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MICROEMULSION – BASED SILICA TEMPLATES FOR MULTIFUNCTIONAL NANOMATERIALS

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The aim of this paper was to present a comprehensive analysis of phase transitions in water/surfactant/alkoxide ternary systems and to show an easy way to identify microemulsion domains as appropriate microemulsion – based silica nanostructured templates for synthesis of multifunctional nanomaterials. For this purpose, different ternary phase diagrams have been experimentally built over a large temperature domain, by using three types of silica precursors, trimethoxymetilsilane, tetraethoxysilane and trimethoxy(phenyl)silane, and a non-ionic surfactant, Triton X-114. The influence of temperature on the phase transitions for different water/surfactant/ alkoxide systems, at a constant mass ratio of alkoxide : water (3:1) was also evaluated. The phase inversion points have been assessed based on Kahlweit diagrams. All these results can be used to pattern silica templates of either water-in-oil or oil-in-water type.

Keywords: ternary phase diagrams, alkoxide, Kahlweit diagrams, silica-nanostructured template

1. Introduction

Microemulsions are clear, isotropic and thermodynamically stable nanodispersions of immiscible liquids like oil and water, stabilized by a monolayer formed by the surfactant molecules between the two phases [1]. These micellar systems depend on the nature and concentration of the components. The micro-heterogeneous nature of the dispersions, enables microemulsions to find applications in various fields of science, technology and medicine [2].

Winsor identified four general types of phase equilibria between the microemulsion transitions [3]. Winsor I (WI), with two phases (O/W, O), where the lower (O/W) microemulsions phase is in equilibrium with the upper excess oil. Winsor II (WII), which has also two phases (W/O, W), in which the upper (W/O) microemulsion phase is in equilibrium with excess water. Winsor III (WIII) has three phases and the middle microemulsion phase (O/W plus W/O, called bicontinuous) is in equilibrium with upper excess oil and lower excess water. Winsor IV (WIV) is a macroscopically single-phase with oil, water and surfactant homogeneously mixed [4]. Winsor types I, II, III or IV are formed

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preferentially depending on surfactant structure and the surrounding environment, the dominant type being related to the molecular arrangement at the interface.

Non-ionic surfactants are, in general, considered superior to ionic ones in some aspects. They are more hydrophobic than ionic surfactants and less sensitive to high electrolyte concentrations or multivalent cations or pH changes [5]. Non-ionic surfactants can be used in food and pharmaceutical industries, as they are generally less toxic, low irritant and exhibit better solubility properties in microemulsions systems [6]. Moreover, nonionic surfactants have the ability to form microemulsion without the assistance of co-surfactant. Non-ionic surfactants belonging to polyethylene oxide family are widely used in industrial and domestic applications. The structure and dynamical properties of the surfactant micelles play an important role in their applications [7]. Triton X-100 is one of the non-ionic surfactants widely used and extensively studied. TX-114 is a non-ionic surfactant which thermo separates in water and forms an aqueous two phase system with a surfactant-depleted top phase and a surfactant-enriched bottom phase [8]. Critical micelle concentration (CMC) and cloud point of the surfactant are 0.17 mM and 22ºC respectively [9].

Solubilization and interfacial properties of non-ionic microemulsions depend upon temperature, the nature and concentration of the components. The determination of phase stability diagrams, the location of different structures formed within these water/non-ionic surfactant/polar oil systems, the alcoxid concentration and the temperature, in terms of variables are, therefore, very important. Using an adequate way of representation, it is possible to describe not only the limits of existence of the single and multiphase regions, but also to characterize the equilibrium between phases.

In this paper, the influence of alkoxide and temperature on the phase behaviour of ternary systems, Water (W)/ Polyethylene glycol tert-octylphenyl ether (TX-114)/trimethoxymetilsilane (MTEOS), Water (W)/ Polyethylene glycol tert-octylphenyl ether (TX-114)/tetraethoxysilane (TEOS) and Water (W)/ Polyethylene glycol tert-octylphenyl ether (TX-114)/trimethoxy(phenyl)silane (PTEOS) are studied. The literature on the phase behavior and structural aspects of microemulsion involving substantial amount of oil (hydrocarbon) and water (as polar and aqueous solvent) stabilized by surfactant (s) is numerous [10,11]. However, this study is important as helps to understand how ordered or complex structures are formed by a spontaneously self – assembling approach, and in which way such processes are controllable in order to prepare structures with predefined structure and, consequently, predetermined properties. Therefore, for delimiting and further use of microemulsion domains in optimum and adequate conditions for a specific purpose, a detailed study is realised on the phase transitions in various water-oil-surfactant systems. As the stability and functionality of the final silica materials can be affected by the local environment of the entrapped structures, different physical-chemical parameters such as polarity, phase inversion temperature (PIT) and phase composition have been also investigated.

2. Experimental section

2.1. Materials

Polyoethylene glycol tert-octylphenyl ether (TX-114) was provided from SIGMA. Trimethoxymetilsilane (MTEOS), tetraethoxysilane (TEOS) and trimethoxy(phenyl)silane (PTEOS) were purchased from MERCK. Ultra-pure water (Millipore Corporation) was used.

2.2. Phase diagrams

Ternary phase diagrams were constructed using the surfactant titration method at two temperatures (25^{o}C), the room temperature and the phase inversion temperature (PIT), following a procedure already known. [12]. This involves successive addition of small quantities of surfactant in water/oil mixtures. In order to establish the PIT, Kahlweit diagrams were built in the range 17 ÷ 70 ^{o}C. The samples were taken in sealed test tubes and shaken vigorously using a magnetic stirrer to ensure a proper mixing and then kept in a thermostatic device at desired temperature. .

3. Results and discussion

3.1. Phase Diagrams in Ternary System Water/Surfactant/Alkoxide

The ternary phase diagrams were determined visually by mixing the surfactant with solvent/water mixtures until an isotropic liquid appeared. This method is advantageous as using the minimum surfactant quantity all types of microemulsions can be obtained. Three different types of silica precursor, with aliphatic tails (trimethoxymetilsilane, tetraethoxysilane) and phenyl ring (trimethoxy(phenyl)silane), have been chosen in order to obtain various and interesting silica template domains. A non-ionic surfactant, polyethylene glycol tert-octylphenyl ether, has been used as self-assembling agent. This non-ionic surfactant was used as it can form microemulsion without the assistance of co-surfactants.

The phase diagrams drawn in ternary system water/surfactant/alkoxide are shown in Figure 1. From this figure one can observe that the solubilization of water and alkoxides increases proportional with the surfactant concentration for a given water/oil volumetric ratio, R = V_W/V_O. Even more, as the alkoxides hydrophobic properties are increasing in the series MTEOS < TEOS < PTEOS, their compatibility with TX-114 surfactant is different. As a result, in the case of MTEOS as oil phase, the WI microemulsion area is more narrow and begins at lower surfactant concentrations (~ 7%). WIV single-phase microemulsion appears for a MTEOS concentration ranging between 17 and 30%.

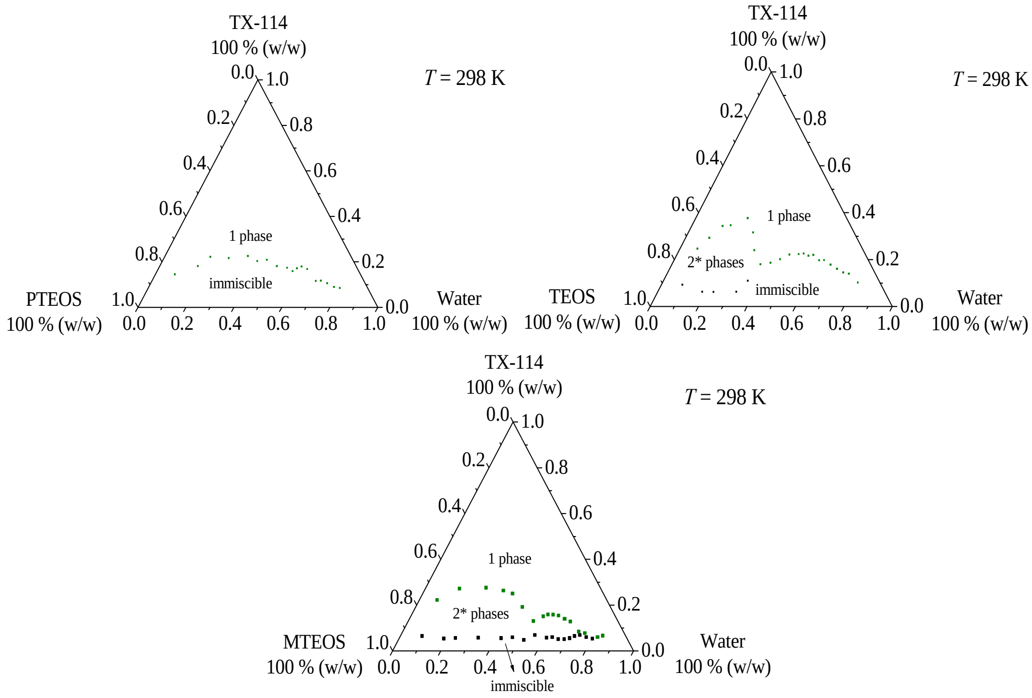

Fig. 1. Phase diagrams in water/surfactant/oil ternary system at 298 K: 1 phase – micellar solution (reverse or direct), microemulsion W IV, gel or liquid crystals; 2* phases – system W I (microemulsion O/W, O)

The affinity of TX-114 towards MTEOS is weakened do to its aromatic character and this leads to a decrease of surfactant solubility into alkoxide solution. In this case, a possible explanation could be correlated with strengthening of the solution hydrophobicity, which hinders the formation of microemulsions at low surfactant concentrations. Moreover, the slightly more hydrophobic character of TEOS as compared to MTEOS leads to an accentuated water immiscibility, which leads to larger biphasic microemulsion areas (~ 10 to 40% TX-114). On the other hand, single-phase systems require more surfactant amounts (from 25 to 40% TX-114). The hydrophobic nature of TX-114/TEOS solution is more pronounced than that of TX-114/MTEOS system and this can be seen by the fact that W II domain doesn’t form. This behaviour is supported by the fact that TX-114 has a small solubility in MTEOS and TEOS and a high solubility in water. Thus, the adequate concentration for obtaining various types of microemulsion is higher.

When an aryl alkoxide (PTEOS) was used, the phase diagrams (Figure 1) indicate the presence of only one microemulsion phase, namely WIV present at small concentrations of surfactant.

Therefore, there are many single-phase microemulsion domains and oil-in water phases that can be successfully applied as soft silica-templates able to solubilise active hydrophobic compounds [13-16].

3.2. Temperature Effect on Phase Equilibrium in Nonionic Ternary Systems

The temperature plays an essential role on non-ionic surfactants solubilisation and on the microemulsion type, as the increase of temperature is known to induce the hydration level decrease of polyoxyethylene chains, and change the phase behaviour of surfactant [17]. This is way its effect on the phase transitions is evaluated in this study.

An increase in temperature for the polyoxyethylene surfactants leads to a decrease in the number of hydrogen bonds, which raises the micellar mass and decreases the CMC. If the temperature continues to increase, the micelle becomes so large and the number of intermicellar interactions increase to such an extent that a sudden onset of turbidity is perceptible even to the naked eye. This temperature is called the cloud point. A further rise in temperature causes the solution to begin to separate into two phases, one surfactant-rich and the other surfactant-depleted with no or few micelles present.

The temperature influence on the phase transitions for the water/surfactant/alkoxide systems, at a constant mass ratio alkoxide:water (3:1) and over temperature ranges delimited by the alkoxide gelling point, was experimentally shown by the Kahlweit diagrams. These results are presented in Figure 2. From these figures, one can see that the type of microemulsion that forms in a water/poly(oxyethylene glycol) alkyl ether surfactant/oil system is highly dependent on temperature. At low temperatures, the surfactant is mainly soluble in water giving rise to W I microemulsions. At high temperatures, the surfactant is preferentially soluble in oil and the WII phase is then formed. At an intermediate temperature, the hydrophilic-lipophilic properties of the non-ionic surfactant are balanced [18] and the phase-inversion temperature (PIT) appears. Here a transition from WI to WII microemulsions takes place and a bicontinuous WIII phase is obtained [19,20].

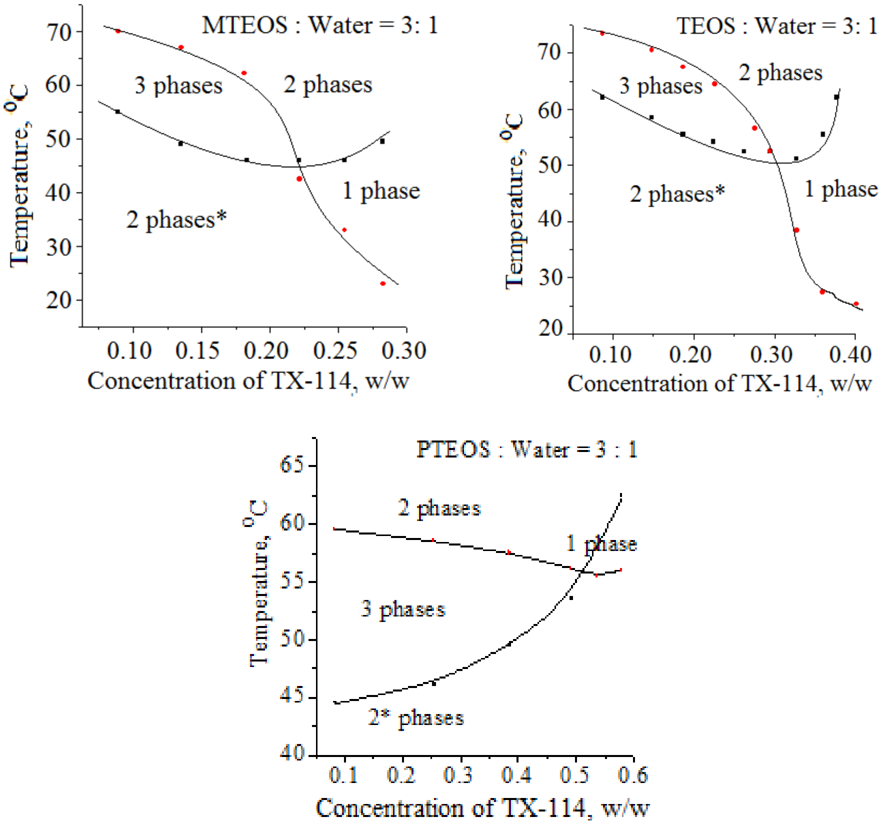

Fig. 2. Kahlweit diagrams for water/surfactant/alkoxide systems, at a constant mass ratio alkoxide : water = 3 : 1. 1 phase – micellar solution (reverse or direct), microemulsion W IV, gel or liquid crystals; 2 phases* – system W I (microemulsion O/W, O); 2 phases – system W II (microemulsion W/O, W); 3 phases – system W III (W, microemulsion, O)

The mass ratio alkoxide:water (3:1) was chosen as it corresponds to the hydrolysis reaction stoichiometry of the sol-gel process (1 mol of alkoxide : 4 moles of water). In this way, two solubility curves were obtained, one for the solubility of the surfactant in water and the other for the solubility of the surfactant in alkoxide. This kind of representation provides information about the conditions in which microemulsions are formed, meaning structural aspects and temperature influence. Also, this approach is useful in practice, especially for obtaining O/W microemulsions from an organic surfactant solution by successively adding water in small amount. The increase in temperature brings with it a diminishing of lateral interactions among the surfactant molecules. This is explained by the increase of the average surface occupied by a surfactant molecule at the interface. Thus the curvature at the interface is reversed from convex towards oil to planar, when the surfactant has no a preferential behaviour towards any of the two components (water and alkoxide), and finally convex towards water.

The phase inversion temperatures of the water/surfactant/alkoxide systems are shown in Table 1. The phase inversion occurs as the surfactant solubility in water is decreasing and its solubility in alkoxides is increasing. After the inversion temperature has been established, the conditions for obtaining microemulsions for a certain purpose can be adequately chosen.

Table 1

The phase inversion temperatures for water/surfactant/alkoxide systems

System	PIT, K
MTEOS/TX-114/Water	318
TEOS/TX-114/Water	324
PTEOS/TX-114/Water	329

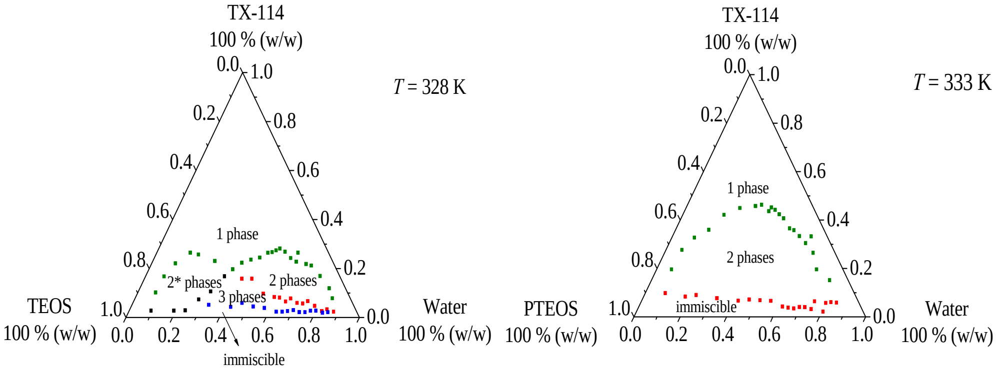

Fig. 3. Phase diagrams in ternary system water / surfactant / oil associated to microemulsions at high temperatures: 1 phase – micellar solution (reverse or direct), microemulsion W IV, gel or liquid crystals; 2 phases* – system W I (microemulsion O/W, O); 2 phases – system W II (microemulsion W/O, W); 3 phases – system W III (W, microemulsion, O)

Phase diagrams for other temperatures than room temperature were also drawn as the working stages for preparing nanostructured silica materials might suppose a thermal treatment. These are shown in Figure 3. According to these phase diagrams, the increase in temperature significantly enhances the W IV microemulsion phase and also the formation of the W II microemulsion, which is extended over a large part of the working domain, even for small concentrations of surfactant.

O/W microemulsion is the first stage for the preparation of hybrid nanocomposites based on formation of the silica network around the colloidal aggregates within the microemulsion. It represents a unique method for obtaining monodispersed fullerene nanoclusters [13]. In this case an important feature of the technique has been revealed: the ability of microemulsion to reverse the oil-in-water, where the nanoparticles are synthesized, into water-in-oil type [13]. These materials exhibit improved adsorption efficiency and photostability.

Therefore there are two ways to exploit the TX-114 microemulsion – based silica templates, depending on the microemulsion type: i) water-in-oil, when lyophilic functional components could be incorporated into silica matrix and ii) oil-in-water, when lipophilic functional components could be solubilised into oil droplets which results into hybrid silica nanomaterials.

3.3. Phase transitions in the water/oil/surfactant system

For a proper interpretation and understanding of a phase diagram [21,22], and consequently, a rigorous selection of the appropriate microemulsion templates for silica nanostructures, the working domain will be divided depending on the ratio ($R = V_W/V_O$) between the volumes of the immiscible components and the surfactant concentration as it is illustrated in Figure 4.

For lower concentrations of surfactant, the number of its molecules at the water/oil interface is small and thus its capacity to stabilize the droplets is reduced. Therefore, the droplets will get together to give a continuous phase in a small volume equilibrated by a poor-surfactant phase. If $V_W/V_O > 1$, then $V_W/V_{SF} < V_O/V_{SF}$ and the predominant interactions will be hydrophilic, having a convex inter-phase with respect to water (reverse micelles) ($R>1$). As a result, a W II system will be formed (W/O microemulsion phase in equilibrium with a lower poor-surfactant water phase). In the opposite side of the diagram, where $V_W/V_O < 1$, so $V_W/V_{SF} > V_O/V_{SF}$, the interactions will be mainly lipophilic and a Winsor I system will appear (O/W microemulsion phase in equilibrium with an upper poor-surfactant oil phase) as a consequence of a convex interface formation with respect to oil (direct micelles) ($R<1$). When $R = 1$, the affinities of the surfactant for the two media are comparable to each other, $V_W/V_{SF} = V_O/V_{SF}$, and the W III microemulsion is formed. The surfactant solubilize equal amounts of water and oil (R=1) and is in equilibrium with the two aqueous and organic phases in excess.

When the surfactant concentration is increasing, both, hydrophilic and lipophilic interactions are affected, and the inversion of phases occurs. For a ratio V_W/V_O <1, water will have the role of hydrating the oxyethylenic groups, as it will no longer solubilise the surfactant. In this case the hydrophilic interactions will predominate, R becomes higher than unity and the resulted one-phase microemulsion is similar to the system of reverse micelles. For V_W/V_O >1, the contact surface with water is increasing while that with oil is decreasing. As a consequence, the lipophilic interactions become more important and determine the inversion of the interface geometry: it will no longer be convex towards water (R>1) but convex towards oil R<1), and as a result, W IV microemulsion will be formed similar to the system consisting in direct micelles.

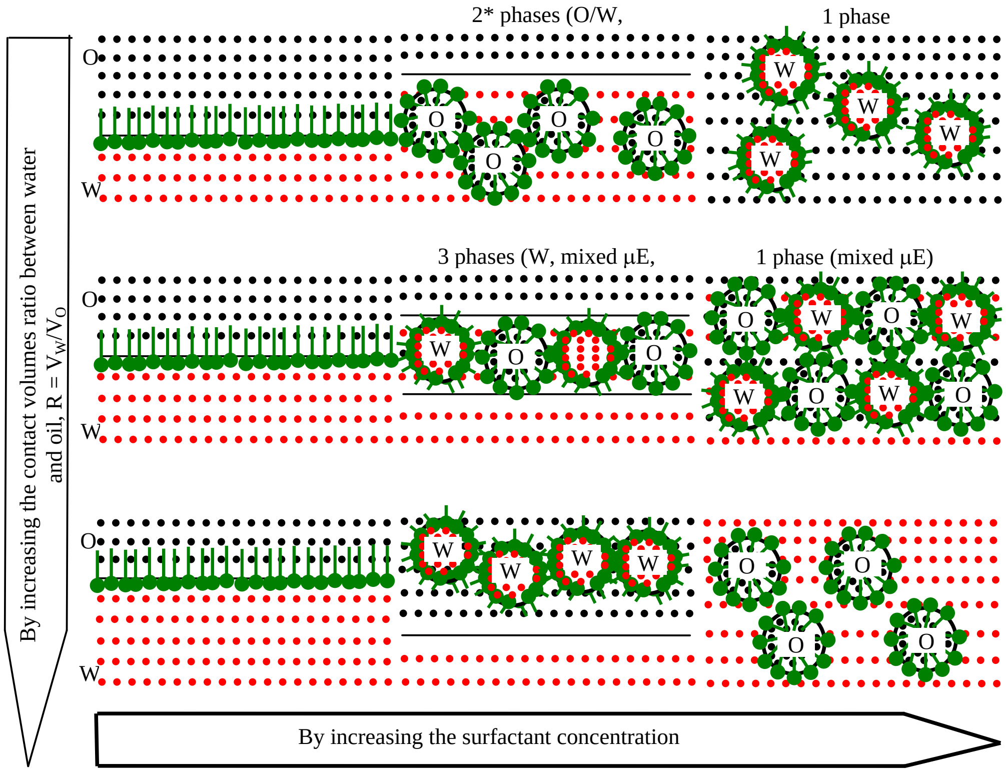

Figure 4. Phase transitions in ternary system water (W)/surfactant (SF)/oil (O) associated to microemulsions: 1 phase – micellar solution (reverse or direct), microemulsion W IV, gel or liquid crystals; 2 phases* – system W I (microemulsion O/W, O); 2 phases – system W II (microemulsion W/O, W); 3 phases – system W III (W, microemulsion, O)

When R=1, isotropic systems are formed that contain aggregates similar to both direct and indirect micelles, relatively equal proportions of water and oil being solubilised. At a surfactant concentration still higher, but close to R=1, its solubilising capacity is significant higher, the interface towards oil is planar, and isotropic rigid structures, gels or liquid crystals are formed.

4. Conclusion

This study showed that different ternary phase diagrams drawn in micro-heterogeneous systems by using a non-ionic surfactant, TX-114 and different silica precursors (MTEOS, TEOS, PTEOS) can be exploited in order to select appropriate microemulsion domains as nanostructured templates for preparing multifunctional silica materials. The experimental approach is based on a detail understanding of phase transitions and adequate selection of appropriate compositions within water/surfactant/alkoxide phase diagrams.

The effect of alkoxide type and temperature on phase transitions is discussed in detail. It was noticed that while at low temperatures, the surfactant is mainly soluble in water giving rise to W I microemulsions, at high temperatures, the surfactant is preferentially soluble in oil and the WII phase is then formed.

The phase inversion point, meaning the transition from water-in-oil to oil-in-water microemulsion, was clearly established by corroboration of information provided by Kahlweit diagrams.

In conclusion, most of the studied systems are able to form a large area of single-phase microemulsion and thus can be applied as silica templates (water/oil or oil/water) for inorganic or hybrid nanomaterials synthesis.

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