MICROEMULSIONS – PROPERTIES, APPLICATION AND PERSPECTIVES

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ABSTRACT

In recent decades, microemulsions as a kind of colloid-dispersed systems have been successfully used as reaction medium allowing the realization of chemical reactions to synthesize various organic and inorganic substances. Based on their thermodynamic stability and simple structure, they are used also as modeling systems. With the development of new technologies like nanotechnology, this feature of microemulsions gradually gained the position of a modern approach to the preparation of nanosized particles. The aim of the present paper is to study and analyze the properties of microemulsion systems, their applications and perspectives for their wider use in industrial technologies and households.

Key words: *W/O microemulsion systems, nanotechnology, nanosized particles, applications*

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INTRODUCTION

Emulsions are widely spread type of heterogeneous dispersed systems both in nature and industry. They usually consist of two immiscible liquids one of which (dispersed phase) is distributed in the other (dispersing phase) in the form of small particles [1].

In recent decades, microemulsions as a kind of colloid-dispersed systems have been successfully used as reaction medium allowing the realization of chemical reactions to synthesize various organic and inorganic substances. A characteristic of the microemulsions is the so called „dynamic exchange process" The emulsion drops in them incessantly integrate and disintegrate, thus exchanging matter between them. With the development of new technologies like nanotechnology, this feature of microemulsions gradually gained the position of interesting alternative reaction medium where relatively small monodispersed colloid particles can be obtained [1÷8].

The aim of the present work is to study and analyze the properties of microemulsion systems, their applications and perspectives for their wider use in industrial technologies and households.

MICROEMULSIONS – PROPERTIES, APPLICATION AND PERSPECTIVES

The microemulsions which are dispersed system by themselves, are thermodynamically stable, transparent and most often contain the components: two immiscible liquids (usually water and oil) and surfactant. They arte obtained from common emulsions and are called micelles emulsions [1].

Depending on the type of the dispersing and dispersed phases, they are classified into two main types: oil –in-water (O/W) and water-in-oil (W/O). The size of the water droplets can vary in wide range depending on the stabilizer nature (from several to several hundred nanometers). The stabilizers used are surfactant of various natures. Surfactants by themselves are high molecular weight substances with pronounced surface activity at certain phase boundary. They consist of hydrophilic and hydrophobic part. In a W/O emulsion, the detergent molecules orient with its hydrophilic end towards water drops to form the so called "reverse micelles" (Figure 1).

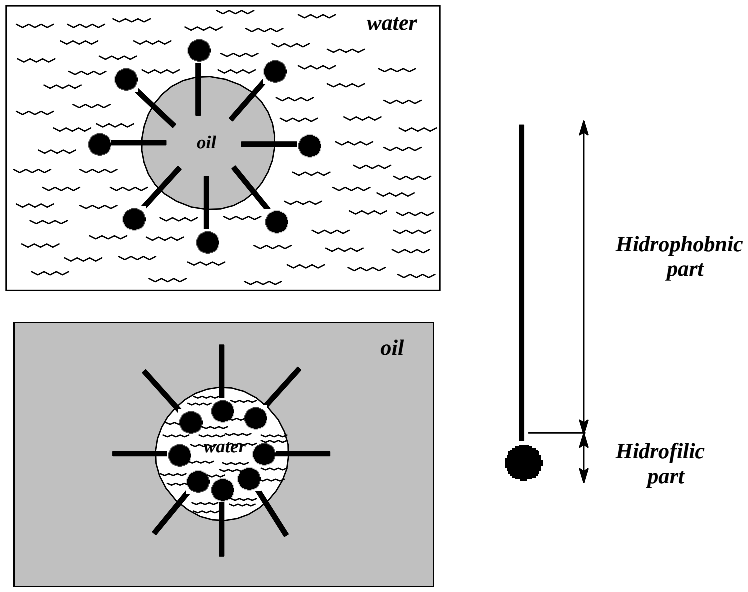

Figure 1. Arrangement of surfactant molecules on W/O emulsion (lower scheme) and in O/W emulsion (upper scheme)

Microemulsions are usually characterised by ternary phase diagrams, the three edges of which are the components of a microemulsion, namely, oil, water and surfactant. Any co-surfactants used are usually grouped together with the surfactant at a fixed ratio and treated as a pseudo-component [1].

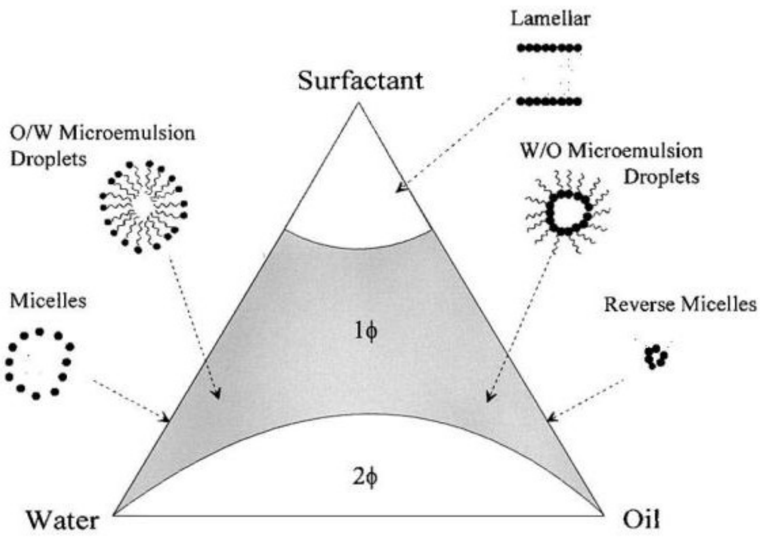

Figure 2. Ternary phase diagram of microemulsion

Figure 2 shows a hypothetical ternary phase diagram of a microemulsion illustrating that two-phase system forms at very high surfactant concentrations.

Microemulsions are industrially relevant due to their applications in a number of areas. The interfacial and rheological properties of microemulsions are important to exploit surfactant-enhanced tertiary oil recovery methods. There are also obvious applications in the food and cosmetics industries, particularly using phospholipid surfactants. The ability to precisely control the size and stability of the microstructure domains of microemulsions makes them useful for applications in liquid membrane technology [5].

Microemulsions also provide compartmentalized liquid structures having high surface area and can therefore be used as novel and versatile media for chemical synthesis. This is significant for potential applications in enzymic reactions in microemulsions. Another potential use of the fluid but structured nano-size domains of microemulsions is in the preparation of sub-micron or nano-particles of a desired size or shape, reflecting the structure and environment of the aqueous droplets [1÷6]. These potential technological applications have led to the development of several new techniques for the synthesis of various types of nanoparticles in recent years. These include gas-phase techniques such as gas evaporation, laser vaporization and laser pyrolysis; vacuum synthesis techniques like sputtering, laser ablation, and ionized beam deposition, as well as and liquid phase techniques like precipitation from homogeneous solutions, sol-gel processing, freeze drying [1÷8], etc.

The present paper is focused on the use of the aqueous cores of water-in-oil microemulsions as reactors for the synthesis of nanoparticles. Microreactor shape depends on the specific reaction conditions [3, 8].

Precipitation reactions in microemulsions offer a novel and versatile technique for the synthesis of a wide variety of nanophase materials with the possibility for precise control of the size and shape of the particles formed. It also offers a unique method to control the kinetics of particle formation and growth by varying the physicochemical characteristics of the microemulsion system. In W/O microemulsions, the aqueous droplets continuously collide, coalesce and break apart which results in a continuous exchange of solute content. The collision process depends on the diffusion of the aqueous droplets in the continuous media, i.e. oil, while the exchange process depends on the attractive interactions between the surfactant tails and the rigidity of the interface, as the aqueous droplets approach close to each other. For reactions in microemulsions involving reactant species totally confined within the dispersed water droplets, a necessary step prior to their chemical reaction is the exchange of reactants by the coalescence of two droplets. When chemical reaction is fast, the overall reaction rate is likely to be controlled by the rate of coalescence of droplets [1÷8].

Therefore, the properties of the interface such as interfacial rigidity are of major importance. A relatively rigid interface decreases the coalescence rate and, hence, leads to a low precipitation rate. On the other hand, a substantially fluid interface in the microemulsion enhances the rate of precipitation. Thus, by controlling the structure of the interface, the reaction kinetics in microemulsions can be changed by an order of magnitude. It has been further shown that the structure of oil, alcohol and ionic strength of the aqueous phase can significantly influence the rigidity of the interface and the reaction kinetics [1]. Conceptually, if one takes two identical water-in-oil microemulsions and dissolves reactants A and B respectively in the aqueous phases of these two microemulsions, upon mixing, due to collision and coalescence of the droplets, the reactants A and B come in contact with each other and form AB precipitate. This precipitate is confined to the interior of the microemulsion droplets and the size and shape of the particle formed reflects the interior of the droplet. This is one of the principles utilized in producing nanoparticles using microemulsions (see Figure 3a). However, nanoparticles can also be produced in microemulsions by the adding a reducing or precipitating agent in the form of liquid or gas, to a microemulsion containing the primary reactant dissolved in its aqueous core. Figure 3b shows the formation of metallic nanoparticles by adding reducing agents such as hydrazine or hydrogen gas in a microemulsion containing metal salt. Figure 3c shows the formation of oxide, hydroxide or carbonate precipitates by bubbling gases like O_2, NH_3, or CO_2 through a microemulsion containing soluble salts of the cations. In the past decade or so, several researchers have used these techniques to synthesize nanoparticles in microemulsions.

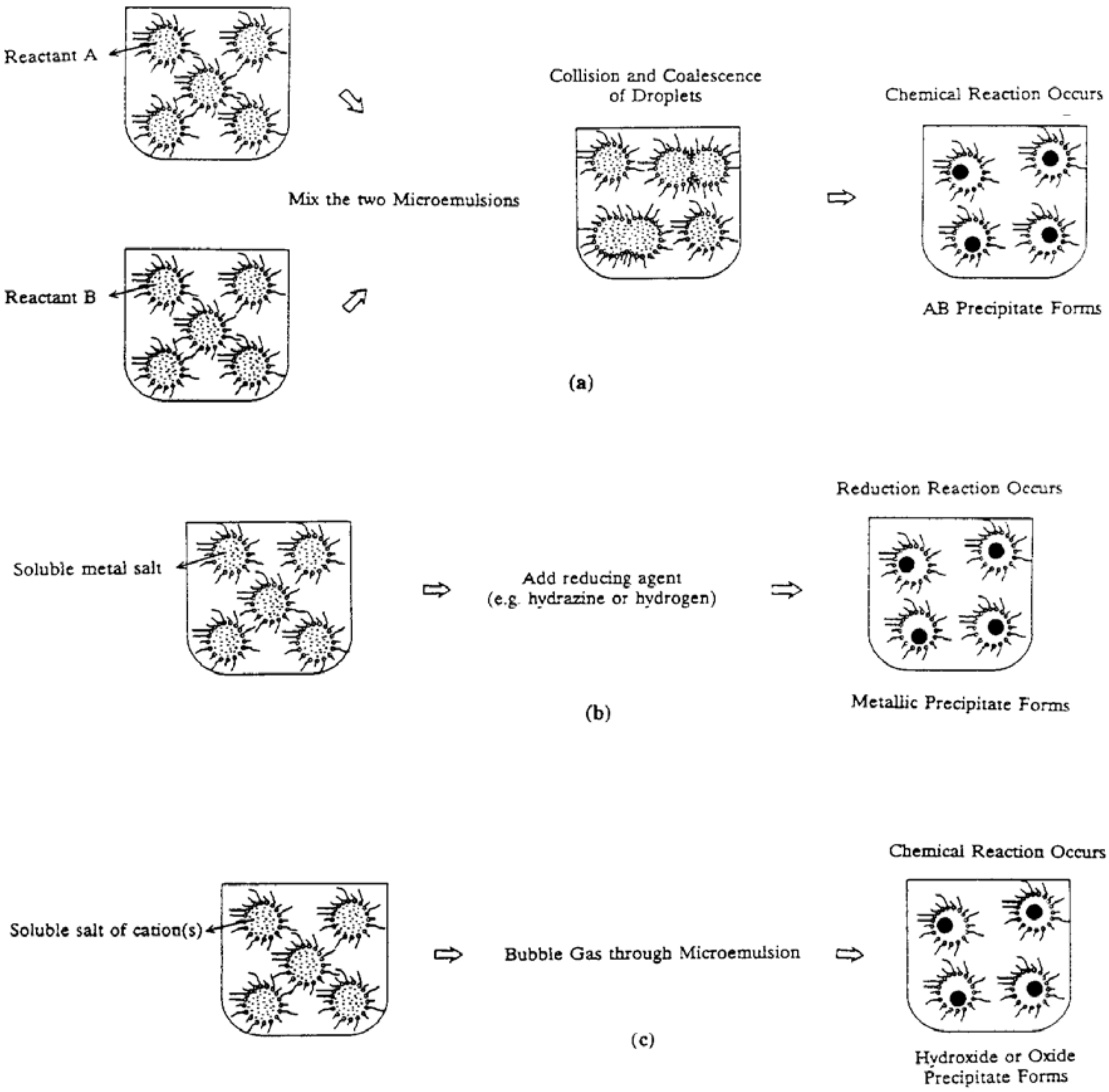

Figure 3. Schematic representation of synthesis of nanoparticles in microemulsions: (a) using two microemulsions; (b) by adding a reducing agent to a microemulsion; and (c) by bubbling gas through a microemulsion.

Nanosized particles of $BaCO_3$, $BaSO_4$, $CaCO_3$, etc, have been synthesized in reverse micelles (water/oil microemulsion) by carbonizing the solution. Different solvents were used, e.g. cyclohexane, decane, heptane. Attempts have been made to study the effect of mole ratio of the components and solvent type. To some extent, the influence of the latter on the size and nature of the carbonate particles have been investigated. However, these attempts reported in the literature lack completeness and have not been fully analyzed [2, 3].

Therefore, the efforts of the team in recent years were devoted to the development of a method, apparatuses and studies on the process of preparation of carbonate nanoparticles using microemulsion technique. The method developed is non-contaminating the environment, uses small amounts of raw materials and allows preparing nanostructures with reproducible distribution of particles by size. The results obtained from studies carried out earlier confirmed the opinion that the synthesis of nanoparticles in microemulsion (w/o) is to be preferred among the other known methods [6÷8]. The dynamic exchange process characteristic for the microemulsions activates the mass transfer in emulsion drops. Besides, the amount of substance dissolved in them is small, so it could be expected that small particles of about the same size would be obtained. This once again confirms the advantages of the method discussed.

CONCLUSION

Colloid-dispersed systems are microheterogeneous systems with dispersity by the order of 1÷100 nm. They possess a number of important properties stipulated by the size of the colloid particles and their structure. Based on their thermodynamic stability and relatively simple structure, they can be still more used as modeling systems.

The microemulsion method of synthesis of nanostructures increases homogeneity at nano-level. Its main idea is to limit the irregularities through the small volume of the microemulsion drops. The water-in-oil (W/O) microemulsion can be regarded s special microreactor allowing the realization of various chemical reactions, preparation of different by nature nanoparticles and control of the synthesis conditions.

Studying the multitude of synthesis parameters to find the variable values most suitable for monitoring and control of particles properties would allow wider use of microemulsion systems in industrial technology and households. It would also make the nanostructures obtained available to technical implementation.

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