



# Thermodynamics of the micellization process of carboxylates: A conductivity study



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## ABSTRACT

The micellization behaviour of the long-chain carboxylates: sodium octanoate (NaC8), sodium decanoate (NaC10), potassium decanoate (KC10), caesium decanoate (CsC10) and sodium dodecanoate (NaC12) in aqueous solutions were studied using electrical conductivity measurements between the temperatures (278.15 and 328.15) K. By using the pseudo-phase separation model and Gibbs–Helmholtz equation, the thermodynamic parameters for the micellization process were obtained from the temperature dependence of the critical micelle concentration, CMC, and the degree of micelle ionisation,  $\beta$ . The heat capacity of micellization,  $\Delta_{\text{mic}}C_p^0$ , estimated from the temperature dependence of enthalpy of micellization,  $\Delta_{\text{mic}}H^0$ , were correlated with the size of the non-polar accessible surface area of the solvent, which is removed from contact with water during micellization. In all systems investigated, results suggest that the micelle core is still in contact with water molecules.

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## 1. Introduction

Interactions between anions and cationic surfactants have been widely studied, whereas less attention has been devoted to influence of cations on the micellization of anionic surfactant systems. Despite sodium dodecylsulfate (NaDS, SDS) being one of the most studied surfactants, there is only one systematic investigation of the counter ion effect on the thermodynamics of micellization of lithium, sodium, potassium and caesium decyl and dodecyl sulphates. This was carried out by Ropers and co-workers [1]. It was found out that the critical micelle concentration, CMC, and enthalpy of micellization,  $\Delta_{\text{mic}}H$ , decrease in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$  at a given temperature and for a fixed chain length. Values for the degree of micelle ionisation,  $\beta$ , at  $T = 298.15$  K are reported for dodecylsulfates by Mukerjee *et al.*, [2] and are ranked in the following order:  $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+$ . While selective binding of alkali metal ions to anionic surfactant films, the air/solution interface has been investigated using ion flotation by Haverd and Warr [3]. They found that alkali metal ions display only weak selectivity on adsorbed films of dodecyl phosphate monoanion, the hexadecyl phosphate dianion, bis(2-ethylhexyl) phosphate, dodecanoate, and dodecyl sulfate. These results were confirmed by electromotive force measurements [4].

It is surprising that long-chain carboxylate micellar systems are rarely the subject of systematic investigations. In 1959 White and

Benson investigated aqueous potassium octanoate (KC8) solutions from  $T = (288.15$  to  $298.15)$  K using electrical conductivity measurements [5]. Campbell *et al.* studied the electrical conductivity of sodium octanoate (NaC8) at  $T = 298.15$  and  $T = 308.15$  K in water but no micelle formation was detected [6]. They extended their work to aqueous solutions of sodium decanoate (NaC10), sodium dodecanoate (sodium laurate, NaC12) and sodium tetradecanoate (sodium myristate, NaC14) by applying surface tension and electrical conductivity measurements [7]. Volumetric and thermochemical properties of NaC10 in water were studied by de Lisi *et al.* from  $T = 275.15$  and  $T = 318.15$  K [8]. The same system was investigated by Álvarez-Silva *et al.* [9] recently by density, speed of sound, surface tension and electrical conductivity measurements, but their results are not in good agreement with the values reported by Lisi *et al.* [8].

More recent investigations have examined the interactions that occur between two- and trivalent metal ions represented by calcium (II), aluminium (III) and chromium (III) and NaC8, NaC10 and NaC12 in aqueous solutions. The results demonstrate how a combination of cation hydration, inter-chain hydrophobic interactions, and specific head group binding leads to the precipitation process [10,11].

Long-chain carboxylates were included in thermodynamic studies of mixed micellar systems [12–14] but no detailed thermodynamic study of “pure” carboxylates in aqueous solutions has been reported. Thus, in this work the micellar properties of sodium octanoate (NaC8), decanoate (NaC10) and dodecanoate (NaC12) in aqueous solutions are investigated using electrical conductivity

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measurements. To examine possible ion effects, potassium (KC10) and caesium decanoate (C10) were also included whereas in lithium decanoate (LiC10) aqueous solutions no micelles were detected.

Experiments were performed at temperatures from  $T = 278.15$  K to  $T = 328.15$  K for NaC8, NaC10 and CsC10. The insufficient solubility at lower temperatures meant that for KC10 and NaC12 measurements there were not possible.

The standard thermodynamic parameters of micellization, Gibbs free energy,  $\Delta_{\text{mic}}G^\circ$ , enthalpy  $\Delta_{\text{mic}}H^\circ$ , entropy,  $\Delta_{\text{mic}}S^\circ$ , and heat capacity,  $\Delta_{\text{mic}}C_p^\circ$ , for all systems have been estimated using a pseudo-phase separation model [15,16]. The results, taking into account those reported in the literature for KC8, are compared and discussed in terms of chain length and the nature of the counter ion.

## 2. Experimental

### 2.1. Materials

Table 1 gives details about the compounds used including the following: CAS numbers, molar mass, supplier and mass fraction purity. Sodium octanoate (NaC8), sodium decanoate (NaC10) and sodium dodecanoate (NaC12) were used as received. Potassium (KC10) and caesium decanoate (CsC10) were synthesized by neutralisation between decanoic acid and potassium and caesium hydroxide. The products were isolated from the reaction mixture by lyophilisation and dissolved in ethanol. The products were then precipitated by adding acetone and removed by filtration. Re-crystallisation was repeated several times. The final products were then dried (KC10 at  $T \sim 363$  K and CsC10 at  $T \sim 393$  K) and stored in vacuum over  $P_2O_5$ . Product purity was checked using IR spectroscopy, CHN and TGA analysis.

De-mineralized water was bi-distilled in a quartz apparatus (DESTAMAT Bi18E, Heraeus). The final product, with a specific conductivity of less than  $5 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ , was distilled and stored under nitrogen.

Stock solutions with a concentration 10 times higher than the CMC were prepared by adding a known amount of water to a known amount of the surfactant.

### 2.2. Conductivity measurements

Electrical conductivity was recorded using a PC-interfaced LCR Meter (Agilent 4284 A) with an AC voltage source and connected to a three-electrode measuring cell as described in [17]. The conductivity cell with the volume of  $\sim 320 \text{ cm}^3$  and cell constant ( $2.2130 \pm 0.0003$ )  $\text{cm}^{-1}$  was calibrated using dilute potassium chloride solutions [18] and immersed in a high precision thermostat [19]. The monoethylene bath was set to each temperature with a reproducibility  $>0.005$  K and stability of  $\pm 0.003$  K. The temperature was also checked using a calibrated Pt100 resistance

thermometer (MPMI 1004/300 Merz) connected to an HP 3458 A multimeter.

For measuring the conductivity of aqueous solutions of NaC8, NaC10 and CsC10, the conductivity cell was filled with a known mass of water. After measuring water conductivity at the programmed temperatures, known amounts of the surfactant stock solution were added. Molal concentrations  $m$  were then determined from the masses.

Stock solutions of KC10 and NaC12 are unstable and for these two systems the described procedure was performed at only a single temperature within 24 h.

An in-house developed software package was used for temperature control and the acquisition of conductance values. The measurement regime, including corrections and extrapolation of the sample conductivity to an infinite frequency, is described in [19]. After taking into account experimental error (calibration, measurements and impurities), the relative standard uncertainty of specific conductivity is about 0.5%. All experiments were carried out at atmospheric pressure,  $p = 0.1$  MPa. The measured conductivity results of all systems investigated are given in tables A and B in the Supplementary data.

## 3. Critical micelle concentration, degree of micelle ionisation and thermodynamics of micellization

The critical micelle concentration, CMC, of the surfactants was determined from the intersection of two straight lines on the (conductivity + concentration) plots above and below the change in the slope [20,21]. The ratio of the slopes above and below the break gives an estimate of the degree of micelle ionisation,  $\beta$ .

According to the pseudo-phase separation model [22,23], the standard Gibbs free energy of micellization,  $\Delta_{\text{mic}}G^\circ$ , was calculated from the following:

$$\Delta_{\text{mic}}G^\circ = (2 - \beta)RT \ln x_{\text{CMC}}, \quad (1)$$

where  $x_{\text{CMC}}$  is the mole fraction of the surfactant at the CMC.

Knowledge of the temperature dependence of the CMC and  $\beta$  enables the standard enthalpies of micelle formation,  $\Delta_{\text{mic}}H^\circ$ , to be calculated from the Gibbs–Helmholtz relation [16,24,25]

$$\Delta_{\text{mic}}H^\circ = -RT^2(2 - \beta) \left[ \frac{\partial \ln x_{\text{CMC}}}{\partial T} \right]_p, \quad (2)$$

which has been widely used as an indirect method for determining  $\Delta_{\text{mic}}H^\circ$ .

The term  $(\partial \ln x_{\text{CMC}} / \partial T)_p$  was calculated by fitting a second order polynomial to the  $\ln x_{\text{CMC}}$  versus temperature plots and by taking the corresponding temperature derivative. The coefficients of polynomials are given in table C in the Supplementary data.

The standard entropies of micellization,  $\Delta_{\text{mic}}S^\circ$ , were obtained from the following relation:

**TABLE 1**  
Provenance and mass fraction purity of the compounds investigated compounds with their CAS number and molar mass.

Chemical name	CAS number	Molar mass/(g · mol <sup>-1</sup> )	Supplier	Mass fraction purity
Decanoic acid	334-48-5	172.26	SAFC for Sigma–Aldrich	>0.98
Sodium octanoate	1984-06-1	166.19	Sigma–Aldrich	>0.99
Sodium decanoate	1002-62-4	194.25	Sigma–Aldrich	>0.98
Sodium dodecanoate	629-25-4	222.30	Sigma–Aldrich	>0.99
Potassium decanoate	13040-18-1	210.30	Synthesized	>0.99
Caesium decanoate	23852-69-9	304.14	Synthesized	>0.99
Potassium hydroxide	1310-58-3	56.11	Merck	EMSURE® 0.85–1.00
Caesium hydroxide	21351-79-1	149.91	Sigma–Aldrich	0.5 aqueous solution

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