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Examination of the pseudophase model of monomer-micelle interconversion in cetylpyridinium chloride

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Abstract

The $^{35}Cl^-$ NMR chemical shift and line width and the ^{1}H chemical shifts of cetylpyridinium chloride, CPyCl, change abruptly at the critical micelle concentration, indicating conversion of monomeric surfactant into micelles within a very small range of concentration. The simple pseudophase treatment fits these results up to 0.05 M CPyCl, but there then appears to be a modest change in micellar structure. Premicelles of single chain surfactants, detected kinetically or photochemically, are probably formed by interactions between reactant(s) and surfactant.

Keywords: Micellization; Premicelles; Pseudophase treatment; NMR spectroscopy

1. Introduction

Aqueous surfactants self-associate to form micelles at the critical micelle concentration, cmc. This structural change is identified by changes in bulk physical properties, including surface tension, electrolytic conductance of ionic surfactants, changes in the spectra of hydrophobic dyes, and increases in light scattering [1–4], although different methods, especially the use of hydrophobic dyes, usually give differences in the cmc. These changes occur over a narrow range of [surfactant] and can be regarded as a gradual change of composition over this range, following a mass action relationship, or as an abrupt change, such that the solution contains only monomeric or micellized surfactant. The evidence can be rationalized in terms of either treatment, because they become essentially equivalent with high aggregation numbers [1–4].

This second description is often used in interpreting micellar effects upon reaction rates and equilibria in terms of the so-called pseudophase model [5]. The cmc is regarded as the concentration of monomeric surfactant and reaction rates, for example, change as micelles form and then provide a reaction region distinct from the bulk solvent. Rates depend on rate constants in water and micelles and the partitioning of reactants between the two regions. The reaction region in aqueous ionic micelles is assumed to be the interface between water and micelles which encompasses the surfactant head groups and adjacent methylene groups. Dimensions of this region probably depend on the nature of the reactants and hydrophobic substrates may penetrate the apolar micellar core.

The pseudophase, ion-exchange, PIE, model fits extensive data on competition between reactive and inert counterions [5–7], although for reactions involving multivalent metal ions and their complexes some simplifying assumptions of this treatment are unsatisfactory [8,9]. Kinetic data can also be treated in terms of distributions of initial and transition states between water and micelles [9,10]. The pseudophase and transition state models differ only in their description of transfers between regions and the choice between them is a matter of convenience [11].

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The pseudophase treatment is qualitatively robust, at least for reactions involving organic molecules and most simple inorganic ions, provided that we accept the limitations of some assumptions at very low or high surfactant concentrations [5–7]. Typically rate constants do not change abruptly at the cmc, but at a lower [surfactant]. This deviation from the simple model is often ascribed to reactant-induced micellization, consistent with extensive evidence on solute effects on the cmc [5–8]. However, there are spontaneous and bimolecular ionic reactions for which observation of rate maxima at [surfactant] close to the cmc demonstrates that reactions can occur in premicelles as well as in micelles [5,12,13]. These observations do not demonstrate the existence of premicelles in the absence of reactants, although that explanation is not excluded [14].

The second weakness of the simple PIE treatment is evidence of deviations from the predicted relationship between rate constants and concentrations of surfactant and added electrolyte. The simple PIE treatment involves the assumption that the fractional micellar charge, α, is constant [5,7]. This assumption fails in high [electrolyte], and a decrease in α is consistent with theoretical treatments of ion binding which fit kinetic data over a wide range of surfactant and electrolyte concentrations [15,16]. The kinetic data in high [electrolyte] can also be accommodated by minor adjustments to the PIE pseudophase treatment [17], and α probably varies modestly with [surfactant] even without added electrolyte [15,16,18].

Evidence on micellar structure may involve the use of spectral probes, which are typically large polarizable ions or molecules and may perturb micellar or premicellar structure. However, evidence from NMR spectroscopy can, in favorable cases, be used in the absence of probes [19]. For example, ^{1}H and ^{13}C chemical shifts of organic groups and line widths, or relaxation rates, of counterions, e.g., Cl^- or Na^+, change on micellization and also provide information on micellar growth [20–23].

In the present work we examined variations of ^{35}Cl NMR line widths and ^{1}H and ^{35}Cl chemical shifts of cetylpyridinium chloride over a range of concentrations from below the cmc to 0.1 M. Much of the kinetic data which lead to the development of the PIE and similar models involved reactions of hydrophilic monoanions, e.g., OH^- or halide ion, with very dilute organic substrates in this range of [surfactant] [5–7]. Cationic micelles with Cl^- as counterion do not grow rapidly with increasing $[Cl^-]$, unlike the corresponding bromides [24], which simplifies analysis of the data. All measurements were at 25 °C generally in H_2O:D_2O 4:1 v/v and no added solutes.

The binding of Cl^- or Br^- to cationic micelles can be monitored by the increasing line width of the NMR signal in going from free to micellar-bound ions [19,23]. Provided that the solution contains only free and micellar-bound Cl^-, Cl_W^- and Cl_M^-, respectively, the increase in line width, B, should fit Eq. (1), at least in dilute surfactant, where, with no micellar growth B_M, for bound Cl^- should be constant, and B_W, for free Cl^- is measured below the cmc,

$$B = (1 - \chi_M)B_W + \chi_M B_M \tag{1}$$

and χ_M is the mole fraction of bound Cl^-.

At the simplest level the line width below the cmc should be approximately constant and increase abruptly at the cmc, but if premicelles and micelles coexist there may be a gradual change in the line width at [CPyCl] near to the cmc. The $^{35}Cl^-$ chemical shifts, or the ^{1}H or ^{13}C chemical shifts in an organic group in the surfactant, also change on micelle formation [19]. All ^{35}Cl and ^{1}H NMR measurements were with cetylpyridinium chloride, CPyCl, in H_2O–D_2O or D_2O. This surfactant is convenient for examination of ^{1}H NMR chemical shifts because signals of the head group and the $C_{16}H_{33}$ group are well separated.

2. Experimental

2.1. Materials

Cetylpyridinium chloride was a sample used earlier [25]. Solutions were made up in D_2O (99.9% D) or its mixtures with deionized, redistilled, H_2O.

2.2. Methods

The NMR chemical shifts and line widths were monitored on a Varian Inova instrument (500 MHz for ^{1}H) at 25 °C with 5 and 10 mm NMR tubes for ^{1}H and $^{35}Cl^-$ spectra, respectively. The ^{1}H chemical shifts were referred to external TSP (sodium 3-(trimethylsilyl) propanesulfonate) in D_2O, but samples generally contained small amounts of dioxane as an internal reference, and its chemical shift, relative to TSP was 3.770 ± 0.001 ppm. For measurements of $^{35}Cl^-$ chemical shifts, a spectrum of 0.05 M NaCl in H_2O:D_2O 4:1 v/v was obtained between each measurement of CPyCl in this solvent. This procedure avoids overlap of the signals of NaCl and CPyCl. Line widths of $^{35}Cl^-$ were calculated by using line broadening to improve the signal to noise ratio with standard Varian software.

3. Results and discussion

3.1. Variation of $^{35}Cl^-$ line widths

The concentration of Cl^- in the aqueous pseudophase, $[Cl^-]_W$ is the sum of the cmc and the amount released from the micelle,

$$[Cl^-]_W = \text{cmc} + \alpha\big([\text{CPyCl}] - \text{cmc}\big). \tag{2}$$

Equations (1) and (2) can be rewritten as

$$B[\text{CPyCl}] - B_W\text{cmc} = \big(\alpha B_W + (1-\alpha)B_M\big)\big([\text{CPyCl}] - \text{cmc}\big). \tag{3}$$