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Review

Mass spectrometric characterization of the non-ionic gemini surfactant Surfynol 465 and a microcalorimetric study of its micelle formation in water

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ABSTRACT

Electrospray ionization mass spectrometry was applied to determine the molecular weight distribution and the number average molecular weight of the commercially available gemini surfactant α,α′-[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ω-hydroxylpoly(oxyethylene)], Surfynol 465 (S465), with NaCl and KCl as the cationization agents. The enthalpies of S465 micelle formation in aqueous solution were measured over a range of temperature by thermometric titration with a MicroCal VP-ITC microcalorimeter. The critical micelle concentration (cmc) of S465 decreased as the temperature was increased from 298 K to 348 K. The variation of the calorimetric enthalpy of micelle formation with temperature was markedly linear in this range of temperature, which allowed extrapolation to slightly higher temperatures. The van't Hoff enthalpies calculated from the temperature dependence of the cmc, were in excellent agreement with the directly measured calorimetric enthalpies. It could be established that S465 micellization changed from endothermic to exothermic as the cmc passed through a minimum at 357 K. The thermodynamic analysis indicated that micelle formation is favoured by entropy and opposed by enthalpy up to this temperature, after which the aggregation is favoured by both entropy and enthalpy. The enthalpy–entropy compensation resulted in a slight decrease in Gibbs free energy with increase in temperature.

Contents

1. Introduction

Gemini (also called dimeric) surfactants are a new generation of synthetic amphiphiles in which two conventional (monomeric) surfactant molecules are interconnected with a spacer group close to the hydrophilic heads [1–6]. These surfactants have significantly lower cmc's and better surface-active properties than the corresponding monomeric species. The synthesis of gemini surfactants from fine chemicals is generally expensive, and the possibilities for the commercial uses of geminis are therefore currently rather limited. Cost-effective technology was developed by Air Products and Chemicals, Inc. to produce the Surfynol 400 family, which is suitable for a variety of industrial applications, including water-borne coatings, fountain solutions, latex dipping, agricultural chemicals, metal-working lubricants, electroplating and acid pickling, pressure-sensitive adhesives, concrete and oil well cementing [7–10]. These acetylenic diol-based non-ionic surfactants are obtained by reacting various amounts of ethylene oxide (EO) with 1,4-diisobutyl-1,4-dimethylbutynediol (Surfynol 104). The addition of EO to Surfynol 104 increases the hydrophilic

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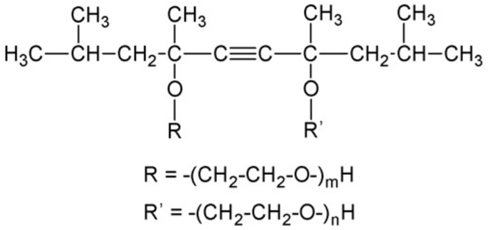

Fig. 1. The structure of S465 surfactant; m + n = 11.4.

nature (HLB) of the product, thereby modifying its water solubility, defoaming, wetting and adhesion characteristics.

A number of academic studies have demonstrated the potential usefulness of Surfynol surfactants, e.g. for the synthesis of silica-bound stationary phases for applications in gas and liquid chromatography [11]; for complex formation with a variety of polymers in order to improve the quality of water-based printing inks [12]; for their reducing and stabilizing abilities in the preparation of gold nanoparticles [13]; and for their wetting efficiency in the aqueous colloidal processing of ceramics [14].

The molecular structure and the physico-chemical properties of the surfactant Surfynol 465 (S465) have been studied by ^{1}H-nmr spectroscopy [15], ^{13}C-nmr spectroscopy [16], pulsed-field gradient spin-echo nmr spectroscopy [17], surface tension measurements [10,17], solution calorimetry [18], osmometry [19], mass spectrometry [20–22], small-angle neutron scattering and dynamic light scattering measurements [23]. The number average molecular weight of the S465 monomer lies in the range 600–730 [19–21]; the cmc at 298 K is ~12 mM [15,16,18,19]; the aggregation number at this temperature is ~13 [19]; the equilibrium surface tension is 26 mJ m^{-2} [10]; the micelle radius has been determined to be 2–3 nm [15,16,18,23]; and the enthalpy of micelle formation at 298 K has been found to be 24 kJ mol^{-1} [18].

The present paper is concerned with the thermodynamics of S465 micelle formation in aqueous solution over a range of temperature. The cmc and the enthalpy of micelle formation were determined by titration microcalorimetry. The Gibbs free energy and the entropy term of micellization were calculated via the mass action model and the Gibbs–Helmholtz relation [24–28].

2. Experimental

2.1. Materials

Surfynol 465 is α,α′-[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ω-hydroxylpoly(oxyethylene)], with a total of ~11 EO units (Fig. 1). The surfactant, a colourless liquid, was a gift from Air Products Netherlands BV (lot no. A512151); it was used as received. Deionized water was produced with a Milli-Q filtration system.

2.2. Methods

2.2.1. Mass spectrometry

The molecular weight distribution of S465 was determined by electrospray ionization mass spectrometry (ESI-MS) by using the Agilent 6120 Single Quadrupole instrument. The mobile phase (water) was percolated at a flow rate of 0.33 mL min^{-1} by using an HPLC pump (Agilent 1200). Sample solutions (1 g L^{-1}) were prepared in water in the presence of a cationization agent; NaCl or KCl. The solutions were introduced into the spray chamber of the MS instrument by using an electric injection valve equipped with a 2-μL sample loop. Spraying conditions: capillary voltage, 3 kV; ionization temperature, 523 K; drying gas (N_2) flow rate, 10 mL min^{-1}; nebulizer pressure, 1810 Torr. The ESI source was connected with the quadrupole analyzer of the MS, which in turn was connected to the detector maintained under a pressure of 5×10^{-5} Torr. The mass range was scanned from 100 to 1200 Da. In the absence of a cationization agent, no signals could be observed in the ESI-MS spectrum of S465, indicating that the measurements were made under conditions that were sufficiently mild to avoid unwanted fragmentation and ionization of the sample.

2.2.2. Titration microcalorimetry

Thermometric titration experiments were performed in the temperature range 298.15–348.15 K, using a Microcal VP-ITC power-compensation microcalorimeter with a cell volume of 1.4163 mL. For the study of demicellization, 10-μL aliquots (25–28 injections) of a surfactant solution (100 mM, i.e. ~10 times the cmc) at periodic time intervals (10 s per injection, 5 min between injections) were titrated into pure water in the calorimetric cell. The heat evolved during the stepwise dilution experiment was recorded in the form of a series of calorimetric peaks. The enthalpogram (calorimeter power signal vs time) was evaluated with Origin 7 software. The errors of the cmc and enthalpy determination were 1.3% and 3.0%, respectively.

3. Results and discussions

The thermodynamics of micelle formation can be described in terms of the Gibbs free energy ($\Delta_{\rm mic}G$), the enthalpy ($\Delta_{\rm mic}H$) and the entropy term ($T\Delta_{\rm mic}S$) of micellization. However, a commercial surfactant sample often consists of a mixture of oligomers or homologues, e.g. the Triton-X, the Brij and the Igepal series, which are the prototypes of commercial non-ionic surfactants possessing a series of EO oligomers as the hydrophilic head group. The description of the thermodynamic potential functions of a polydisperse surfactant on a kJ mol^{-1} basis is therefore not completely straightforward: the molecular weight distribution and the number average molecular weight are key fundamental properties for such a thermodynamic analysis. The number average molecular weight ($M_{\rm N}$), the weight average molecular weight ($M_{\rm W}$) and the polydispersity index (PD) are defined as follows [20,21]:

$$M_{\rm N} = \frac{\sum_i M_i N_i}{\sum_i N_i} \tag{1}$$

$$M_{\rm W} = \frac{\sum_i (M_i)^2 N_i}{\sum_i M_i N_i} \tag{2}$$

$$\mathrm{PD} = \frac{M_{\rm W}}{M_{\rm N}} \tag{3}$$

where M_i is the mass of the i-th oligomer in the distribution and N_i is its intensity. These quantities can be calculated from the distribution of observed peak areas obtained by gas chromatography, size exclusion chromatography, nmr spectroscopy or a variety of MS techniques [20–22]. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements suggested that, upon cationization, the two EO side-chains of the surfactant are folded to allow the cations to be chelated by oxygen atoms via multicoordination [20,21]. We applied ESI-MS to determine the molecular weight distribution of S465. The intensities (N_i/total counts) of the S465 oligomers cationized by Na$^+$ and K$^+$ are plotted against the individual ion masses (M_i/Da) in Figs. 2 and 3, respectively. The present experimental conditions resulted in charges of +1 for the surfactant oligomers. Each M_i is composed of the backbone diol (Surfynol 104), the total mass of the EO segments in the i-th oligomer species and the mass of the metal cation. Neighbouring peaks are separated by 44 Da, the mass of one EO unit. The MS spectra were transformed to molecular weight distributions and quantified further by using