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Procedures for DSC analysis of percolative microemulsions

Donatella Senatra*

Dipartimento di Fisica, Università di Firenze, Gruppo INFM (Istituto Nazionale di Fisica della Materia),
Largo Enrico Fermi 2, 50125 Firenze, Italy

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Abstract

In this paper we report about the procedure for investigating the thermal properties of three-component water-in-oil microemulsions exhibiting a percolative behavior. The thermal properties of these highly disperse systems are analyzed both on freezing the liquid samples and upon their melting. A thermal cycle suitable for evidencing the higher order phase transition at the percolative threshold temperature is presented. Since the latter transition was found to depend on the system's thermal history, a modification of the DSC set up is described that allows the refilling of the liquid nitrogen Dewar without requiring the removal of any of the instrument parts and enables to maintain the calibration assessment through long time lasting measuring runs. The change in the specific heat, at constant pressure, at the percolation transition was evaluated. The thermal hystheresis associated with the transition is also discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: DSC; Complex self-association liquids; Percolation transition by DSC; Microemulsions by thermal analysis

1. Introduction

A water-in-oil microemulsion (w/o) is a complex multicomponent, isotropic and transparent liquid, consisting of water (W), oil (O) and a surface active agent (S) [1].

The water is dispersed in the oil in the form of small spherical droplets (diameter ca. 10 nm) coated with a surfactant monolayer. Microemulsions, either w/o or o/w, are thermodynamically stable systems that form spontaneously. The formation of these systems can be explained in terms of the surfactant self association mechanism [2,3].

The structural characterization of microemulsions is obtained by quasi-elastic light scattering (QUELS) and small angle neutron scattering techniques (SANS) [4–6].

The properties of several microemulsion systems have been investigated by the author by dielectric spectroscopy, electrical conductivity measurements [7–10] and thermally stimulated depolarization techniques [11,12].

Differential Scanning Microcalorimetry was applied for the first time by Senatra et al. [13–15] to four-component non-percolative microemulsions and later on extended to three-component percolative ones with the aim of investigating the percolation transition as well as the extent to which the percolative nature of the microemulsion affects the system's thermal behavior [16,17].

Percolative microemulsions are systems in which, for a given value of the droplet concentration Φ_p (volume fraction: W + S/total), the presence of short

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* Fax: +39-55-229-330.
E-mail address: donatella.senatra@fi.infn.it (D. Senatra).

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range attractive interactions between the droplets, favors a clustering process of the dispersed phase leading to the formation of a connecting path through the system [18]. The volume fraction at which the system is internally connected is defined as the percolative threshold and the phenomenon as percolation transition.

In w/o microemulsions a percolative transition may also occur as a function of the temperature for a given and fixed Φ value. The evaluated temperature at which the transition occurs is called percolation temperature (T_p) [19–24].

The latter aspect suggested the possibility of investigating the percolation process by DSC methods.

The study of the electrical conductivity against temperature offers a rather direct mean for evidencing the percolative behavior of a system. A possible percolative trend must show a change in the electrical conductivity of four or more orders of magnitude. Greater details about this topic may be found in [20–24].

The microemulsion systems analyzed in this work are fully characterized as far as the structure, dielectric behavior and percolative properties is concerned [25–27].

2. Experimental

2.1. Materials

Two w/o microemulsions were investigated namely, a water/decane and a water/isooctane with Na(AOT) as surfactant (sodium di-2-ethylhexyl sulfosuccinate).

Water was taken from a Millipore-Q-System. The surfactant, of Micro Select > 99% quality, was supplied by Fluka. Decane oil ($C_{10}H_{22}$) of 99.5% quality was supplied by Sigma and isooctane (C_8H_{18}) of purity >99.5 (GC) was also from Fluka.

Besides the aforementioned systems, also a heavy-water/decane microemulsion was formulated. The deuterium oxide (D_2O) was supplied by Carlo Erba Chemicals with isothopic purity >99%D.

The composition of the three systems is given in Table 1. The percolative behavior of the D_2O/decane microemulsion was ascertained in our laboratory by electrical conductivity measurements as a function of temperature. The percolation temperature and the exponents of the scaling laws governing the type of percolative process involved, were evaluated following the procedure described in [10].

2.2. DSC method

The thermal analysis was performed with a Mettler TA 3000 Differential Scanning Microcalorimeter equipped with a TC 10A processor and two low temperature cells, a DSC 30 and a DSC 30 silver. The standard sensor was set in the medium sensitivity position. The temperature interval investigated extends from 333 K down to 110 K: nitrogen gas of 5.5 purity was used to purge the cell. A flow of 20 ml min^{-1} was used. The nitrogen gas was further purified by flowing through two Millipore cartridges to both adsorb small particles, if any, and residual humidity. Aluminum pans of equal mass were employed for both the reference and the sample. The mass accuracy was ±2 μg. The temperature accuracy, at the thermal rate of 2 K min^{-1} was evaluated as ±0.01 K.

DSC measurements were performed as a function of temperature upon the freezing of the liquid samples as well as during their melting. The thermal cycle

Table 1
Composition of percolative water-in-oil microemulsions

System	Φ^a (ml ml^{-1})	W_0^b (mol mol^{-1})	T_p^c (K)
Water/Na(AOT)^d/decane	0.35	40.8	300
D_2O/Na(AOT)^d/decane	0.35	40.7	312
Water/Na(AOT)^d/isooctane	0.31	37.0	306

[a] Volume fraction (water + surfactant)/total.

[b] Molar fraction water/surfactant.

[c] Percolation temperature.

[d] Sodium di-2-ethylhexyl sulfosuccinate.

described in [16] was followed. After an isothermal period at $T = T_p$ of the given sample, the heat flow rate (dH/dt) was measured as a function of decreasing temperature down to $T = 110$ K. This measure was labeled DSC-EXO run. After a second isotherm at $T = 110$ K, dH/dt was measured against increasing temperature up to a temperature T_L at which the system is again in the liquid, microemulsion state. The latter part of the cycle was named DSC-ENDO. A 2 K min^{-1} scan speed was applied in both the DSC-EXO and ENDO runs. The temperature T_L was about 40 K lower than the percolative temperature of the sample under test. After a third isotherm at the T_L temperature, the phase transition associated with the percolative process was measured by applying a higher thermal rate of 8 K min^{-1}. The latter measure was called C_p run. During the C_p run the purging gas was stopped.

The thermal cycle allows: (i) the analysis of first-order phase transitions associated with both the freezing and the melting of the system's massive phases water and oil [14,15]; the control of the systems' thermal history; the detection of the percolative transition occurring in the liquid microemulsion samples by using a higher scan speed to trigger the process. Moreover, it was found that the thermal rate suitable for the detection of the percolation process, depends on the type of surfactant used [16,17].

The thermal events in the DSC spectra were identified as reported in [13–15]. We assumed as reference melting temperatures and enthalpy values the experimentally measured data gathered on the pure liquids used to formulate the different systems.

Although first-order phase transitions are rate independent, the latter behavior was controlled to apply also to both liquid massive phases in the microemulsion state. For any component the reference data were taken at 2 K min^{-1}. The same applies to the enthalpy values for any liquid tested. Whenever necessary, the corresponding deuterated liquids were used for the water and the oil phase in order to exclude any ambiguity in the identification of any given thermal event, provided that the melting temperature of the deuterated liquid differs by about 4 K from that of the normal, undeuterated one and that the systems formulated do share a common monophasic region in the phase diagrams. Finally, we recall that, being microemulsions liquid systems consisting of liquid components, overcooling phenomena occur upon lowering the temperature.

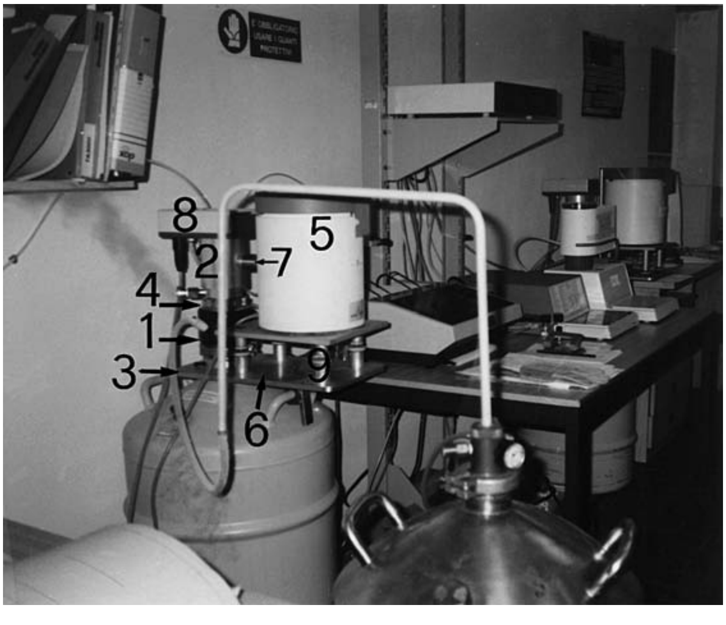

Fig. 1. Technical modification of the DSC set up adopted for increasing the autonomy of the instrument (see text for explanation).

2.3. Technical modification

In order to improve the autonomy of the DSC set up and to maintain its calibration assessment, a modification was made which allows the refilling of the liquid nitrogen Dewar without requiring the removal of both the low temperature DSC 30S head and the nitrogen heater.

With reference to Fig. 1: a flange coupling joint (1) is placed between the flange with the safety valve (2) and the base plate (3). Both the top and the bottom of the joint are fixed with chain clamps (4). The DSC low temperature cell (5) is positioned over a second aluminum plate (6) in order to allow the alignment of the liquid nitrogen heater opening (7) with the DSC head connecting tube (8). The second plate (6) is provided with adjustable knots (9) to facilitate the leveling of the DSC cell. The base plate (3) is placed on top of the liquid nitrogen Dewar as in the unmodified set up. The joint is thermally insulated by a suitable rubber tape. With this assessment the lowest working temperature is 113 K. For lower temperatures another joint was built equipped with a coaxial chamber with an outlet tube to a vacuum pump. The thermal insulation is improved by producing the vacuum in the gap between the internal and the external walls of the joint chamber. In this way it is possible to reach and to maintain the lowest working temperature of the instrument $T = 103$ K. In both cases the joints are provided with a lateral inlet tube that allows the refilling of the nitrogen reservoir. The refilling of the latter can be performed while the DSC set up is in a standby state at a temperature that does not require the nitrogen heater to be energized too much in order to reduce the waste of liquid nitrogen.

2.4. ΔC_p evaluation

To detect the percolation transition as a function of temperature by a DSC technique on a system that is in the liquid state and does not show, even if observed by SANS, at the threshold temperature, any particular change, may present some difficulty. The percolation transition is expected to be a higher order phase transition. With a TA 3000 equipment, based on a DTA conception, even the raw detection of the thermal event associated with the percolation process, without any "driving tool" as, for instance, the electric field in the conductivity measurements, is not trivial at all.

In order to afford the above problem, the thermal properties of samples of Rochelle or Seignette salt were studied. The Rochelle salt exhibits an anomaly in the specific heat at $T = 296.7$ K [28] just as at a Curie point of ferromagnetic materials, a behavior very similar to the behavior one would expect at the percolation transition. The Rochelle salt was considered as a reference system for learning how to deal with higher order phase transitions in the particular, simpler case, of a well known solid. The result of the DSC measurements with Rochelle salt samples, both pressed powder pellets and single crystals, is summarized in Fig. 2. The salt, sodium potassium tetrahydrate ($C_4H_4KNaO_2.4H_2O$) of 99% purity, was supplied by Sigma.

The above study has shown that, with our equipment, two parameters play a fundamental role in this type of transitions namely, the control of the sample thermal history and the thermal rate. On the basis of the former finding the thermal cycle previously described was worked out.

The change in the specific heat, at constant pressure, was evaluated: (i) by simply using a Blank procedure to account for a residual weight difference between the sample and the reference crucibles; (ii) by evaluating experimentally a kind of τ "lag" constant with both

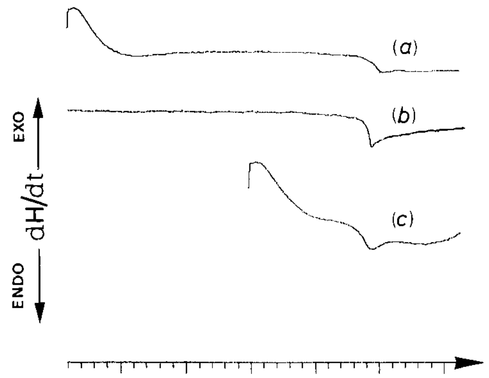

Fig. 2. DSC recordings of the transition at ca. 300 K of Rochelle salt samples. Different temperature intervals (ΔT) were tested. Curve (a): pressed powder pellet, ΔT (278–323 K); curve (b): single crystal, ΔT (173–313 K); curve (c): single crystal, ΔT (293–313 K). Heating rate: 5 K min^{-1}. Only the significant aspect of the curves is plotted.

the reference and the sample pans filled with the system under test and entering the calculated value in the configuration list of the instrument during the C_p run; (iii) by applying a Blank correction with the reference pan filled with the (Oil + Surfactant) mixture, without added water [29]. As in point (ii) the latter procedure was applied only in the C_p run.

As a last step, also the temperature and the time dependence of the percolation process was investigated to evidence the presence of thermal hysteresis. To this aim both the last measuring run at the percolation transition and the thermal cycle "in toto", were repeated at regular intervals of time.

3. Results and discussion

The melting spectra of the three systems investigated are assembled in Fig. 3. The identification of the different thermal contributions in the recordings confirms that the two main components, the water and the oil, by melting at the melting temperatures of the corresponding pure liquids, do behave as massive phases. Since, from a thermodynamic point of view, the formation of these systems as a distribution of droplets of either water or oil into a continuous oily or water medium can be justified in terms of the concentration and interacting energies of the only surfactant at the water/oil or oil/water interphase, under the assumption that the dispersed liquid behaves as a bulk phase, the DSC results plotted in Fig. 3, offer a rather direct confirmation of the above working hypothesis [2,3].

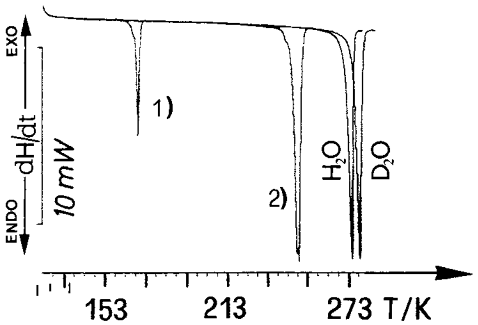

Fig. 3. Melting endotherms of three samples differing in the oil used as continuous phase. (1) Water/isooctane system; (2) water/decane system and (b), in the dispersed phase: the spectrum of the D_2O/decane sample is observable just because of the higher melting temperature of the heavy water component. Heating rate: 2 K min^{-1}.

From the DSC endotherms it also emerges that the dispersed phase maintains its droplet identically independent from the particular oil used, if the surfactant is always the same. In other words, the droplet water core, enclosed by a surfactant shell, ignores its oily partner. The latter finding is in agreement with previously reported results on four-component microemulsions [14,15].

Knowing the sample composition and therefore the "a priori" expected enthalpy value for each one component, from the measured heat content associated with each one thermal event, it is possible to evaluate the amount of water that behaves as free water (melting at 273 K), as well as the amount of water bound to the hydrophilic groups of the surfactant. The same applies to the oil. If the surfactant, as in the present case, is soluble in both the water and the oil, from the enthalpy value measured for the oil, besides the percentage of free oil, also the fraction of oil trapped between the surfactant's hydrophobic chains will result as shown in Table 2. In the case the surfactant is insoluble in either phases, the total amount of oil contained in the system will be obtained as reported in [14].

For the water there will be always a missing fraction from the total sample water content, because of the amount bound to the hydrophylic heads of the surfactant. The latter result is anyhow a probe for estimating the interphasal area of the microemulsion [30].

As far as the freezing behavior is concerned, it was found that the percolative nature of the system plays a role. Depending on the starting temperature (T_{st}) of the thermal cycle, it emerges that if $T_{st} \ll T_p$ the thermal events in the DSC-EXO spectra are sharp, well shaped peaks as depicted in Fig. 4, while at $T_{st} \cong T_p$ (internally connected system), as well as at $T_{st} > T_p$ (multiconnected system), a spreading in the exotherms associated with the water phase occurs. In Fig. 5 an example is given of the latter behavior for each one the system studied. For sake of completeness, the freezing exotherms of both a pure, bulk water and decane sample are shown.

The freezing behavior of the water/decane system explains why the heavy water/decane microemulsion was formulated. Because of the overcooling phenom-

Table 2
Example of evaluated data from DSC analysis of w/o microemulsions (S^o: surfactant Na(AOT))

System	Free water (%)	Free oil (%)	Bound water/AOT (mol mol^{-1})	Bound oil/AOT (mol mol^{-1})
H_2O/S^o/decane	82.4	89.6	7.2	1.1
D_2O/S^o/decane	82.1	93.0	7.4	0.8
H_2O/S^o/isooctane	81.4	49.9	6.8	7.1

enon, the thermal events associated with the water and the oil nearly merged together and even bypasses each other. The heavy water was therefore used with the aim of separating the two thermal events, the one due to the dispersed phase from that due to the oil. The higher melting temperature of heavy water, and thus its lower freezing temperature was used to distinguish between the two thermal contributions.

3.1. The percolative transition

The recording of the raw DSC spectra at the percolation transition are shown in Fig. 6. The trend of the specific heat against temperature is reported in Fig. 7 for two samples of the water/isooctane and the heavy water/decane systems. The latter measure, curve (1), was plotted on purpose. It was taken for a sample of 18 mg, too large. The result shows that, within the confined temperature interval of the C_p run, the sample temperature lags behind the reference temperature and the transition "appears" to develop at a lower temperature with respect to the evaluated one. This type of effect can be minimized by reducing the sample mass, as shown in the second example of curve (2) where the measure was performed with a sample of 5 mg.

Only the Blank correction of point (i) was used to evaluate the ΔC_p. The other two methods did not significantly improve the measure. The use of the (oil + surfactant) mixture did not work because, due to an unavoidable amount of residual water in the surfactant, the latter shows a slightly viscoelastic

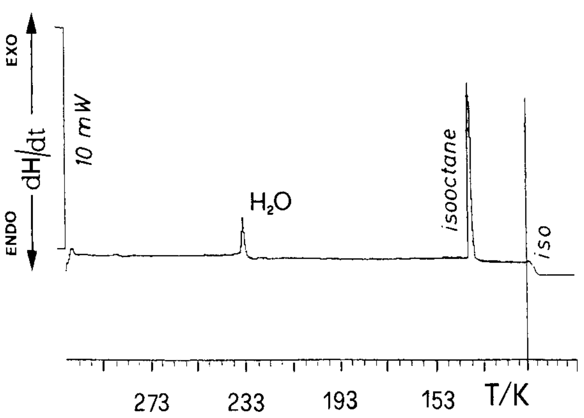

Fig. 4. Freezing exotherms of a water/isooctane sample measured at a starting temperature lower than the evaluated percolative threshold temperature. T_{st} = 293 K. Heating rate: 2 K min^{-1}.

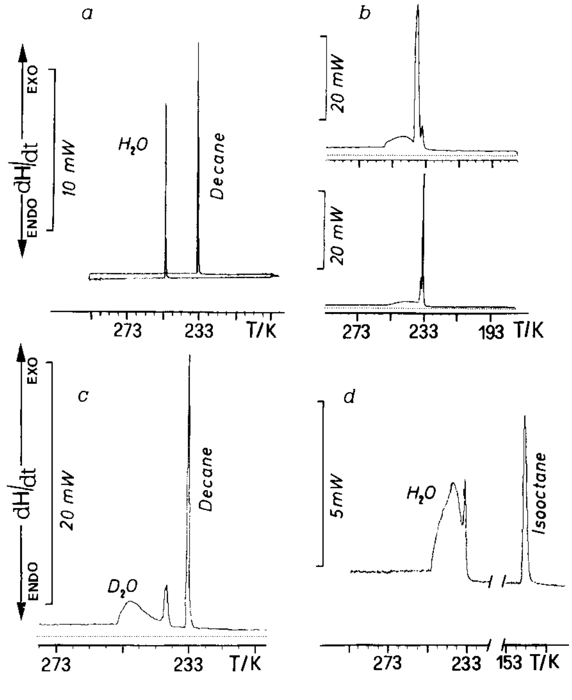

Fig. 5. Freezing exotherms of microemulsion samples taken at $T = T_p$ in the very first isotherm of the thermal cycle. (a) DSC-EXO spectra of a pure water and a pure decane sample; (b) water/decane system: spreading exotherms exhibited by two samples both taken at the same temperature T_p; (c) heavy water/decane system; (d) water/isooctane system. Heating rate: 2 K min^{-1}.

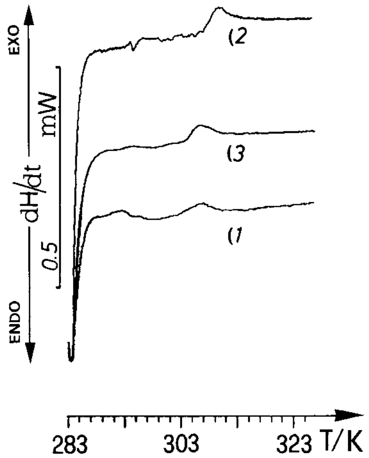

Fig. 6. DSC recordings of the percolation transition. Curve (1): water/decane system; curve (2): heavy water/decane system; curve (3): water/isooctane system. Heating rate: 8 K min^{-1}.

behavior. With the procedure of point (ii), the change in specific heat, within the experimental errors, was found to be exactly the same. Therefore, since to apply the latter procedure, the reference pan must be substituted for the C_p run, it was decided to follow the simpler experimental method of point (i) by using, during all the thermal cycle, the same empty pan as reference.

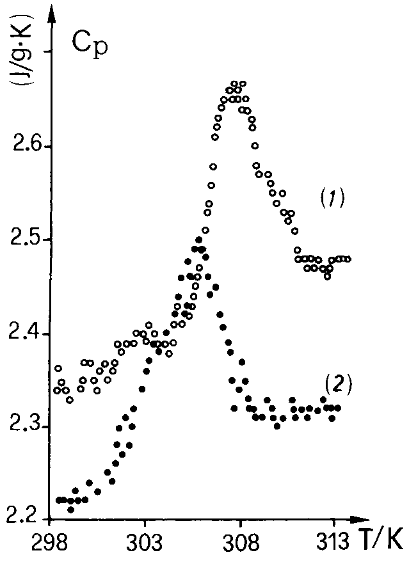

Fig. 7. Specific heat at constant pressure against temperature. Curve (1): heavy water/decane system; curve (2): water/isooctane system.

It is worth noting that, being the percolative temperature an evaluated temperature, [18] it may happen that, if one fails in detecting the transition, by repeating the measure, starting the very first isothermal period of the thermal cycle, at a temperature slightly different from T_p, the transition will occur just because the evaluated T_p was not exactly the real percolative threshold temperature.

3.2. Thermal hysteresis

It was found that once the percolative transition has occurred, it is not possible, immediately after, to redetect the transition, neither by repeating the C_p run, nor by repeating the complete thermal cycle. For a given sample the percolative transition can be measured again after several hours [16]. It is anyhow remarkable that the system "remembers" its thermal trial even after being frozen and thereafter liquified.

4. Conclusions

The investigation of both the properties and the structure of complex liquids like microemulsions, requires obviously a multidisciplinary experimental approach. However, the DSC analysis described in this paper shows that the study of the thermal behavior of microemulsions, offers notable amount of very specific information. Namely, from the analysis of first-order phase transitions, it emerges the behavior as true massive phases of the two main components water and oil; from the evaluation of the amount of water bound to the surfactant hydrophilic groups as well as from the amount of oil trapped between the surfactant hydrophobic tails, a description is obtained of the role played by the two "sides" of the amphiphile at the water/surfactant and at the surfactant/oil interphase.

The study of the percolation transition by DSC confirms the critical nature of the percolative process [20–24]. The exothermal events associated with the freezing of the water phase demonstrates that the percolative character of the microemulsion affects the thermal behavior of these systems. The spreading in the freezing exotherms was interpreted in terms of the freezing of different water domains linked with the dimension of the cluster(s) connecting the system [16].

References

[1] Progress in Microemulsions, Ettore Majorana International Scientific Series, vol. 41, Plenum Press, New York, 1989.

[2] J. Israelachvili in Surfactants in Solution, vol. 4, K.L. Mittal and P. Bothorel Eds. 1989. p. 3–33 (Plenum Press).

[3] J. Israelachvili, Physics of amphiphiles: micelles, vesicles and microemulsions, Proceedings of the International School of Physics Enrico Fermi, Italian Physical Society, course XC, 1983, p. 23.

[4] Horizons in small angle scattering from mesoscopic systems, R. Giordano, G. Maisano, J. Teixeira, R. Triolo and A.J. Barnes Eds. J. Molecular Structure, 383. Elsevier, Amsterdam. 1996.

[5] R. Pecora, Dynamic Light Scattering Application of Photon Correlation Spetroscopy, Plenum Press, New York, 1985.

[6] Structure and dynamics of strongly interacting colloids and supramolecular aggregates in solution, S.-H. Chen, J.S. Huang and P. Tartaglia Eds. NATO ASI Series C: Mathematical Physical Science, vol. 369. Kluwer Academic Publishers. 1992.

[7] D. Senatra, G. Giubilaro, J. Colloid Interface Sci. 67 (1978) 457–458.

[8] M.G. Giri, M. Carlà, C.M.C. Gambi, D. Senatra, A. Chittofrati, A. Sanguineti, Meas. Sci. Technol. 5 (1993) 627.

[9] C.M.C. Gambi, M.G. Giri, M. Carlà, D. Senatra, A. Chittofrati, Phys. Rev. E 56 (1997) 4356.

[10] M.G. Giri, M. Carlà, C.M.C. Gambi, D. Senatra, A. Chittofrati, Phys. Rev. E 50 (1998) 1313.

[11] D. Senatra, C.M.C. Gambi, A. Neri, J. Colloid Interface Sci. 79 (1981) 443.

[12] D. Senatra, C.M.C. Gambi, A. Neri, Lett. Nuovo Cimento 28 (1980) 433–603.

[13] D. Senatra, G.G.T. Guarini, G. Gabrielli, M. Zoppi, J. Physique 45 (1984) 1159.

[14] D. Senatra, G. Gabrielli, G.G.T. Guarini, Europhys. Lett. 2 (1986) 455.

[15] D. Senatra, Z. Zhou, L. Pieraccini, Prog. Colloid Polym. Sci. 73 (2987) 66.

[16] D. Senatra, R. Pratesi, L. Pieraccini, J. Thermal Anal. 51 (1998) 79.

[17] D. Senatra, C.M.C. Gambi, M. Carlà, A. Chittofrati, J. Thermal Anal. Cal. 56 (1999) 1335.

[18] M. Carlà, C.M.C. Gambi, M.G. Giri, L. Pieraccini, D. Senatra, A. Chittofrati, A. Sanguineti, IEEE Trans. Dielectrics and Electrical Insulation 4 (1994) 716.

[19] B. Lagourette, J. Peyrelasse, C. Boned, M. Clausse, Nature 281 (1979) 60.

[20] S. Kirkpatrick, Rev. Modern Phys. 45 (1973) 574.

[21] A.L. Efros, B. Shlovskii, Phys. Status Sol. 76 (1976) 475.

[22] S. Gary, I. Webman, S.A. Safran, A.C.R. Bug, Phys. Rev. A 33 (1986) 2842.

[23] M. Moha-Ouchane, J. Perelasse, C. Boned, Phys. Rev. A 35 (1987) 3021.

[24] J. Peyrelasse, M. Moha-Ouchane, C. Boned, Phys. Rev. A 38 (1988) 904.

[25] S.H. Chen, J. Rouch, F. Sciortino, P. Tartaglia, J. Phys.: Condens. Matter 6 (1994) 10855.

[26] S.H. Chen, Ann. Rev. Phys. Chem. 37 (1986) 351.

[27] C. Cametti, P. Codastefano, P. Tartaglia, J. Rouch, S.H. Chen, Phys. Rev. Lett. 64 (1994) 1461.

[28] A. Rusterholz, Helv. Phys. Acta 8 (1935) 39.

[29] D. Vollmer, J. Vollmer, H.F. Eicke, Europhys. Lett. 26 (1977) 574.

[30] D. Senatra, Z. Zhou, Prog. Colloid Polym. Sci. 76 (1988) 106.