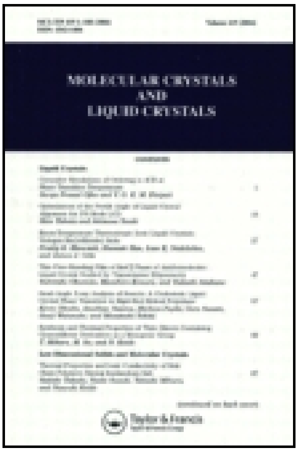

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THE INFLUENCE OF SURFACTANTS ON THE CRYSTALLIZATION OF CALCIUM OXALATE HYDRATES.

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Abstract The influence of sodium dodecyl sulphate, SDS, dodecyl ammonium chloride, DDACl and octaethylene glycol mono-n-hexadecyl ether, $C_{16}EO_8$, on the crystallization of calcium oxalate from 0.3 molar sodium chloride solutions is discussed. Under the given experimental conditions the thermodynamically stable monohydrate, COM was the predominant crystal form. Both ionic surfactants inhibited growth and aggregation of COM and, by preferential adsorption at different crystal faces, induced different habit modifications. In addition, micellar solutions of SDS promoted crystallization of the metastable calcium oxalate dihydrate, COD. The nonionic surfactant, $C_{16}EO_8$, stimulated nucleation and/or initial crystal growth of COM, most probably by providing active centers for heterogeneous nucleation.

INTRODUCTION

Micellar solutions of surfactants have been used as reaction catalysts for a long time[1], but the possibility to use them as crystallization modifiers in process technology has only recently been demonstrated[2,3]. It seems, however, that such applications may have great potential because of the special properties of surfactants and their ready availability in many different designs. It was therefore of interest to investigate systematically the influence of surfactants on crystallization processes (nucleation, crystal growth and aggregation) in relation to their specific properties. In this paper we summarize recent results concerning the influence of the aggregation state of surfactants and the charge of their headgroup on the crystallization of calcium oxalate hydrates.

MODELS: CRYSTALLIZATION SYSTEM AND SURFACTANTS

Calcium oxalate crystallizes in the form of three different hydrates, i.e. the thermodynamically stable monoclinic monohydrate ($CaC_2O_4.H_2O$, COM), the metastable tetragonal dihydrate ($CaC_2O_4.(2+x)H_2O$, COD) and the triclinic trihydrate, ($CaC_2O_4.(3-x)H_2O$, COT) where ($x \leq 0.5$). COM and COD are the main mineral constitutents of kidney stone and occur in many different types of plants and sediments of biological origin. COT[4-6] has been produced mainly in the laboratory. Crystal structure determinations of COD have shown[7] that the fractional portion of x water molecules per mole is zeolitic, i.e. included in disordered water channels. The three forms can be easily recognized by their different morphologies and optical properties. COM crystallizes in the form of birefringent hexagonal platelets with frequent twinning, while COT forms birefringent, large elongated platelets and COD crystallizes in the form of nonbirefringent octahedral bipiramids[6,8]. IR spectra[8] and X-ray powder patterns[9] are characteristic of each of the three hydrates and can thus be used for identification. When precipitation of calcium oxalate is initiated from aqueous or electrolyte solutions, experimental conditions will determine whether COM or COT are the prevailant crystallizing forms[6], while COD, which seems to have a very low nucleation rate, does not crystallize in any reasonable amount without the presence of additives[6,10,11].

As model additives the following surfactants have been used (critical micellar concentrations determined in 0.3 molar NaCl are given in mol dm^{-3}): sodium dodecyl sulphate, SDS, CMC $5x10^{-4}$ (ref.12) dodecyl ammonium chloride, DDACl, CMC $1.0x10^{-3}$ (ref.13) and octaethylene glycol mono-n-hexadecyl ether, $C_{16}EO_8$, CMC $7.2x10^{-6}$ (ref.3). In the presence of the electrolyte the CMC-s of the ionic surfactants are significantly lower than in aqueous solutions, which is due to electrostatic interactions of counterions with the charged surfactant headgroups. The CMC of the nonionic surfactant is unaffected by the presence of strong electrolyte[3].

CRYSTALLIZATION EXPERIMENTS

Crystallization of calcium oxalate was initiated by mixing equal volumes of solutions of calcium chloride (2×10^{-2} moldm^{-3}) and sodium oxalate (5.5×10^{-4} moldm^{-3}), both 0.3 molar in sodium chloride and precipitation kinetics was followed by Coulter counter. Under the given conditions, without additives, COM was the prevailant crystal form (row 1 in Table 1). Molecular or micellar solutions of the surfactants were added to one of the reactant solutions before mixing so that the additive was present during all stages of precipitate formation. Precipitates were routinely observed by means of a polarized microscope and selected precipitates were in addition observed by scanning electron microscope and/or characterized by X-ray powder patterns, thermogravimetric (TG) and differential thermal (DT) analysis. The latter methods permit a quantitative estimate of two different hydrates in a mixture on the basis of the amount of water evolved.

The influence of ionic surfactants

Both SDS and DDACl inhibited crystal growth and aggregation of calcium oxalate as demonstrated by precipitation kinetics [12,13] and by significant, but different effects on the crystal growth morphology (DDACl promoted the formation of rhomb-like COM crystals[13], while SDS induced needle-like crystal growth (to be published). However, in comparison, the overall inhibitory activity of SDS was significantly weaker than that of DDACl[3]. Microscopic observations and X-ray diffraction powder patterns pointed to the reason for this difference: it became apparent that, while strongly inhibiting crystal growth of COM, SDS (but not DDACl) promoted nucleation and/or growth of COD[3,12]. Some of the quantitative results obtained by thermal analysis from precipitates prepared in the presence of different concentrations of SDS, i.e. below the CMC, at the CMC and above the CMC are listed in Table 1.

The results listed in Table 1 show that the ability of SDS to promote COD crystal growth depends on the aggregation state of the surfactant, i.e. at and above the CMC a reversal in precipitate composition occurs (for more details see refs. 3,12).

TABLE I: Results of thermal analysis of precipitates formed in the presence or without SDS. Initial reactant concentrations in moldm^{-3}: Ca 1x10^{-2}, C_2O_4 3x10^{-4}, NaCl 0.3, reaction time 60 min, temp. 310 $^{+}$ 0.1K.

c(SDS)·10^4	Mass % H_2O		Mass %*	
mol dm^{-3}	313-353K**	393-423K	COM	COD
-	-	12.48	98.4	1.6
1.0	-	12.2	100	-
5.0	0.4	20.2	12.6	87.4
10.0	1.2	21.0	10.1	89.9
50.0	0.7	20.7	13.3	86.7

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* Calculated from mass% of water evolved at 393-423K assuming the presence of mixtures of COM + COD (as shown by X ray powder patterns).

** In the presence of COD a small amount of water evolved at lower temperatures. This was ascribed to zeolitic water and was not included in the calculations.

Precipitation conditions seem to be less critical, i.e. a similar effect has also been observed at room temperature if oxalate ions were in excess (unpublished results). The COD crystals that emerged were remarcably monodispersed, size distribution histograms (by number) show sizes between 2-5μm with a maximum of 80% at 2-3μm (ref. 3). Their morphology was affected by adsorption of the surfactant at the high energy tip of the octahedral bipiramid which resulted in inverted bipiramids with occasional holes in the middle of the crystal. Within 24h the crystals aggregated, but no significant phase transformation into COM occured.

The influence of the nonionic surfactant

When calcium oxalate was precipitated in the presence of $C_{16}EO_8$ no significant changes in solid phase composition or crystal growth morphology occurred. In the presence of molecular solutions of the surfactant (concentrations below the CMC) no significant changes in precipitation kinetics were observed and the precipitates appeared as aggregates of COM crystals which were in the average smaller than in the controls. However, micellar solutions of $C_{10}EO_8$ had a surprising effect. In Fig.1 the kinetics of crystallization of COM in the presence of such a solution ($c(C_{10}EO_8)$ = 10xCMC) is compared with the respective control systems (shaded area).

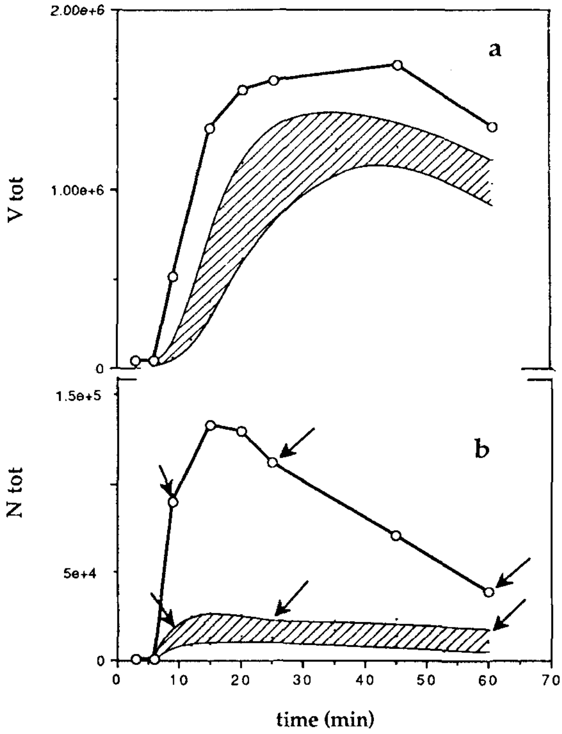

FIGURE 1. Kinetics of crystallization of calcium oxalate (total precipitate volume, V_t in μm^3 per 0.1 cm^3, and number of particles, Nt per 0.1cm^3 , vs time curves) obtained in the presence of a micellar solution of $C_{16}EO_8$ (full lines, c=CMCx10). Shaded areas represent three control systems. Arrows mark points corresponding to the particle size distributions represented in Fig.2

It is seen that in the presence of the surfactant both the rate of precipitation (from the initial slopes of the kinetic curves) and the amount of precipitate formed (from the V_t vs time curves, Fig.1a) were significantly enhanced. The enhancement of the total number of particles (Fig.1b) is particularly striking. The curve passes through a maximum (at approx. 20 min) after which N_t gradually decreases indicating that aggregation in the system was not significantly inhibited.

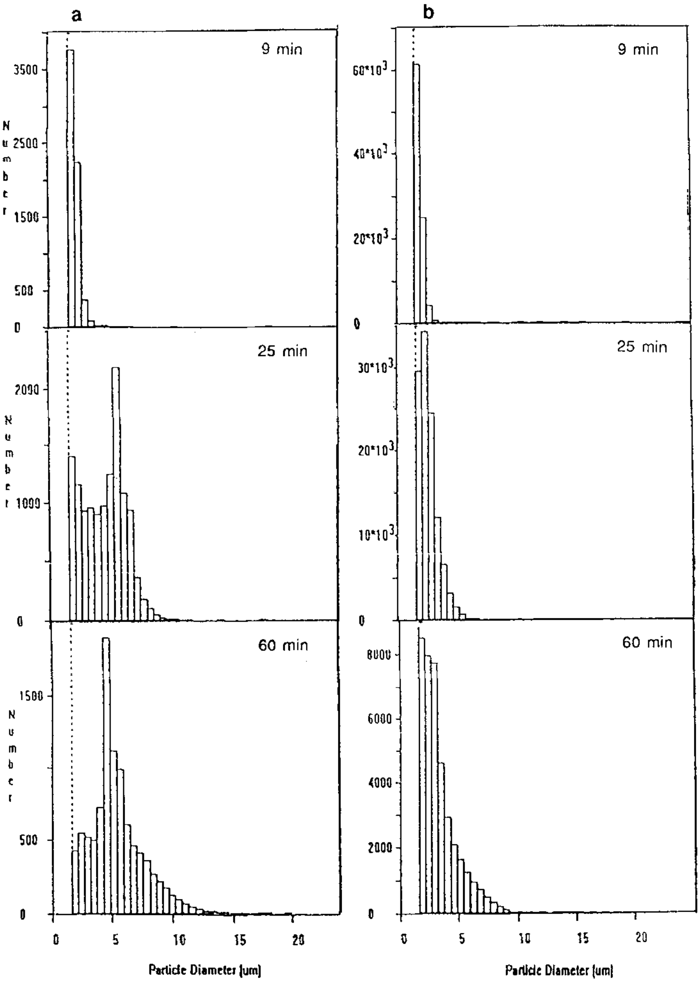

FIGURE 2. Particle size distributions (number) of calcium oxalate precipitates obtained at three different times (see arrows in Fig. 1b) in the presence (b) and without (a) $C_{16}EO_8$ micelles. Number of particles given per 0.1 cm^3.

Particle size distribution histograms show that unlike in the controls (Fig.2a), in the presence of surfactant micelles (Fig.2b) small particles (equivalent diameters <5µm) prevailed throughout the kinetic run. Note, that even at an early time (9 min), where small particles prevailed in both systems, approx. 15 times more particles were counted in the presence of $C_{16}EO_8$. It seems reasonable to conclude that this effect was caused by enhancement of nucleation and/or initial crystal growth in the presence of the surfactant micelles.

DISCUSSION

We have shown that, depending on their headgroup charge and state of aggregation, surfactants affect crystallization of calcium oxalate in several different ways: (i) ionic surfactants inhibit crystal growth and/or aggregation and, by preferential adsorption at certain crystal faces induce habit modifications (ii) the investigated nonionic surfactant, $C_{10}EO_8$ stimulates crystallization of the stable polymorph, COM (Figs.1,2) and (iii) the investigated anionic surfactant, SDS, initiates preferential crystallization of COD on account of the thermodynamically stable polymorph, COM (Table 1). Effects (ii) and (iii) occur prevailantly in micellar solutions and are thus related to the aggregation state of the surfactant.

In order to explain the observed enhancement of the rate of nucleation and/or initial crystal growth (Figs.1,2), we first consider that under our experimental conditions calcium oxalate is formed by heterogeneous nucleation and 2-D crystal growth upon nonspecific impurities[14]. Additives may then behave as active centers for nucleation which are more or less effective than the impurities[15]. We consider in addition the ability of micellar solutions to solubilize and concentrate solute molecules[1]. It is thus conceivable that $C_{16}EO_8$ micelles concentrate oxalate ions at the micelle/solution interface and thus become specific nucleation centers for calcium oxalate. In the above system, in which because of the large excess of calcium ions the availability of oxalate ions determines the amount of precipitate formed, the above effect should be quite pronounced.

Preferential crystallization of COD in the presence of surfactant micelles (Table 1) has also been observed with sodium cholate[16] an anionic surfactant which is a component of bile salt. Some other additives, citrate ions, RNA[10] and certain aminoacids[14] have been reported to promote crystallization of COD to a certain extent. The effect seems to be facilitated by preferential inhibition of COM crystal growth by the additive molecules but involvement of the surfactant micelles as nucleating centers for COD cannot be excluded.

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