



Thermodynamics of micellization of homologous series of alkyl mono and di-glucosides in water and in heavy water



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Dedicated to the memory of the late Professor Manuel Ribeiro da Silva

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ABSTRACT

In this study, isothermal titration calorimetry was used to follow the micellization of two homologous series of alkylglucoside surfactants from heptyl to nonylmonoglucosides and from octyl to dodecyl diglucosides over the temperature range from (15 to 65) °C. These measurements allowed the calculation of the thermodynamic parameters associated with micelle formation, viz.: Gibbs free energy, enthalpy, entropy and heat capacity changes. Moreover, micellization of one of these surfactants, nonylmonoglucoside, was also investigated in heavy water, D₂O, at different temperatures for comparison.

Overall, these results conformed very well with the behaviour displayed by other surfactants with respect to changes within the homologous series. Use of additivity schemes provided estimates of contributions from the polar head group and the methylene units to these thermodynamic functions. The good agreement between the results for alkylglucosides micellization and literature data for other surfactants confirms that, with respect to the hydrophobic interior, their micelles display similar properties. The same can be said about the temperature dependence for micellization, which follows that of other surfactants. Two specific issues were investigated. First the contributions from one versus two glucoside units in the surfactant chemical structure were assessed, which turned out to be essentially the same because the data for the two families of surfactants could be superimposed within their experimental uncertainty. The second addressed possible differences regarding micelle formation in normal and heavy water. In this respect, data for the micellization of one of these surfactants provided values for the thermodynamic functions in D₂O that could be considered only slightly different from those in H₂O.

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1. Introduction

Alkylglucosides are non-ionic surfactants obtained from raw materials which ally their origin from renewable materials with very interesting properties such as total biodegradability and almost absence of toxicity to humans [1]. They can be typically obtained from vegetable sources such as corn and fatty acids, becoming an alternative in commercial products to polyglycol ethers, which are normally obtained from non-renewable sources (most notably petroleum). For these properties, they are termed as green surfactants and this appeal has added significant interest in the study of their surface-active properties. The first publication on their physico-chemical properties dates from the 1950s [2,3] but only more recently other reports started to appear in the scientific literature, most likely due to their commercial availability as their production becomes economically interesting. Nowadays, many chemical companies supply these surfactants which can be used for various chemical and pharmaceutical applications.

Phase diagrams for binary mixtures of these surfactants with water have been reported [4] that display mesophases, which are also formed by other non-ionic surfactants such as ethoxylated surfactants. One clear difference with respect to the solution behaviour of ethoxylated surfactants is the small temperature dependence on the phase borders in the phase diagrams of alkylglucoside surfactants.

Some earlier studies on the thermodynamics of their micellization have been reported [5–8] and in most of these, isothermal titration calorimetry has been employed. This is a technique most suitable to this kind of study because it provides direct determination of the three thermodynamic functions, with high precision and accuracy [9]. In addition, when results for the homologous series are available, these data can be treated by additivity principles to provide the contributions from surfactant head groups and hydrocarbon chains (typically expressed per methylene unit). Additionally, the possibility of performing experiments at different temperatures allows the determination of changes in heat capacity associated with this process that have been shown to provide important information on solvation, most notably the so-called hydrophobic effect [10–13].

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The aim of the present study was to explore the potential of titration calorimetry in the investigation of the homologous series of mono and dialkylglucoside surfactants over a wide temperature range to provide a complete thermodynamic description of their micellization trends. For nonylmonoglucoside, micellization in heavy water was also studied and the results compared with those obtained in normal H₂O.

For the sake of simplicity, alkylglucosides will be referred here-in often as *CmGn* where *m* is the number of carbon atoms in the hydrophobic chain and *n* means the number of glucoside units.

2. Experimental

2.1. Chemicals

The full description of the provenance and purity of the chemicals used in this study is provided in [table 1](#).

2.2. Equipment and procedure

Two titration calorimeters were used. Most of the experiments were performed with a VP-ITC MicroCal, and only for the experiments with heptylmonoglucoside, at temperatures of (15 and 25) °C. Another calorimeter, Thermometric 2277 TAM was used, to allow for measurements of greater power values associated with the use of more concentrated solutions required by the larger CMC values of this surfactant. For TAM, electrical calibration was performed before each experiment, while the ITC calorimeter was checked by chemical calibration using propanol dilution [14,15].

In both cases, solutions around 20 times the estimated CMC values were used for titration with addition of aliquots of around 10 μL into cells containing 1.44 mL (VP-ITC) or 4 mL (TAM). In the case of the former, the cell is filled and there is an overflow of solution accompanying each injection, which is taken into account for concentration calculations. Titration proceeded until there were no more significant changes in the enthalpies measured above CMC. At least two independent experiments were performed for each condition and deviations are shown in some figures, but they are typically smaller than the size of the data points.

CMC values were determined at the inflection point of the titration curves, and the enthalpy change associated with micellization was determined from the extrapolation of enthalpy values before and after micellization, calculated at the inflection point. This procedure has been described in more details elsewhere [9,16]. This enthalpy difference was also corrected to account for the amount of non-aggregated surfactant in the syringe, as follows [9]:

$$\Delta_{\text{mic}}H = \Delta_{\text{mic}}H^{\text{obs}}[C/(C - \text{CMC})], \quad (1)$$

where $\Delta_{\text{mic}}H^{\text{obs}}$ is the enthalpy difference directly determined from the titration curve, *C* and *CMC* are, respectively, the surfactant concentration in the syringe and at the CMC.

Values for the Gibbs free energy change associated with micellization were calculated as:

$$\Delta_{\text{mic}}G = RT \ln \text{CMC}, \quad (2)$$

and the respective entropy changes calculated from the enthalpy and Gibbs free energy change values.

Changes in the heat capacity associated with micelle formation were calculated from the enthalpy values determined within this temperature range (15 to 65) °C, as follows

$$\Delta_{\text{mic}}C_p = (\delta\Delta_{\text{mic}}H/\delta T)_p. \quad (3)$$

Some measurements were also performed using a high-sensitivity DSC, a VP-DSC from MicroCal, Inc., to determine the temperatures at which micellization occurred, the so-called critical micellization temperatures (cmt). These are taken as the temperature at the maximum for each transition peak. Experiments were performed using surfactant solutions close to CMC (from 0.9 to 2 times CMC values at 25 °C), at scanning rates of (0.5 to 1) °C · min⁻¹.

3. Results

A typical set of titration curves is shown in [figure 1](#), for decyldigluco-side, from (15 to 65) °C in H₂O. These results indicate a significant change in the values of the enthalpy of micellization, which start positive at low temperatures, becoming negative at higher temperatures. CMC values and, particularly, the Gibbs free energy values do not change as much and, consequently, entropy values should also vary to compensate for the variation of enthalpy values. This is typical behaviour displayed in aqueous systems, including surfactant solutions, referred to as enthalpy–entropy compensation [5,17].

[Figure 2\(A\)](#) and [\(B\)](#) display the currently determined CMC values and the thermodynamic functions of micellization for decyldigluco-side, along with a set of literature data [5] that reveal very good agreement among the different data sets. It is worth mentioning that [figure 2\(A\)](#) represents a diagram displaying conditions (temperature and concentration) at which micellization occurs, with minimum in CMC values around 35 °C. From the van't Hoff approximation, the change in CMC (or $\Delta_{\text{mic}}G$) values allows one to estimate the corresponding enthalpy changes. In this work, we found no reason to derive actual van't Hoff enthalpies, due to the greater uncertainty associated with these values with respect to calorimetric results, but the changes in CMC with temperature are consistent with an endothermic process below 35 °C, and an exothermic one above this temperature, agreeing the with calorimetry results.

For this reason, micellization could be also induced by temperature changes, that would appear as vertical lines in [figure 2\(B\)](#), moving from one region to another crossing the micellization border. This property was explored by performing high sensitivity DSC measurements in solutions with surfactant concentration close to the CMC, which produced calorimetric curves similar to those represented in [figure 3\(A\)](#). This approach has been previously described by Kresheck [18] and Blume and co-workers [5]. The latter was seen for some glucoside surfactants and, once more, both data sets fit the same trend, as can be seen in [figure 3\(B\)](#) and in [supplementary material](#) accompanying this paper.

The availability of a comprehensive data set as the one produced by this study allows determination of a series of thermody-

TABLE 1
Provenance and purity information for chemicals used in this study.

Chemicals	Source	Mass fraction purity ^a	Treatment
Heptyl, octyl and nonylmonoglucosides	Anatrace Inc.	>0.99	None
Octyl, nonyl, decyl, undecyl and dodecyldigluco-sides	Anatrace Inc.	>0.99	None
Water, H ₂ O	Milli Q	Milli Q grade	None
Heavy water, D ₂ O	Goss Scientific Instruments	0.999	None

^a As stated by the suppliers.

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