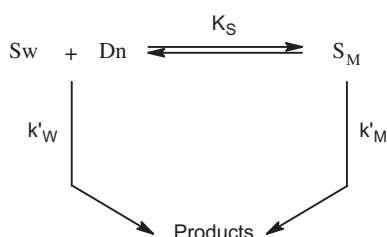
2. Materials and methods

2.1. Materials

Preparation and purification of MeONs and surfactants were carried out following standard procedures [26,29,30].

2.2. Kinetic measurements

Reaction was followed spectrophotometrically at 326 nm at the various temperatures (± 0.1 °C) in double beam UV–Vis 2401 PC Shimadzu spectrophotometer. Freshly prepared solutions of MeONs in MeOH were added to 3 ml of the reaction solutions, and the substrate concentration in the cuvette was 1×10^{-4} M, whereas the reaction mixture contained 1% organic solvent. Integrated pseudo-first-order rate plots were linear for up to 3–4 half-lives. Good ($R^2 > 0.99$) pseudo-first-order kinetic plots were



Scheme 1. Substrate distribution and reaction in each pseudophase.

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