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DSC SPECTRA AS THERMAL FINGERPRINTS OF PERCOLATIVE MICROEMULSIONS

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Abstract

Three component percolative W/O microemulsions were studied by differential scanning calorimetry. Water–AOT–Decane, D_2O–AOT–Decane, Water–AOT–Isooctane and Water–$Ca(AOT)_2$–Decane systems were analyzed. Thus by changing, in the order, the dispersed phase, the dispersing medium, and by modifying the interphase region. The thermal history of the samples was monitored by a suitable thermal program. Following the latter, first order phase transitions associated with the freezing and/or melting of the two massive phases were obtained, as well as the higher order phase transition associated with the percolation process. From the melting spectra an estimate of the amount of water bound to the hydrophilic groups of the AOT as well as of that of oil bound to the hydrophobic surfactant tails was obtained. The latter result shows a difference in the behaviour of the continuous oily phase at the O/W interphase. From the freezing spectra, the percolative character of the microemulsion was evidenced by the exotherms associated with the freezing of the water phase.

Keywords: DSC, fingerprints, percolative microemulsions

Introduction

The main purpose of the present study is the analysis by DSC of both the first and the higher order phase transitions occurring, as a function of temperature, in three-component W/O microemulsions that exhibit a percolative transition [1–6].

The thermal behaviour of the microemulsions was investigated on cooling the liquid samples down to their complete freezing as well as upon heating the frozen systems back to their normal, liquid, microemulsion state. To this aim water in oil microemulsions well characterized for what concerns both the percolative behaviour and the structure were chosen [7, 8].

It will be shown that the above experimental approach, although very general, may offer a rather surprising both qualitative and quantitative description of some of microemulsion main features, including the percolative behaviour.

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Materials and methods

Water–AOT–Decane, Heavy Water–AOT–Decane, Water–AOT–Isooctane and Water–Calcium AOT–Decane microemulsions were analyzed. The composition of the systems is summarized in Table 1.

Table 1 Composition of microemulsion systems

Systems	φ cm^3/cm^3	W_o mol/mol	T_p/K
1) Water/Na(AOT)/Decane	0.35	40.8	306
1b) Na(AOT)/Decane	0.36	12.4	–
2) HeavyWater/Na(AOT)/Decane	0.35	40.7	312
3) Water/Na(AOT)/Isooctane	0.31	37	300
4) Water/Ca(AOT)$_2$/Decane	0.302	24.3	–

Na(AOT)=sodium di-2-ethylhexyl sulfosuccinate
W_0=molar fraction water/surfactant
φ=volume fraction (Water+Surfactant)/(Total).

Since it is very difficult to obtain samples identical with those formulated by other researchers, the percolative behaviour of the samples was controlled by electrical conductivity measurements as a function of temperature, and the critical exponents and percolative temperature (T_p) evaluated (Table 1).

The thermal analysis was performed with a Mettler TA3000 Differential Scanning Calorimeter equipped with a low temperature DSC-30 Silver cell. The (dH/dt) measuring range, in the actual configuration, was 50 mW, the temperature interval analyzed extends from 333 K down to 103 K. Each complete measuring run lasts about 5 h, therefore, in order to keep the samples continuously temperature monitored, we modified the equipment in order to allow the refilling of the liquid nitrogen Dewar, without removing the DSC low-T head, while the instrument is on.

Our calorimeter is basically a DTA, the calibration procedure – heat flow, temperature, blank measures, evaluation of the reference enthalpies of the microemulsion compounds and, centering of the sample holder device – requires an accuracy up to a paranoic level! And this mostly, for what concerns the detection of thermal events associated with transitions in which there is no latent heat involved. Aluminum pans of equal weight were used with an accuracy ±2 μg. After each measuring run, the mass of the sample pan was checked in order to exclude any leakage during the measure. The opening of the sample pan causes a notable drift in the DSC recordings.

The suitable sample mass (mg) for the actual study, was chosen taking into account the following main points: 1) The constant pressure condition must be satisfied in DSC measurements on condensed state systems. Therefore the sample pan cannot be completely filled, because at a higher order phase transition an expansion of the system may very likely occur; 2) Samples with components with high enthalpy values (Table 2), if too large (>18 mg) would give rise to output signals that may fall outside the measuring range of the instrument. 3) The samples cannot be too small (<5 mg) either, because the thermal event associated with a change in the specific heat, at constant pressure, (C_p) would escape detection. Thus, depending on the system studied, sample masses between 8 and 15 mg were selected.

The calorimetric reference data used to formulate the microemulsions are reported in Table 2. The enthalpy values, the melting and freezing temperatures were measured with our equipment on the pure, bulk compounds.

Table 2 Calorimetric parameters

	T_m/K	T_{fz}/K	ΔH_m/J g^{-1}	System	$\frac{\text{Bound H}_2\text{O}}{[\text{AOT}]}$ mol/mol	$\frac{\text{Bound oil}}{[\text{AOT}]}$ mol/mol
H_2O	273	233–253	333.42	1	7.2	1.1
D_2O	277	237–257	313.54	2	7.4	0.8
Decane	243	233	202.25	3	6.8	7.1
Isooctane	166	145	89.73	4	13.1	12.9

In order to become familiar with higher order phase transitions we used α-aluminum oxide powders, and Rochelle or Seignette salt both crystals and powders. The latter study was very useful because, as it is well known, Rochelle salt exhibits an anomaly in the specific heat just as at the Curie points of ferromagnetic materials, a behaviour very similar to that one would expect at a percolation transition [9].

Experiments with Rochelle salt have been very instructive. At the beginning we did not observe a thing: perfectly flat and cleaned DSC recordings were obtained, not even Michelangelo could draw them any better. After an endless procedure of trials and errors we learned that to detect a higher order phase transition the following parameters play a fundamental role namely, the sample thermal history and the thermal rate applied in the DSC analysis. The main result of the above study is synthesized in Fig. 1, where we report the thermal program that must be followed in the investigation of the thermal properties of microemulsions by means, obviously, of the actual DSC equipment.

One starts by keeping the liquid microemulsion sample isothermally for 20 min at a temperature T_0 around T_p. The DSC spectra associated with the freezing of the sample (DSC-exo) are recorded by applying a thermal rate of 2 K min^{-1}. The lowest temperature reached depends on the temperature at which

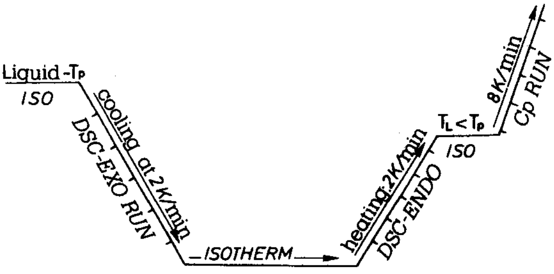

Fig. 1 The thermal program followed in the present study. The DSC analysis begins by taking the liquid samples at a temperature T_0 around the evaluated percolation temperature T_p

freezes the component with the lowest melting point. Because of the overcooling phenomena, to make sure that the sample is really frozen, it is wise, if possible, to broaden the low-T range of about 40 K. After a second isotherm at the final temperature reached in the DSC-exo run, the melting curves are recorded by applying the same scan speed of 2 K min^{-1} (DSC-endo).

From the above two DSC runs, the thermal event associated with first order phase transitions are obtained. Thereafter the DSC-endo measure is stopped at a temperature T_L about 20 K lower than T_P. While the samples, again liquid, are kept isothermally at T_L for 10 min, refilling of the liquid nitrogen Dewar is made.

The last DSC measure, labelled C_P run, is carried out by applying a rather high thermal rate of 8 K min^{-1} in a temperature interval from T_L to 313 K.

The DSC analysis of the percolative transition of liquid microemulsion samples, by equilibrium measurements or, by small isothermal steps, failed. It was necessary to trigger in some way the transition. The only tool we had for a system that is a liquid and has its own dynamics, was the thermal rate. The scan speed suitable for the C_P run was found to depend on the particular surfactant used. For AOT containing microemulsions this rate was of 8 K min^{-1}.

For first order phase transitions, the analysis of the calorimetric data was performed as reported in [10]. Following the temperature program here described, it was possible to control the thermal history of the samples and, also, to obtain the complete analysis of the thermal properties of a given microemulsion.

Results

The results gathered can be summarized as follows:

In the case of Water/Decane microemulsion the DSC exotherms depicted in Fig. 2 show a freezing behaviour of the two massive phases water and oil which is different from the one found in not percolative microemulsions described in reference [10–12]. In the actual case, the two thermal events bypass each other randomly. The latter behaviour was observed despite the T_0 temperature at which the samples were kept isothermally at the very beginning of the DSC

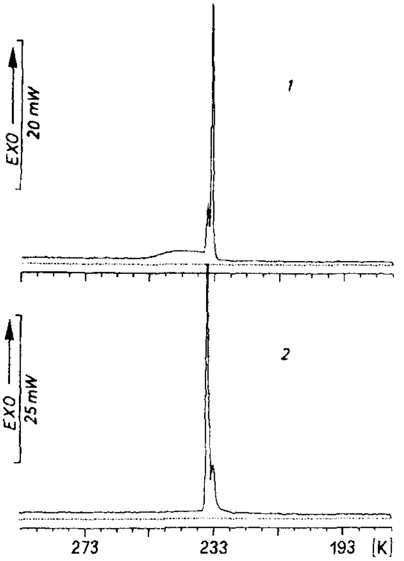

Fig. 2 Freezing exotherm of Water/Decane samples. The thermal events of the two massive phases bypass each other even if the temperature T_0=300 K was the same in both cases

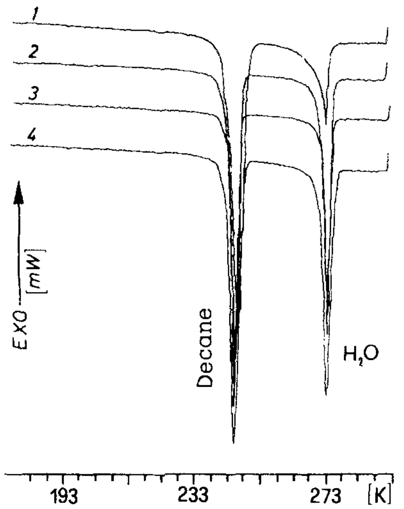

Fig. 3 Melting endotherms of system 1. The family of curves 2–3–4 was obtained on samples of different masses. Curve 1: a sample with a lower water content

analysis was the same. On the other side, the melting endotherms (Fig. 3) follow the schedule: the two massive phases melt at the temperature of the bulk pure components. The evaluation of the enthalpies associated with the melting of the known amounts of both water and oil contained in the samples, allows detection of the third component, the surfactant. As a matter of fact the measured enthalpies are lower (taking into account the measurement errors) than the estimated ones for the corresponding components. The difference between the a priori known and the measured enthalpies offers, therefore, an estimate of the amount of water bound to the surfactant hydrophilic groups, as well as of that of oil trapped between the surfactant hydrophobic tails. This result is consistent with the fact that the AOT amphiphile is soluble both in the water and in the oil phase. The calculated data are reported in Table 2 for the four systems investigated.

In order to understand the unusual freezing behaviour of the Water/Decane microemulsion, a systematic investigation was carried out. We studied microemulsion systems by substituting: i) the dispersed phase (Fig. 4); ii) the dispersing medium (Fig. 5); and iii) by modifying the interphase region. To this aim Calcium AOT [13] surfactant was used instead of Sodium AOT. In this case two surfactant tails are bound to the Ca ion. System 4 was found not to percolate in the temperature range from 263 to 333 K.

The melting endotherms (Figs 4 and 5 bottom) did not show any novelty. However the freezing exotherms did (Figs 4 and 5 top). Both in the D_2O/Decane

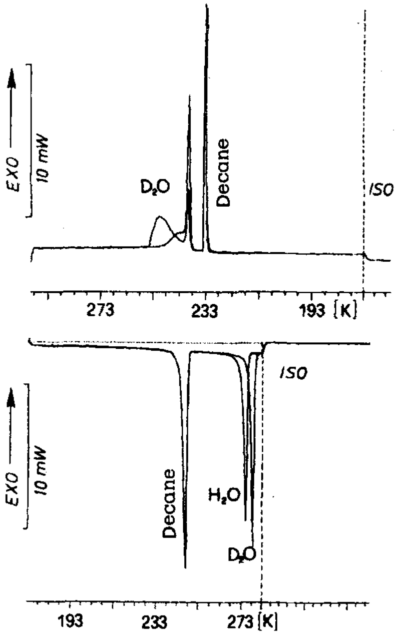

Fig. 4 Top: DSC-exo spectra of system 2. The 4 K difference in the D_2O melting temperature with respect to that of H_2O, helps to distinguish between the freezing contribution of the two massive phases and, shows the spreading of the exothermal peaks due to the freezing of the dispersed phase. Bottom: The corresponding endo spectrum compared with a DSC recording of system 1. The isothermal part of the measurement is also shown

and in the H_2O/Isooctane system the thermal event associated with the freezing of the dispersed phase did not show a sharp, well shaped peak but rather, a distribution of thermal events not always well separated. A possible interpretation could be that, around the percolation temperature, besides the cluster of water droplets that connects the system, clusters of smaller size as well as isolated droplets form. On cooling, obviously, the droplet concept vanishes, but water pools differing in their size may very likely occur, leading to freezing exotherms at different temperatures. The smaller the water pool, the lower its freezing temperature.

The results of the thermal analysis of the Water–Ca(AOT)$_2$–Decane system, are reported in Fig. 6 (DSC-exo and Fig. 7 (DSC-endo). The thermal events due to the freezing of the two massive phases, did not bypass each other. Both families of spectra, the exo and endo respectively, are perfectly overlapping and totally independent on the system's thermal history.

Because of the overcooling phenomenon, in the exo-spectra, the two peaks nearly stick together: the two massive phases freeze at about the same temperature. The corresponding bulk samples do not (Table 2). In W/O microemulsions the water is confined in environments of low dimensionality, the droplets. The latter are self cleaning containers. Impurities, if any, migrate toward the inter-

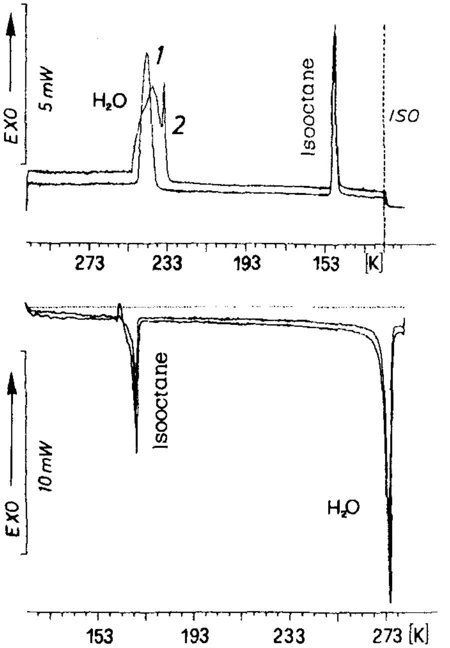

Fig. 5 DSC-exo (top) and endo (bottom) spectra of two samples of system 3. The isooctane, by freezing at 145 K, does not influence the thermal behaviour of the water phase. Curve 1: T_0=313 K; curve 2: T_0=300 K. The small exotherm in the melting curve is due to recrystallization

phase; in the microemulsion state really cleaned and nucleation center free water cores may stay overcooled down to temperatures even 20 K lower than those of a bulk water sample.

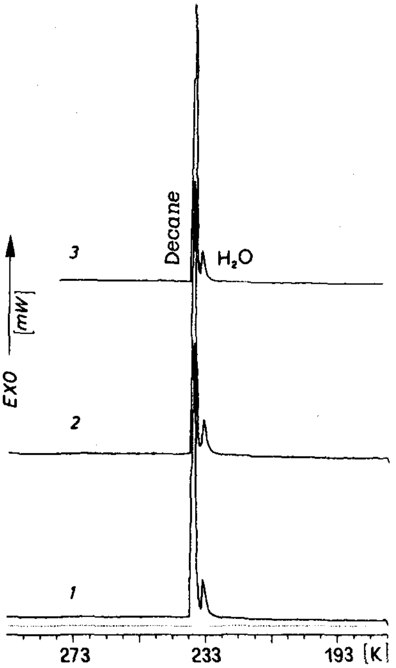

Fig. 6 DSC-exo spectra of system 4. The $H_2O/Ca(AOT)_2$/Decane microemulsion does not percolate. Curve 1: T_0=308 K; curve 2: T_0=298 K; curve 3: T_0=283 K

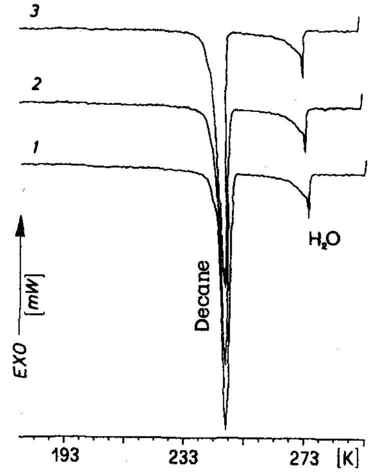

Fig. 7 DSC-endo spectra of system 4. See text for explanation

The two freezing peaks were identified by verifying the enhalpy values of the corresponding melting spectra, under the hypothesis that the heat absorbed on melting should be equal to that released on freezing!

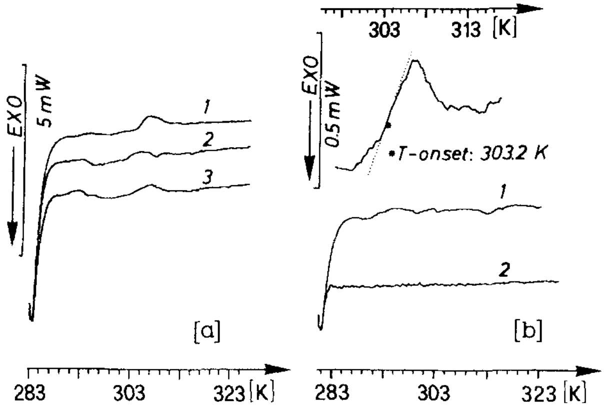

Fig. 8 a) DSC recordings of the percolative transition of Water/Decane samples: 1) T_0= 303 K, mass 18.250 mg; 2) T_0=278 K, mass 13.413 mg; 3) T_0=302 K, mass 10.259 mg
b) Top: Onset analysis of the transition of curve 3) of part a). Curve 1: oscillating trend by measuring a second time the higher order phase transition with or without following again the temperature program. Curve 2: example of failure recorded on a sample of system 1. By applying a scan speed of 4 K min^{-1}, during the C_p run, the percolative transition escapes detection

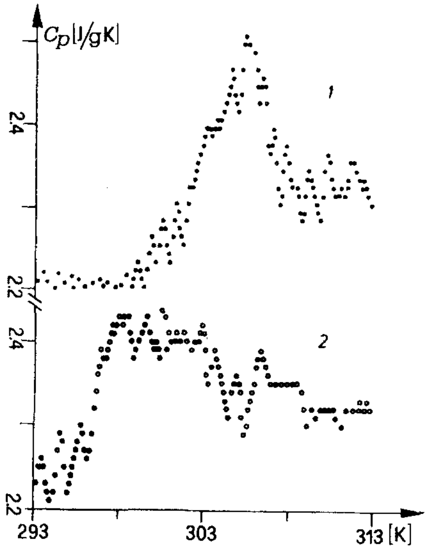

Fig. 9 Water/Decane microemulsion: the behaviour of C_p *vs*. temperature. Curve 1: a sample taken at T_0=302 K, near T_p; curve 2: a sample taken at T_0=283 K, much lower than T_p

The results of the DSC study of the percolation transition are assembled hereafter:

– In Fig. 8 part a) we report a family of DSC recordings (d*H*/d*t* *vs.* *T*) for the W/Decane system;

– In Fig. 8 part b) the analysis is shown, by the Onset method, of curve 3 of part a); curve 1 : an example of the oscillating recording obtained by repeating the C_p-run a second time immediately after the occurrence of the percolation transition; curve 2: a typical result of a DSC measure obtained by applying the wrong thermal rate of 4 K min^{-1} during the C_p-run.

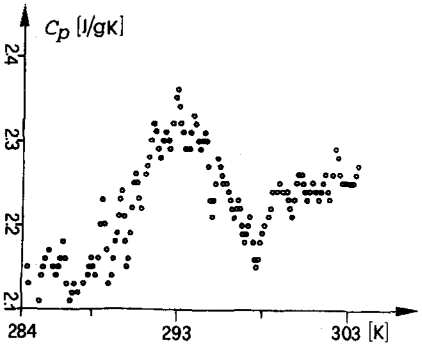

Fig. 10 W/Isooctane microemulsion. C_p as a function of temperature. T_0=300 K

– In Fig. 9 the trend as a function of temperature of C_p is plotted for two samples of system 1 differing in the temperature at which they were kept at the very beginning of the DSC analysis. The corresponding study on the W/Isooctane microemulsion is depicted in Fig. 10. The result, beside a difference in the order of magnitude of ΔC_p, presumably arising from having used as reference a water-oil mixture, is substantially in agreement with the one reported by Vollmer and coworkers [14].

Discussion

The result of the DSC analysis of percolative microemulsions reported in this work, shows that the study of the thermal behaviour of these highly disperse systems, both on freezing the liquid samples and, upon their melting, offers a notable amount of very specific information about some of the microemulsion main characteristics.

i) The DSC-endo spectra prove that the two main phases, water and oil, do behave as true massive phases, in agreement with the working hypothesis advanced by Israelachvili in his thermodynamic approach to the mechanism of formation of microemulsion systems [15].

ii) For the first time it was possible, by a single experimental run, to obtain an estimate of the amount of water bound to the hydrophilic groups of the surfactant, as well as of that of oil trapped between the surfactant hydrophobic tails. The result has also evidenced a substantial difference in the behaviour of the two oils, decane and isooctane, at the interphase of the system. Reasoning in terms of mass percent of the oil contained in the sample, it follows that, in system 1 the 89.60% of the decane melted, while in system 3, only the 49.90% of the isooctane contributed to the melting peak.

iii) The DSC-exo spectra confirmed once more, that the W/O microemulsion can be very useful for studying the properties of water confined in environments of low dimensionality [16, 17].

iv) The percolative nature of the microemulsion was found to emerge directly from the first order exotherms associated with the freezing of the dispersed phase. The spreading of the H_2O and D_2O exotherms shown in Figs 4 and 5 could be a consequence of having frozen the samples after an isothermal period at a temperature around the percolative one. The oil phase does not appear to be responsible for the above behaviour. The exo-spectra obtained on the samples with the isooctane oil that freezes at a temperature about 100 K lower than that of the decane, supports the above conclusion (Fig. 5). The control of the sample thermal history allows a well reliable comparison with the DSC recordings of the systems studied and, *a posteriori*, confirms that, if a modification in the thermal program has no effect on the DSC-exo events associated with the freezing of the water phase, then, very likely, the microemulsion does not exhibit a percolative behaviour.

v) The result that the type of surfactant used and therefore of the interphase formed, rules the thermal rate required to detect the percolation transition, confirms the fundamental role played by the interphase region in governing the microemulsion properties.

vi) The finding that it is impossible, under our experimental condition, to re-detect the percolation transition a second time immediately after it has occurred (Fig. 8b, curve 1) suggests that liquid samples, first frozen and thereafter liquified again, maintain the memory of the thermal history they went through. The latter result signifies that the sample shows a strong thermal hysteresis, a behaviour highly suggestive of a crytical type of transition. The time required by the sample to recover was of the order of several hours.

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