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Phase diagrams of microemulsions containing reducing agents and metal salts as bases for the synthesis of metallic nanoparticles

Reza Najjar [a,*], Cosima Stubenrauch [b]

[a] Faculty of Chemistry, University of Tabriz, 29 Bahman Blvd., Tabriz, Iran
[b] School of Chemical and Bioprocess Engineering, Centre for Synthesis and Chemical Biology (CSCB), SFI-Strategic Research Cluster in Solar Energy Conversion, University College Dublin, Belfield, Dublin 4, Ireland

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ABSTRACT

We studied the phase diagrams of microemulsions with a view to using these systems for the synthesis of metallic Pt, Pb, and Bi nanoparticles as well as of intermetallic Pt/Pb and Pt/Bi nanoparticles. The microemulsions consisted of H_2O/salt–*n*-decane–SDS–1-butanol. The salt was either one metal precursor ($H_2PtCl_6{\cdot}6H_2O$, $Pb(NO_3)_2$, or $Bi(NO_3)_3{\cdot}5H_2O$), a mixture of two metal precursors ($H_2PtCl_6{\cdot}6H_2O + Pb(NO_3)_2$ or $H_2PtCl_6{\cdot}6H_2O + Bi(NO_3)_3{\cdot}5H_2O$), or the reducing agent ($NaBH_4$). In addition, other salts needed to be added in order to solubilize the metal precursors, to stabilize the reducing agent, and to adjust the ionic strength. Combining the microemulsion (µe1) that contains the metal precursor(s) with the microemulsion (µe2) that contains the reducing agent leads to metallic nanoparticles. To study systematically how the shape and size of the synthesized metallic nanoparticles depend on the size and shape of the respective microemulsion droplets, first of all one has to find those conditions under which µe1 and µe2 have the same structure. For that purpose we determined the water emulsification failure boundary (*wefb*) of each microemulsion as it is at the *wefb* where the water droplets are known to be spherical. We found that the ionic strength (I) of the aqueous phase as well as the hard acid and hard base properties of the ions are the key tuning parameters for the location of the *wefb*.

1. Introduction

Fuel cells working at low temperatures with methanol or ethanol are of special interest because of their low production cost and easy availability. The anodic material of these fuel cells should have reasonable catalytic properties for the oxidation of the related alcohols. Platinum is one of the materials used for this purpose [1,2]. However, apart from the high price, its catalytic activity decreases dramatically over time. This is because of the adsorption of oxidation products such as CO, COH$^{\cdot}$, OH$^{\cdot}$ on the catalyst sites causing permanent blockage. The costs can be reduced by using Pt nano-crystallites deposited on less expensive materials (such as vitreous carbon) but still the poisoning of the catalyst is an issue [1]. Another way to overcome this problem is to modify Pt by adding other elements such as Sn, Bi or Pb, i.e. by synthesizing intermetallic phases (alloys). This has proved to be a solution to the problem as it prevents the fast poisoning of the catalyst [1,3–10]. Different mechanisms were suggested for the role of the added modifying element, namely (a) adsorption of the alcohol molecules on Pt and oxygen derivatives generated from the decomposition of water on the added element (for example Pb, Sn) [11–13], (b) "ligand effect" (electronic interaction of the added element with Pt which changes the adsorption energy of the adsorbate on Pt) [14], and (c) homogeneous catalytic reactions which was confirmed by the presence of complexed cations of the added element in the reaction media [12,15]. Hence, because of their expected specific catalytic activities and selectivities, intermetallic (nano)particles synthesized by different techniques [16–19] are gaining in importance. For example, Abruna and co-workers [20,21] have prepared Pt/Pb intermetallic phases by heating metals to ca. 1000 °C under vacuum in a sealed quartz tube and used them as catalyst for fuel cells. Moreover, they have prepared Pt/Pb and Pt/Bi nanoparticles using solvochemical reduction techniques [22–25]. In both cases the resulting alloys have shown improved performance as electrocatalysts for the oxidation of small organic molecules compared to the pure Pt catalyst.

A simple technique for the synthesis of metallic nanoparticles under very mild reaction conditions (e.g., at room temperature) is the use of water-in-oil (w/o) microemulsions. Using microemulsions instead of the above mentioned solvochemical reduction techniques allows us to synthesize nanoparticles of low polydispersity and tuneable size [26–28]. Microemulsions are thermodynamically stable mixtures of at least three components, namely,

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* Corresponding author.
E-mail address: najjar@tabrizu.ac.ir (R. Najjar).

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water, oil, and a surfactant with domain sizes of 5–50 nm [29]. The domains can be discrete (water or oil droplets) or bicontinuous [30]. As it is known how to tune the structure and size of the domains, microemulsions are becoming increasingly important as micro-reactors and/or templates. Although w/o-microemulsions have been widely used to synthesize monometallic nanoparticles, the synthesis of intermetallic nanoparticles via w/o microemulsions is still a challenge and has been successful only in the case of metals with similar reduction potentials (e.g., Pt/Ag [31], Pt/Au [32], Pt/Pd [33]). The synthesis of intermetallic nanoparticles of metals with largely different reduction potentials has not yet been achieved. The difficulties mainly arise from the need to "co-reduce" two metals with largely different redox potentials and from the low water stability of most reducing agents. As already mentioned Pt/Bi and Pt/Pb intermetallic compounds exhibit unique catalytic properties in fuel cell applications [20,24–27] compared to the catalytic activity of pure Pt. Thus introducing new routes towards the synthesis of intermetallic Pt/Bi and Pt/Pb nanoparticles ($[PtCl_6]^{2-}/[PtCl_4]^{2-} = +0.68$ V, $[PtCl_4]^{2-}/Pt = +0.76$ V,[1] $Bi^{3+}/Bi = +0.22$ V, and $Pb^{2+}/Pb = -0.13$ V) and testing their catalytic activity in fuel cells is of prime importance. Studying the phase behaviour of the microemulsions is a very important part of the work, which requires a careful determination of the water emulsification failure boundary (*wefb*) because it is at the *wefb* where discrete water droplets in a continuous oil phase are formed.

SANS, NMR self-diffusion, static and dynamic light scattering measurements performed along the oil emulsification failure boundary can be self-consistently interpreted in terms of spherical oil-swollen micelles, interacting through a hard sphere potential over a large concentration range. The presence of spherical micelles can be understood in terms of the flexible surface model where structure and stability are governed by the curvature and the elastic properties of the surfactant monolayer [30,35–39]. From extensive phase studies it is known that the oil and the water emulsification phase boundaries, respectively, play the same general role [30]—they are just located on different sides, namely the water- and the oil-rich side, of the phase diagram. Not surprisingly, SANS measurements at the water emulsification failure boundary can also be interpreted in terms of spherical water-swollen micelles interacting through a hard sphere potential [35,36,40]. A further proof of the spherical nature of water droplets at the *wefb* was obtained via transmission electron microscopy [41]. The diameter d of the spherical droplets at the *wefb* can be calculated according to [42]

$$d = 6\delta \frac{\phi_{\text{disp}}}{\phi_{\text{C},i} + \phi_{\text{D},i}} \approx 6\ \text{nm} \frac{w_\text{A} + \gamma}{\gamma}, \tag{1}$$

where $\delta \approx 1$ nm is the thickness of the amphiphilic interfacial film, ϕ_{disp} is the volume fraction of the dispersed phase, and $\phi_{\text{C},i}$ and $\phi_{\text{D},i}$ are the volume fractions of the surfactant and co-surfactant forming the interface.

The final aim of our work is to synthesize intermetallic Pt–Bi and/or Pt–Pb nanoparticles via w/o-microemulsions. For this purpose first of all one has to find a suitable microemulsion system as well as the experimental conditions under which w/o-microemulsions are formed. Secondly, the conditions for the co-reduction of two metal salts whose reduction potentials are quite different have to be specified. The starting point of our study was the model system H_2O/NaCl–n-decane–SDS–1-butanol. First, the water emulsification failure boundary (*wefb*) of this system was determined. Based on this phase diagram, we studied the influence of (a) different types and amounts of electrolytes, (b) the reducing agent, and (c) different metal precursors on the location of the *wefb* to preserve the desired w/o-microemulsion structure. To our knowledge these extensive phase studies are usually not carried out and we only could find one detailed study of this kind [43]. Generally two microemulsions with a fixed water/surfactant ratio are prepared without taking into account the influence the added metal salt or the reducing agent has on the size and the structure of the dispersed water droplets. In our previous study we indeed adjusted changes of the phase boundaries caused by adding the different salts. However, we did not determine the location of the complete *wefb* but rather the location of one point on the *wefb* [28]. With the present study we want to fill this gap. Detailed phase diagrams will be presented and the influence of the different salts on the *wefb* will be discussed. Knowing the location of the complete *wefb* will allow us to efficiently use these microemulsions as reaction media for the synthesis of nanoparticles in following studies.

2. Experimental

2.1. Materials

The following chemicals were all used as received without any further purification: sodium chloride, NaCl (Merck, 99.5%), sodium borhydride, $NaBH_4$ (Sigma-Aldrich, 98%), sodium dodecyl sulfate, SDS (Sigma-Aldrich, 99.0%), chloroplatinic acid hexahydrate, $H_2PtCl_6{\cdot}6H_2O$ (Sigma-Aldrich, ACS reagent), lead(II) nitrate, $Pb(NO_3)_2$ (Aldrich, 99.999%), n-decane (Aldrich, 99%), bismuth(III) nitrate pentahydrate, $Bi(NO_3)_3{\cdot}5H_2O$ (Sigma, 99.999%), sodium hydroxide, NaOH (BDH, 99.999%), nitric acid, HNO_3 (BDH, 69.5%), sodium nitrate, $NaNO_3$ (Fluka, 99.99%), 1-butanol (Romil, 99.9%). Fresh milli-Q water was taken from a Millipore unit.

2.2. Determination of phase diagrams

Phase diagrams were measured using glass water basins comprising of an immersion thermostat, a magnetic stirrer, a light source, and a thermometer. The temperature of the basin was monitored with ±0.01 °C precision (thermometer model 1521, Hart Scientific). A halogen lamp was used as light source (Gerhardt Optic, Germany). For the determination of the phase diagrams, aqueous solutions containing metal precursors and reducing agent, respectively, were prepared. Afterwards the desired amounts of these solutions, n-decane, and SDS (sodium dodecylsulfate) were weighted into test tubes, which were then sealed with stoppers. The test tubes were placed in the water basin at 21.0 °C and stirred for 5 min. While stirring 1-butanol was added and the resulting phase changes were monitored**.**

A, B, C, and D denote the aqueous phase (with or without electrolytes), oil, surfactant, and co-surfactant, respectively. The composition of the samples is given by the following definitions:

γ_b—mass fraction of surfactant in the oil phase,

$$\gamma_\text{b} = \frac{m_\text{C}}{m_\text{C} + m_\text{B}}; \tag{2}$$

w_A—total mass fraction of aqueous phase (with or without electrolytes),

$$w_\text{A} = \frac{m_\text{A}}{\sum_i m_i}; \tag{3}$$

ε—mass fraction of dissolved inorganic salt in the aqueous phase,

$$\varepsilon = \frac{m_{\text{salt}}}{m_{\text{salts}} + m_\text{A}}; \tag{4}$$

and w_D—total mass fraction of co-surfactant,

$$w_\text{D} = \frac{m_\text{D}}{\sum_i m_i}. \tag{5}$$

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[1] $H_2[PtCl_6]$ was found to be reduced from Pt^{4+} to Pt via Pt^{2+} [34].