sequence—with respect to the spectrum of the so-called solid and volatile products. As it has been shown, there is a clearcut difference between the reactive behaviour of alkaline earth metal and transition-metal carbonates: the decomposition of the former always leads to the corresponding metal oxide MO, which in turn can be reversibly transformed into the carbonate. The degradation of the latter leads to transition metal oxides MO, with varying oxygen stoichiometry and to elemental transition metals. The observation of different volatile carbon species gives evidence for the in situ formation of catalytically active transition-metal compounds. This means also, that in reducing atmospheres these transition-metal species are in many cases active catalysts for the conversion of the volatile products CO₂ and CO into reduced and, therefore, interesting carbon compounds, mainly CH₄. The combination of alkaline earth metal carbonates with transition-metal carbonates allows not only to lower the decomposition temperatures drastically, but also to produce finely dispersed, catalytically active transition-metal compounds on a selected support material. As example a combination of any transition-metal compound with simultaneously formed appropriate supports such as the well-established support materials MgO or ZnO can be thought of. The knowledge of the influences of experimental parameters such as temperature program, inert or reactive gas atmosphere, or even the type of energy impact onto kinetics and mechanism of the degradation of the initial carbonates allows the optimization of the solid products. Depending on the experimental conditions, in situ formation of catalysts can take place. Simultaneously, the evolved volatile species can be catalytically transformed during the degradation process of the initial carbonate. Therefore, the palette of volatile carbon compounds gives a hint for the catalytic potential of the system under investigation. The study of the reactivity of metal carbonates obviously leads into a multidisciplinary field, comprising aspects of heterogeneous solid-state chemistry, heterogeneous catalysis, thermochemistry, photochemistry, an 'interface' between inorganic and organic chemistry, and—last but not least—some more details on the most interesting reactive behaviour of CO₂. These studies are also related to the research topic of chemical solar energy conversion, i.e. to convert radiation energy into useful chemical forms (see e.g. [20][21]). The results of these investigations elucidate the need of multidisciplinary approaches and concepts for the description and understanding of the initially underestimated complexity of the reactivity of metal carbonates.

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Self-replicating Reverse Micelles

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Abstract. Conditions are described, under which the hydrolysis of octyl octanoate (O-OA) takes place at the interface of reverse micelles formed by sodium octanoate (OA) in isooctane. Since the micelle-mediated hydrolysis affords fresh OA, which spontaneously assemble into new micelles, the reaction can be seen as a self-replicating process. The kinetics and the spectroscopy of this self-replication process are presented.

Introduction

Reverse micelles can be seen as small droplets of H₂O (with a radius in the range of 10–100 Å) which are stabilized in organic solvents by a layer of surfactant. Reverse micelles are usually monodisperse, and their physical properties depend primarily on the molar ratio of H₂O to surfactant, usually denoted as wₜ (wₜ = [H₂O]/[surfactant]): e.g. the radius of the H₂O pool depends almost linearly on wₜ [1–3]. To an organic chemist, reverse micelles are also of interest as micro-reactors: a series of H₂O-soluble compounds can be solubilized in the H₂O pool of the micelles, thus permitting reactions between hydrophilic compounds essentially in a bulk aprotic solvent [4][5].

Quite recently, a new type of a chemical reaction in reverse micelles has been proposed [6], one which brings to self-replication of the micelles themselves. The principle is the following: the reverse micelle hosts a reaction which yields the very surfactant which builds the micelle. The so-produced fresh surfactant accumulates at the micellar interface; however, the micelle cannot grow in size, since H₂O is limiting. Actually, since wₜ decreases, the thermodynamic constraints impose formation of a

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larger number of smaller micelles. Since this increase in number is due to a chemical reaction which takes place within the domain of parent micelles, it is appropriate to view the micelle population growth as a 'self-replication' process. A couple of other self-replicating systems have been proposed already in the chemical literature, based on the quite different principle of template reactions [7][8]. In our system, the emphasis is on the replication of geometrically closed structures.

Such a self-replicating micelle system has been presented in a preliminary communication without kinetic data and without discussing the ongoing spectroscopic events [6]. The aim of this paper is to provide this additional and still missing information and to further discuss the principle of self-replication in reverse micelles.

Results and Discussion

It may be worthwhile to recall that the system consists of an apolar solvent mixture, i.e. isooctane/octan-1-ol 9:1 (v/v), and that the reverse micelles are built by sodium octanoate (OA). Octan-1-ol (OL) is at the same time co-solvent and co-surfactant. LiOH in a concentration of 2.86M (chosen over NaOH for its greater solubility in reverse micelles) is confined in the H$_2$O pool at $w_o = 9.2$ (23 mm LiOH overall concentration), whereas excess of octyl octanoate (O-OA) is dissolved in the system, being localized mostly in the bulk solvent and partly at the micellar interface, where the hydrolysis reaction takes place. The resulting fresh OA and OL lead to new micelles.

A pictorial representation of the system is given in the Scheme, whereas the time progress of a typical reaction is illustrated in Fig. 1.

The time progress of the reaction has been followed by Fourier transform IR spectroscopy. The principle of the method has already been described in another context [9]. As the ester is hydrolyzed, the intensity of the C=O(s) band around 1744 cm$^{-1}$ decreases, while at the same time the intensity of the C=O(s) of the octanoate around 1570 cm$^{-1}$ increases (Fig. 1B). The formation of octan-1-ol during the reaction can be monitored in the O-H(s) region of the IR spectrum, by looking at the increase in the intensity of the band which is centered around 3250 cm$^{-1}$ (Fig. 1A). The kinetics of the reaction can be analyzed by following the decrease of the ester band at 1744 cm$^{-1}$. For this spectroscopic characterization, we have first carried out a calibration at this wavenumber with known amounts of octyl octanoate in isooctane and then determined the extent of hydrolysis as a function of time.

As expected [10], the hydrolysis reaction is second order with respect to the ester, with an overall rate constant of $10^{-3}$ M$^{-1}$s$^{-1}$, as estimated from half-time determinations at different ester concentrations (data not shown). The determined rate constant is comparable to the ester-hydrolysis rate constant obtained for p-nitrophenol octanoate in the reverse micellar system consisting of sodium octanoate, hexan-1-ol, and H$_2$O [11].

The concentration change of the reverse micelles was measured by time-resolved fluorescence quenching [12][13]. According to this technique, the micelles contain a H$_2$O-soluble fluorescent probe – in our case 1-pyrenesulfonic acid – and a quencher – in our case NaI. Since the magnitude of the intramicellar quenching of the probe is proportional to the quencher concentration and inversely proportional to the micelle concentration, the method allows the determination of the concentration of the reverse micelles.

As shown in Fig. 2, the concentration of micelles increases from 1.9 to 3.0 mM while the concentration of octanoate increases from 50 to 68 mM. Since the micelles become smaller, micellar radius and aggregation number of OA must also decrease. This two parameters can be calculated from the measured concentration of micelles by simple geometrical considerations [12], giving a decrease in the micellar radius from 12 to 10.3 Å and a decrease in the aggregation number from 26.1 to 22.4. The mean hydrodynamic radius of the reverse micelles has in addition been determined by quasi-elastic light scattering. From a cumulant analysis of the measured intensity autocorrelation function, the diffusion coefficient of the scattering species can be obtained. Knowing the diffusion coefficient, the hydrodynamic radius can be calculated by the Stokes-Einstein equation. The so determined hydrodynamic radius is 22.7 Å at the beginning of the reaction, and 20.5 Å at equilibrium (at the end of the self-replication process) in good agreement with the micellar radius determined by fluorescence quenching, taking 10.4 Å for the length of an octanoate molecule.
Concluding Remarks

There is a small shortcoming in the reaction illustrated here: since \( w_2 \) (and consequently the radius of the micelles) becomes smaller during replication, the self-replication is not completely warranted. In principle, one could try to avoid this by adding \( H_2O \) so that \( w_2 \) remains constant during reaction, according to a method outlined in [15]. Another possibility is the use of coupled reactions, one of which producing \( H_2O \) (e.g. the use of the enzyme tyrosinase which yields \( H_2O \) upon oxidation of phenol). However, until now none of this was implemented experimentally.

Aside from these details, the reaction presented here, as simple as it is, represents a new class of micellar reactions, which most likely will be considerably developed in the near future. There are already reports indicating that the same self-replication principle can be extended to aqueous micelles [16] and even liposomes [17]. Thus, it is perhaps important to conclude with a couple of general observations.

Micelles and the other supramolecular surfactant complexes can be seen as geometrically closed structures which assemble spontaneously, and this combination of features makes them particularly suitable to model biological replication processes. Of course, given their chemical simplicity, supramolecular surfactant aggregates are very far from the complexity of a cell. On the other hand, precisely this simplicity may permit the understanding of some basic mechanistic steps.

Micellar self-replication offers another point of interest: the linkage with 'autopoiesis'. This notion, as developed by Maturana and Varela [18], tries to define the essential mechanistic aspects of the living; and essentially, an autopoietic system is one which is defined by a boundary, and in which domain a metabolic network of reactions takes place, which bring to the production of components, which then assemble spontaneously in the same bounded structure. As already emphasized [16][17], self-replicating micelles and liposomes offer in principle the challenge of responding to the essential definition of living.

Materials and Methods

Reagents

1-Pyrenesulfonic acid sodium salt (PSA) was from molecular probes and octan-1-ol from Aldrich both of high purity grade. All other chemicals were of highest purity available from Fluka.

Octyl octanoate was synthesized by heating octanoic acid and octan-1-ol in concentrated \( H_2SO_4 \).

Methods

Quasi-Elastic Light Scattering. Quasi-elastic light scattering experiments were carried out with a Malvern 4700 POM/W spectrometer and an Ar ion laser (coherent, Innovox Model 200–10, \( \lambda_e = 488 \text{ nm} \)). Hydrodynamic radii of the octanoate reverse micelles can be determined from a cumulant analysis of the intensity autocorrelation function with a reproducibility of \( \pm 5 \% \).

Time-Resolved Fluorescence Quenching. The fluorescence decay curves of solubilized fluorescent probe and quencher (or probe alone) were obtained by the single-photon counting technique and analyzed according to a non-linear weighted least-squares procedure [12].

For comparison with light scattering data, the hydrodynamic radius can be calculated as the sum of the \( H_2O \) pool radius and the length of the extended surfactant molecule, which is \( 10.4 \text{ Å} \) for octanoate [14].

FTIR Spectroscopy. All Fourier transform IR spectra were recorded on a Nicolet SSX FTIR spectrometer, using a ZnS cell from Textronica AG with a fixed pathlength of 0.1 mm. 36 scans were taken of each sample at a resolution of 4 cm\(^{-1}\).

Preparation of the Reaction Mixture and Quantification of the Reaction

An appropriate amount of 2.88M LiOH was added by a microsyringe (typically 40 \( \muL \)) for 5 ml of reaction solns. to 50 \( \muL \) sodium octanoate in isooctane/octan-1-ol 9:1 (v/v) to give the desired \( w_2 \). The reagents were solubilized by vortexing and sonification, until a clear soln. was obtained. The reaction was started by adding octyl octanoate (25 \( \muL \)) by a microsyringe. The mixture was kept at r.t. without stirring and samples were withdrawn at a desired time and analyzed by FTIR spectroscopy.

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