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Precipitation of calcium carbonate and calcium fluoride in microemulsions. Calorimetric investigation

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Abstract

The enthalpies of precipitation of calcium carbonate and calcium fluoride in water/sodium bis-2-ethylhexyl sulfosuccinate/*n*-heptane, water/didodecyldimethylammonium bromide/*n*-heptane and water/tetraethyleneglycol-mono-*n*-dodecyl ether/isooctane microemulsions were measured by a calorimetric technique. The results indicate that the energetic state of $CaCO_3$ and CaF_2 nanocrystals encapsulated in the aqueous microregions of these microemulsions is strongly different from that in bulk water. Effects due to the smallness of the nanocrystals, interactions between nanocrystals and water/surfactant interfaces and changes of the thermodynamic parameters in nanoscopic water environments are discussed.

INTRODUCTION

Microemulsions are monophasic liquid systems constituted by water, an apolar organic solvent (generally indicated as oil) and one or more amphiphilic substances (surfactants). From a molecular point of view, these systems are characterized by the coexistence of spatially separated polar and apolar microregions stabilized by a monolayer of amphiphilic molecules.

In the case of water-in-oil microemulsions, the water is dispersed in the oil as nanodroplets (diameter 10–100 Å), whereas in the case of oil-in-water microemulsions, the oil is dispersed as nanodroplets in water. These two structures are schematically represented in Fig. 1.

There are also microemulsions characterized by a bicontinuous structure (see Fig. 2). In this case, each pseudophase is characterized by an interconnected network of canalicula of indefinite length. It is interesting to note, however, that as a consequence of the dynamic processes occurring at

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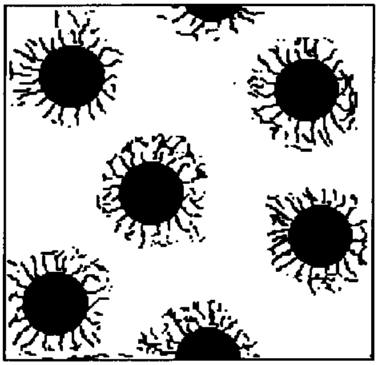

Fig. 1. Schematic representation of the structure of water-in-oil microemulsions (circles delimit water nanodroplets) or of oil-in-water microemulsions (circles delimit oil nanodroplets).

molecular level the same system could show different structures when observed at different timescales.

Given the structural peculiarities of these systems, recently [1,2] microemulsions were employed as suitable media for the synthesis of solid nanoparticles (diameter 5–50 Å). The interest in this field is due to the opportunity to synthesize catalysts with high active surface [3–5] and to model or to mimic biological functions such as the formation of solid constituents of the human body [6–8]. Microemulsions can also be employed to simulate processes such as carbonate formation in continental environments [9, 10]. This is of great interest since the data analysis of geological environments is often a hard task as a consequence of the many uncontrolled and/or uncontrollable parameters influencing the investigated phenomena. However, laboratory experiments often give unrealistic

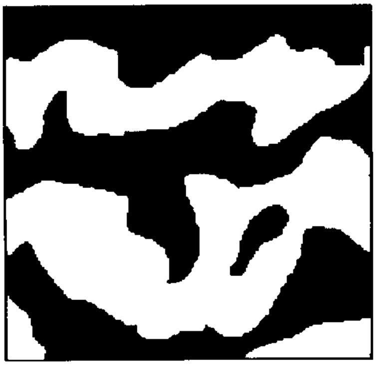

Fig. 2. Schematic representation of microemulsions characterized by a bicontinuous structure. Aqueous microregions (white) and oil microregions (black) are separated by a monolayer of oriented surfactant molecules (for simplicity, the surfactant moelcules are not represented).

results since they refer to conditions very different from those occurring in nature [11–14].

However, while many studies have been devoted to define the photophysical and geometrical properties of nanocrystals in microemulsions, relatively little effort has been devoted to characterize their energetic state [1]. In order to give a contribution in this direction we have investigated the precipitation of calcium carbonate and calcium fluoride in some representative microemulsions by calorimetry. Nanocrystals were obtained by performing the reactions

$$Ca^{2+}2Cl^- + 2Na^+CO_3^{2} \rightarrow CaCO_3(s) + 2Na^+2Cl^-$$

$$Ca^{2+}2Cl^- + Na^+HCO_3^- \rightarrow CaCO_3(s) + Na^+Cl^- + H^+Cl^-$$

$$Ca^{2+}2Cl^- + 2Na^+2F^- \rightarrow CaF_2(s) + 2Na^+2Cl^-$$

in the following microemulsions: (A) water/sodium bis-2-ethylhexylsulfosuccinate (AOT)/*n*-heptane; (B) water/didodecyldimethylammonium bromide (DDAB)/*n*-heptane; (C) water/tetraethyleneglycol-mono-*n*-dodecyl ether ($C_{12}E_4$)/isooctane. This set of microemulsions offers different microstructures and/or different interfaces. In particular, in (A) and in (C) water is dissolved as minute spherical droplets [4,15–17] whereas (B) is characterized by a bicontinuous structure [17,18]. In (C), moreover, the water/oil interface does not show the ionic double layer which is present in (A) or in (B).

EXPERIMENTAL

Methods

Calorimetric measurements were performed at 25°C by the Thermal Activity Monitor (TAM) produced by LKB (LKB 2277) equipped with a mix-flow cylinder (LKB 2277-204) and a perfusion cell (LKB 2277-402). A typical run was carried out as follows. A known amount (about 2 g) of microemulsion (obtained by dissolving in the surfactant/oil solution an appropriate amount of an aqueous solution of $CaCl_2$ at a molar concentration of 0.005–0.01 M) was placed in the perfusion cell. This cell was inserted into the calorimeter and, after thermal equilibration, an aqueous solution containing NaF, Na_2CO_3 or $NaHCO_3$, at a concentration of about 0.1 M, was added by an injection cannula connected to a Hamilton syringe. Generally, the amount of these solutions necessary to obtain the complete precipitation of calcium was reached by 3–5 injections. These quantities (always less than 1 μl) do not change the water content of the microemulsions significantly. The heat effect accompanying the solubilization of pure water in the investigated systems was also determined and used to correct the heat effects observed when precipitation occurs. The estimated uncertainty in the experimental enthalpies was ±0.2%.

TABLE 1

Experimental molar enthalpy of precipitation ($\Delta H_{exp}/n_{CaCl_2}$) of calcium carbonate and calcium fluoride in water and in microemulsions (A, water/AOT/n-heptane; B, water/DDAB/n-heptane; C, water/$C_{12}E_4$/isooctane) as a function of the molar ratio n_X/n_{CaCl_2} (X indicates the added salt); R is the water/surfactant molar ratio

n_X/n_{CaCl_2}	$\Delta H_{exp}/n_{CaCl_2}$ in kJ mol^{-1}
System a: $CaCl_2 + NaF$ in water	
0.060	−0.44
0.181	−1.78
0.484	−6.37
0.786	−9.48
1.089	−11.04
1.573	−11.33
1.996	−11.66
System b: $CaCl_2 + NaF$ in A; [AOT] = 0.268, R = 8.8	
0.289	23.14
0.590	29.65
0.892	54.24
1.181	69.91
1.470	81.48
1.783	93.05
2.072	103.3
System c: $CaCl_2 + NaF$ in B; [DDAB] = 0.994, R = 7.3	
0.096	0.78
0.416	3.14
0.735	5.49
1.377	10.6
2.018	15.3
System i: $CaCl_2 + Na_2CO_3$ in A; [AOT] = 0.268, R = 9.5	
0.297	10.18
0.594	21.06
0.990	34.36
System l: $CaCl_2 + Na_2CO_3$ in B; [DDAB] = 0.831, R = 9.2	
0.0837	1.22
0.3627	7.01
0.6417	19.42
1.004	31.97
System m: $CaCl_2 + Na_2CO_3$ in B; [DDAB] = 8.810, R = 13.9	
0.130	2.92
0.348	17.28
0.565	28.44
1.001	39.61
System n: $CaCl_2 + Na_2CO_3$ in C; [$C_{12}E_4$] = 0.202, R = 9.9	
0.388	9.50
1.03	25.33
System o: $CaCl_2 + Na_2CO_3$ in C; [$C_{12}E_4$] = 0.215, R = 13.9	
0.340	10.15
0.680	15.68
1.020	22.03

System d: $CaCl_2 + NaF$ in B; [DDAB] = 1.07, $R = 10.7$	
0.309	2.78
0.536	5.01
0.769	6.13
1.003	7.24
1.238	9.75
System e: $CaCl_2 + NaF$ in B; [DDAB] = 0.810, $R = 13.7$	
0.251	2.40
0.503	4.20
0.754	5.70
1.005	7.62
1.256	8.82
System f: $CaCl_2 + NaF$ in B; [DDAB] = 1.19, $R = 14.3$	
0.099	0.97
0.296	3.40
0.494	5.09
0.790	7.76
1.008	9.22
1.210	10.67
System g: $CaCl_2 + NaF$ in C; [$C_{12}E_4$] = 0.215, $R = 13.9$	
0.419	10.26
0.755	16.42
1.006	22.58
2.000	40.00
System h: $CaCl_2 + Na_2CO_3$ in water	
0.098	0.72
0.393	4.56
0.589	6.95
0.785	9.12
1.001	10.79
System p: $CaCl_2 + NaHCO_3$ in water	
0.060	0.07
0.256	0.33
0.516	0.80
0.991	1.54
System q: $CaCl_2 + NaHCO_3$ in A; [AOT] = 0.268, $R = 13.2$	
0.189	2.92
0.567	8.03
1.008	12.71
System r: $CaCl_2 + NaHCO_3$ in B; [DDAB] = 1.07, $R = 10.4$	
0.162	1.50
0.326	4.51
0.652	9.02
0.977	12.78
System s: $CaCl_2 + NaHCO_3$ in B; [DDAB] = 0.810, $R = 14.3$	
0.123	2.85
0.369	6.85
0.616	10.27
0.961	14.83
System t: $CaCl_2 + NaHCO_3$ in C; [$C_{12}E_4$] = 0.202, $R = 9.9$	
0.388	1.58
1.034	2.50
System u: $CaCl_2 + NaHCO_3$ in C; [$C_{12}E_4$] = 0.215, $R = 13.9$	
0.355	1.03
0.709	2.65
1.063	4.28

In order to have more experimental evidence on nanocrystal formation, some samples were observed with a transmission electronic microscope (Philips, EM420). The solvent of a dilute sample containing the nanocrystals was gently evaporated before inspection.

Materials

Sodium bis-2-ethylhexylsulfosuccinate (AOT, Sigma, 99%), tetraethyleneglycol-mono-*n*-dodecyl ether ($C_{12}E_4$, Nikkon, 98%) and didodecyldimethylammonium bromide (DDAB, Aldrich, 98%) were used as received. $CaCl_2$, Na_2CO_3, $NaHCO_3$, NaF (Sigma, RPE) were dried under vacuum for several days. *n*-Heptane and isooctane (Merck, >99%) were used as received. All the solutions were prepared by mass.

In Table 1, the experimental molar precipitation enthalpy ($\Delta H_{exp}/n_{CaCl_2}$) is reported as a function of the mole ratio n_X/n_{CaCl_2} (X represents the salt added to the microemulsion).

RESULTS AND DISCUSSION

As shown in Figs. 3–5 there is generally a marked difference between the heat associated with the precipitation reaction in microemulsions and that in water; furthermore different behavior is observed in the three microemulsions examined. Moreover, whereas some systems are characterized by a linear dependence of $\Delta H_{exp}/n_{CaCl_2}$ upon n_X/n_{CaCl_2} (probably due to the formation of nanocrystals with well defined geometries), other systems are characterized by a non-linear trend (probably due to the progressive growing process of the nanocrystals).

In order to analyze quantitatively the experimental data, it is necessary to take into account all the equilibria involved. The following equilibria given in Table 2 have been considered.

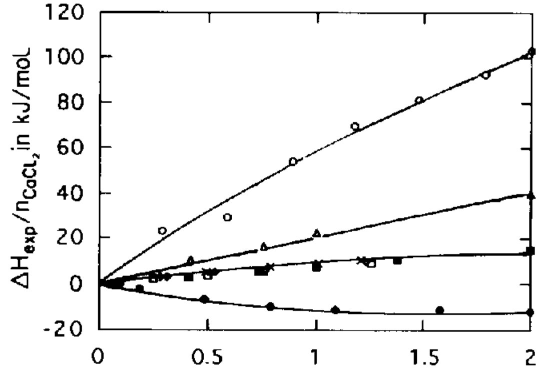

Fig. 3. Molar enthalpy of precipitation ($\Delta H_{exp}/n_{CaCl_2}$) of calcium fluoride in water and in microemulsions as a function of the molar ratio n_{NaF}/n_{CaCl_2}. (Systems: a (●), b(○), c (■), d (□), e (△), f (×), g (▲).)

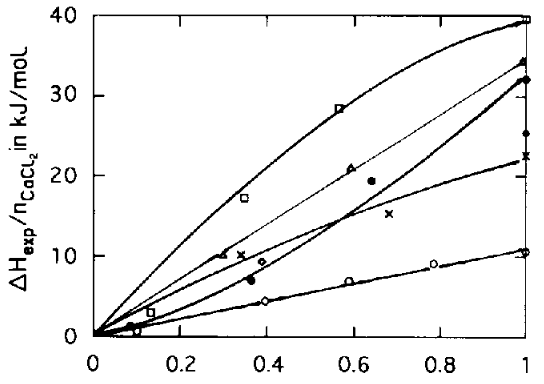

Fig. 4. Molar enthalpy of precipitation ($\Delta H_{exp}/n_{CaCl_2}$) of the calcium carbonate in water and in microemulsions as a function of the molar ratio $n_{Na_2CO_3}/n_{CaCl_2}$. (Systems: h (○), i (△), l (●), m (□), n (◇), o (×).)

The activity coefficients (f) were calculated by the modified Debye–Huckel equation [20]

$$\log f = -0.5\left(\frac{I^{1/2}}{1+I^{1/2}} - 0.3I\right) \tag{1}$$

where I is the ionic strength ($I = 0.5\sum v_i^2 c_i$).

Using an iterative method and the above reported data, theoretical values of the molar enthalpy of precipitation in water ($\Delta H_{th}/n_{CaCl_2}$) were evaluated. These data together with the experimental ones are given in Table 3 where, for simplicity, only the values concerning the complete precipitation are listed. As can be seen, in spite of the approximations introduced for the calculation of the theoretical values, the agreement

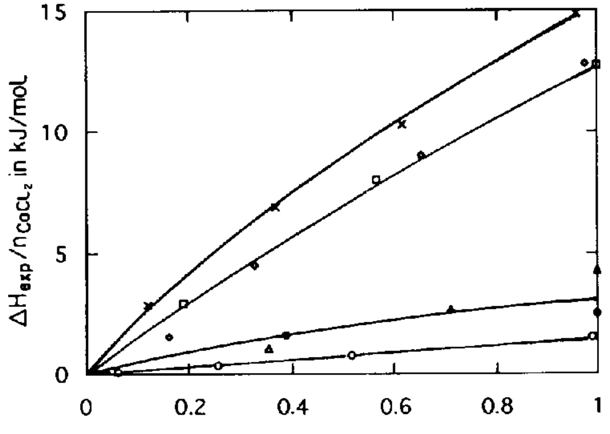

Fig. 5. Molar enthalpy of precipitation ($\Delta H_{exp}/n_{CaCl_2}$) of the calcium carbonate in water and in microemulsions as a function of the molar ratio n_{NaHCO_3}/n_{CaCl_2}. (Systems: p (○), q (□), r (◇), s (×), t (●), u (▲).)

TABLE 2

Equilibria considered for quantitative analysis of experimental data

Number	Equilibrium	K_{eq}	ΔH in kJ mol^{-1}
1	$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$	3.4×10^{-2} [a]	−20.0 [a]
2	$CO_{2(aq)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	4.50×10^{-7} [a]	9.1 [a], 7.6 [c]
3	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.79×10^{-11} [a]	14.9 [a]
4	$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+$	12.9 [a]	11.3 [a]
5	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^0$	1.66×10^3 [a]	14.7 [a]
6	$Ca^{2+} + OH^- \rightleftharpoons CaOH^+$	25 [b]	
7	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$(calcite)	3.31×10^{-9} [a]	9.61 [a]
8	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$ (aragonite)	4.61×10^{-9} [a]	10.8 [a]
9	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$ (vaterite)	1.22×10^{-8} [a]	15.8 [a]
For the formation of calcium fluoride			
10	$Ca^{2+} + F^- \rightleftharpoons CaF^+$	8.7 [d]	17.2 [d]
		18.2 [e]	−10.9 [e]
11	$Ca^{2+} + 2F^- \rightleftharpoons CaF_2$(s)	2.69×10^{-11} [d]	−13.4 [d]
		0.64×10^{-11} [e]	46.0 [e]
12	$HF \rightleftharpoons H^+ + F$	6.75×10^{-4} [f]	32.8 [g]
For both salts			
13	$H^+ + OH^- \rightleftharpoons H_2O$	1.0×10^{-14} [f]	−55.8 [h]

[a] Ref. 19. [b] Ref. 20. [c] Ref. 21. [d] Ref. 22. [e] Ref. 23. [f] Ref. 24. [g] Ref. 25.

between the two sets of data can be considered quite good. In particular, the observed differences for the calcium carbonate can be accounted for in terms of the formation of a precipitate constituted by different crystalline forms.

Because our $\Delta H_{exp}/n_{CaCl_2}$ values in water correspond to the formation of precipitates in spatially uncostrained conditions, it follows that the difference Δ between the value of $\Delta H_{exp}/n_{CaCl_2}$ in microemulsions and that

TABLE 3

Experimental values ($\Delta H_{exp}/n_{CaCl_2}$) and theoretical values ($\Delta H_{th}/n_{CaCl_2}$) of the molar enthalpy of precipitation in water of calcium carbonate and calcium fluoride in kJ mol^{-1}

System	$\Delta H_{th}/n_{CaCl_2}$	$\Delta H_{exp}/n_{CaCl_2}$
CaF_2 in water	−12.8	−11.7
$CaCO_3$ in water (from carbonate)	8.4 (calcite) 9.5 (aragonite) 14.3 (vaterite)	10.8
$CaCO_3$ in water (from bicarbonate)	3.1 (calcite) 3.3 (aragonite) 4.3 (vaterite)	1.5

TABLE 4

Δ values in kJ mol^{-1} for the precipitation of calcium carbonate and calcium fluoride

Systems[a]	Δ		
	CaF_2	$CaCO_3$	
		From carbonate	From bicarbonate
b	115.0		
i		23.6	
q		11.2	
c	27.0		
l		21.2	
r			11.3
d	26.2		
e	26.9		
m		28.8	
f, s	30.1		13.3
n, t		14.5	1.0
g, o, u	51.9	11.2	2.8

[a] See Table 1.

in water can be attributed directly or indirectly to compartimentalization effects occurring in the aqueous microregions characterizing the microemulsion structure.

In particular, the observed Δ values result essentially from contributions due to: (i) formation of crystals of very small dimensions (nanocrystals); (ii) interaction between nanocrystal and water/surfactant interface; (iii) change of thermodynamic parameters of the precipitation process.

Concerning point (i), it must be stressed that the ions residing at the surface of a nanocrystal are both a non-negligible fraction of all the ions and in a higher energetic state. It follows that a contribution to $\Delta > 0$ may be expected when nanocrystals are formed. Actually, the positive values of Δ reported in Table 4 strongly suggest that in the investigated microemulsions the precipitation is stopped at the nucleation stage. Obviously, the dimensions of the aqueous microregions must be retained and are mainly responsible for the regulation of the nanocrystal dimensions [26].

As far as the second point is concerned, since nanocrystals and water/surfactant interfaces have an ionic-dipolar character, it seems reasonable to suppose that their interaction is mainly electrostatic. In addition, since the interface-microcrystal interaction can induce structural changes of the aqueous microregion hosting the nanocrystal or of the nanocrystal itself, further energetic contributions may arise from these effects. At present, unfortunately, the current knowledge does not permit the evaluation of these contributions.

Fig. 6. Electron micrograph of CaF_2 nanocrystals from system g (dimension of nanocrystals about 700 Å).

Finally, it is doubtful whether the values of the thermodynamic parameters (enthalpy changes, equilibrium constants and activities) governing the precipitation process in pure water also hold for the formation of nanocrystals in aqueous microregions. At present, the changes of these thermodynamic parameters are not predictable on the basis of current theories.

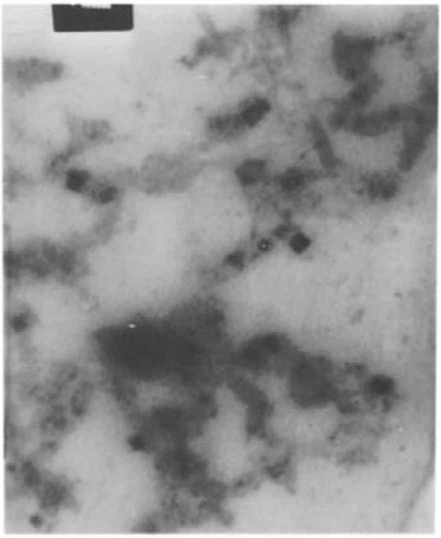

Fig. 7. Electron micrograph of $CaCO_3$ nanocrystals from system o (dimension of nanocrystals about 300 Å).

In conclusion, although it is not possible to give a complete explanation of the processes underlying the formation of nanocrystals in microemulsions, our results show that nanocrystals of calcium fluoride and calcium carbonate are formed in the systems investigated (this was also corroborated by electron microscopy; see Figs. 6 and 7) and that the energetic state of these nanocrystals is very different from that in bulk water.

ACKNOWLEDGMENT

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