

LIPID-SIMILAR THERMAL TRANSITION OF POLYETHYLENE GLYCOL ALKYL ETHER DETERGENTS

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Abstract

A narrow, reversible endothermic main transition is found in the aqueous micellar phase of octaethylene glycol tetradecyl ether ($C_{14}E_8$) by DSC, characterized by a transition temperature of 41°C and a ΔH value of 0.5 kcal mol⁻¹, which is not observed by light scattering. This transition is assigned to a cooperative conformational rearrangement of the assembled amphiphilic detergent molecules and not to a micelle aggregation process. It is suggested that the detergent's polar head group is primarily involved in this rearrangement.

Keywords: $C_{14}E_8$, detergent, DSC, polyethylene glycol tetradecyl ether, thermal transition

Introduction

Nonionic polyethylene glycol (E_y) n -alkyl (C_x) monoether detergents (type C_xE_y surfactants) are of considerable scientific and technical interest. Depending on the detergent concentration in the aqueous environment, these amphiphilic compounds can exist in different phases above their critical micelle concentration (*cmc*). Generally, the phases consist of a micellar phase (L_1), different mesophases or the hydrated detergent phase in the presence of small amounts of water (cf. phase diagrams in [1]). This phase behaviour is very sensitive to temperature and is characterized at high temperatures by a phase separation (cloud point temperature). Above this critical temperature, a detergent enriched and a detergent poor phase (L'_1 and L''_1) coexist, where the latter one is of higher density [2]. Much interest has also been devoted to ternary mixtures of this type of detergents with water and a hydrophobic component (oil), which leads to the formation of microemulsions [3]. Besides these aspects of fundamental importance, nonionic detergents of the C_xE_y type are also widely used in membrane biochemistry (above the *cmc*) for the solubilization of integral membrane proteins under conditions where the protein's functional properties remain [4].

There is a lack of knowledge about the assembly behaviour of type C_xE_y detergents in the temperature range between the L_1 and the coexisting L'_1/L''_1 phases. These are conditions that are relevant for many of the biochemical applications. In a recent study, it has been shown that for $C_{12}E_6$ a temperature-sensitive phase bound-

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ary between globular micelles and large aggregates exists in this intermediate range [5]. The corresponding transition temperature strongly depends on the detergent's concentration. Temperature-induced phase transitions can be easily investigated by thermoanalytical methods such as differential scanning calorimetry (DSC). Employing DSC, it is shown that a narrow thermal transition can be observed in aqueous solutions of some C_xE_y type detergents. The transition is characterized by properties that are similar to those of lipid phase transitions [6].

Materials and methods

Octaethylene glycol tetradecyl ether ($C_{14}E_8$) of quality grade BioChemika and glycerol of grade puriss. p.a. have been purchased from Fluka (Deisenhofen) and ethylene diamine N,N,N',N'-tetraacetic acid (EDTA) of quality grade for analysis from Merck (Darmstadt). The detergent is dissolved at room temperature in a filtered (0.2 μm Millipore) and degassed buffer solution consisting of 30 mM histidine (Microselect quality, Fluka)/HCl and 0.1 mM EDTA pH 6.8 in a N_2 atmosphere.

DSC measurements are performed on the MCS DSC instrument (MicroCal, Northampton). Prior to filling the capillary cell, the detergent solution is thoroughly degassed under reduced pressure. Runs from 10 to 100°C (30°C h⁻¹) are recorded.

Static light scattering measurements are carried out on a Spex 212 fluorimeter (Instruments S.A., Grasbrunn), equipped with a thermostated cuvette holder for a semi-micro 1 ml quartz cuvette from Hellma (Müllheim). Both double monochromators are set to 300 nm. The temperature gradient is achieved with a K4R/R20K thermostat (MGW Lauda, Lauda) and the temperature is measured inside the cuvette with a Pt100 sensor and a Fluke (Ismaning) 2180A RTD digital thermometer.

Results and discussion

As a representative example of type C_xE_y detergents, $C_{14}E_8$ (Fig. 1) has been chosen for a thermochemical investigation employing DSC.

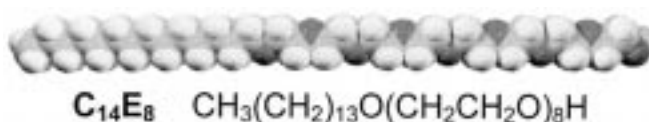


Fig. 1 Structure and molecular model of octaethylene glycol tetradecyl ether ($C_{14}E_8$)

Thermoanalytical curves obtained with a 60 mM solution of this detergent are shown in Fig. 2. The chosen concentration is far above the *cmc*, which is about 0.01 M for $C_{14}E_8$ [2]. The first curve (Fig. 2a) shows an endothermic main transition which is characterized by a transition temperature of 40.6 ± 0.5 , a transition width (*FWHM*) of 9.2 ± 0.8 °C and a transition heat (ΔH) of 0.50 ± 0.05 kcal mol⁻¹. A further increase of temperature leads to a change of the specific heat at about 72°C. This temperature corresponds to that of the cloud point of $C_{14}E_8$, which has been determined by visual examination of a separate solution in a precision heating-apparatus.

The corresponding process, observed by DSC, is thus assigned to the phase separation leading to the formation of the L'_1 and L'_1 phases.

After cooling (the applied DSC instrument does not allow registration upon cooling) and repeating the DSC experiment, part of an exothermic heat change is detected around 10°C in the second curve (Fig. 2b), that has not been observed in the first scan. However, the main transition at 40.6°C and the subsequent specific heat change at 72°C are still observed. Thus, the underlying processes are fully reversible because the transition width and the ΔH value of the endothermic main transition remain unchanged. A third subsequent temperature scan provides the same result as the second thermoanalytical curve. In order to test whether the main transition is solely due to a micelle association process, a DSC experiment is carried out with a 10 mM $C_{14}E_8$ solution. The same principal behaviour is found and the endothermic transition is characterized under these conditions by a transition temperature of 45°C, a width of 14°C and a ΔH value of 0.55 kcal mol⁻¹. Because the transition temperature is slightly higher than for the 60 mM solution, it is concluded that the main transition is influenced by a micelle association phenomenon, which affects the transition temperature, but does not represent the origin of the transition.

Moreover, the reduction of the length of the polar head group and the prolongation of the alkyl chain lead to a marked decrease of the main transition temperature

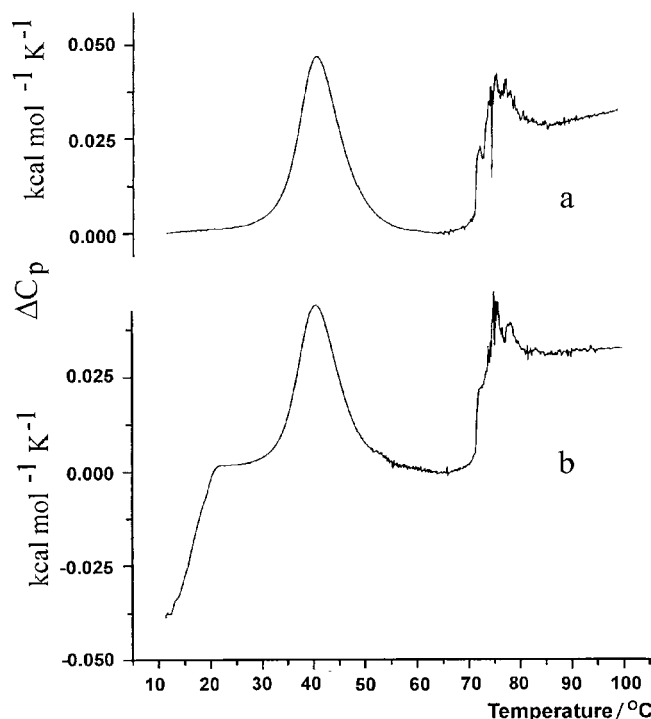


Fig. 2 DSC curves of 60 mM $C_{14}E_8$: a – first run; b – second run. Plot of the specific heat change vs. temperature. The detailed conditions are specified in the experimental section

[7]. This clearly indicates, that the properties of the main transition depend on the structure, respectively chemical nature of the detergent molecule. Modifying in addition the properties of the solvent by adding 25% glycerol (m/m) leads to a decrease of the main transition temperature of about 10°C.

In addition to these thermochemical studies, the temperature dependence of the light scattering intensity of the aqueous 60 mM C₁₄E₈ solution is studied (Fig. 3). The observed scattering intensity is low at low temperatures and remains unchanged up to about 37°C. Above 37°C, a marked, steady increase of the scattering intensity, probably due to the formation of large, aggregated structures that may differ from the association phenomenon mentioned above, is seen up to a temperature of about 70°C. This temperature is close to that of the cloud point of C₁₄E₈. Increasing the temperature further leads to a sudden intensity decrease (Fig. 3) until again a low scattering level is reached in the high temperature region. This intensity decrease is due to a very high turbidity of the sample, which can also be observed by visual examination. Under these conditions, the degree of scattering at the solution interface is so high that only a weak signal can be detected by the photomultiplier. This temperature dependence of the scattering intensity does not correspond to the result of the DSC study in the range of the main transition. Decreasing the temperature slowly (about 50°C h⁻¹) down to 10°C allows the observation of a scattering intensity increase down to 45°C and a subsequent scattering intensity decrease, which levels off at about 22°C. However, the observed intensity changes seen upon cooling are considerably smaller than under the conditions of the temperature increase. This indicates, that the time was too short to allow for a complete redistribution of the two separated phases existing at high temperature. We thus conclude that the heat change observed calorimetrically around 10°C (Fig. 2b) is likely to represent the remaining formation of the homogeneous phase, reformed only partially upon cooling. This conclusion is again consistent with the visual examination of a separate solution

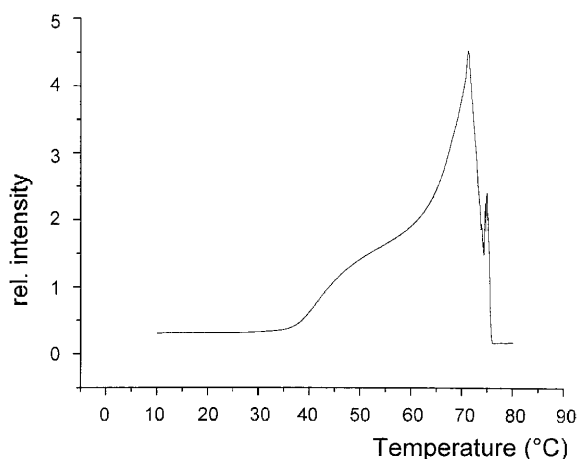


Fig. 3 Light scattering intensity observed at 300 nm of 60 mM C₁₄E₈ as a function of temperature. The detailed conditions are given in the experimental section

treated accordingly. The scattering intensity increase observed above 37°C is likely to represent a micelle association process.

The DSC results concerning the main transition mentioned above are indicative of a cooperative process with a transition temperature at 41°C occurring in the micellar L₁ phase of C₁₄E₈. Although there is no direct correlation, this detergent transition is somehow similar to the thermal transitions observed with phospholipid bilayer systems [6]. In both cases the transition temperature depends on structural properties of the head group and of the alkyl chain. As a consequence of a higher cooperativity, the synthetic lipid systems exhibit much narrower transitions [6]. The fact that the lipid transition temperature increases with increasing alkyl chain length can be regarded as an expression of the fact that this type of detergents does not adopt a bilayer structure under the conditions specified above. Nevertheless, it is surprising to note, that the micellar assembly of amphiphilic detergent molecules differing from that of phospholipid molecules exhibits a similar endothermic transition in a comparable temperature range. Considering the effect of glycerol, which leads to a decrease of the transition temperature, it is suggested that the endothermic main transition reported here may be due to a type of conformational rearrangement of the polyethylene glycol head group (partial melting) coupled to a rearrangement of the alkyl chain. The rearrangement of the polar head group may involve a change of the interaction with solvent molecules. The high temperature conformation might subsequently give rise to an aggregation process, as detected by light scattering. Further investigations will be required to analyze this transition and to characterize it in molecular terms as well as to investigate its relevance with regard to the phase behaviour and properties of this class of detergents.

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