Organic Reactions and Nanoparticle Preparation in CO₂-Induced Water/P104/*p*-Xylene Microemulsions

Rui Zhang, Jun Liu, Jun He, Buxing Han,* Weize Wu, Tao Jiang, Zhimin Liu, and Jimin Du[a]

Abstract: Nanometer-sized gold particles are synthesized by the reduction of $HAuCl_4$ with KBH_4 in the CO_2-induced microemulsion of $(EO)_{27}(PO)_{61}(EO)_{27}$ (P104; EO = ethylene oxide, PO = propylene oxide)/*p*-xylene/CO_2/H_2O. The recovery of gold particles from the microemulsion can be easily accomplished by the venting of CO_2, while the surfactant remains in the organic phase. The effect of the molar ratio of the reductant to $HAuCl_4$, the concentration of the reactants, and the molar ratio of water to EO segments (W_0) in the reverse micelles on the size of the gold particles is studied. The hydrolysis of benzoyl chloride (BzCl) and *p*-nitrophenyl chloroformate (NPhCl) has also been carried out in the microemulsion.

Keywords: carbon dioxide · gold · hydrolysis · microemulsions · nanoparticles

The results show that the observed rate constants k_{obs} of both substrates increase significantly with W_0, and that W_0 has a larger influence on the hydrolysis of BzCl. The different extents of the influence of W_0 on the two reactions can be ascribed to the different reaction mechanisms and the expected changes in nucleophilicity and polarity of water in the reverse micelles.

Introduction

Microemulsions are often good solvents for both hydrophilic and hydrophobic substances.[1–3] Therefore, they have been used as media for enhanced oil recovery,[4, 5] organic[6, 7] and enzymatic reactions,[8, 9] and as a mobile phase in chromatographic solutions.[10, 11] The surfactant-covered water pools in the water–oil microemulsions offer a unique microenvironment for the formation of nanoparticles.[12–18] Formation of nanoparticles in such systems is controlled by the reactant distribution in the droplets and by the dynamics of interdroplet exchange. The surfactant stabilized microcavities provide a cagelike effect that limits particle nucleation, growth, and agglomeration.[14, 19] As a result, the particles obtained are generally very fine.[20] When performing synthetic organic chemistry, one is often faced with the problem of reacting a hydrophobic compound with one that is hydrophilic, for example, water or a salt. One successful approach is to use microemulsions,[21–23] which are pseudohomogeneous mixtures of water insoluble organic compounds, water, and surfactant. In a microemulsion, high concentrations of both hydrophilic and hydrophobic reactants can be dissolved simultaneously. Also, the surface area between water and oil can reach a value as high as 10^5 m²L⁻¹ of microemulsion.[24] Solubilization of immiscible reactants, in the same region of a surfactant assembly, can lead to an increase in reaction rates, while the rates of reaction of segregated reactants are retarded. The nanoparticles usually show novel electronic, magnetic, optical, and chemical properties, that are significantly different from those of the bulk materials, because of their extremely small sizes and large specific surface areas.[25–28] Therefore, they have various potential applications in a diversity of areas, such as, electronic, mechanical devices, engineering materials, superconductors, magnetic recording media, catalysis, dyes, adhesives, drug delivery, and optical and photographic suspensions.[28–32] As a result, a lot of effort has been devoted to the preparation of nanoparticles, and to the study of their properties in recent years. Many methods used to prepare nanoparticles include, the sol—gel, [33] coprecipitation,[34] hydrothermal,[35] gas-evaporation,[36] and sputtering method.[37] Nanoparticle preparation in nanoreactors of microemulsions is one of the best methods.[12–18]

Compressed CO_2 is quite soluble in a number of organic solvents and causes large expansion of the solvent.[38, 39] With the CO_2-expanded solvent medium, it is possible to achieve optimum conditions for some processes. Sometimes the CO_2-expanded solvent may be better than either neat solvents or supercritical CO_2.[40] Compared to liquid solvent mixtures, the

[a] Prof. B. Han, Dr. R. Zhang, Dr. J. Liu, Dr. J. He, Dr. W. Wu, Dr. T. Jiang, Dr. Z. Liu, J. Du
Center for Molecular Sciences
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (P. R. China)
Fax: (+86)10-62559373
E-mail: hanbx@infoc3.icas.ac.cn

easy and complete separation of CO_2 from the liquid solvent after depressurizing is also an advantage.

Recently, we published a short communication to report a novel finding,[41] that compressed CO_2 could induce the formation of reverse micelles of block $(EO)_{27}(PO)_{61}(EO)_{27}$ (P104; EO = ethylene oxide, PO = propylene oxide) in *p*-xylene. The copolymer could not form reverse micelles in the solvent at 40 °C. By using compressed CO_2 to tune the solvent properties, the reverse micelles were formed. The CO_2-induced reverse micelles could solubilize polar and ionic chemicals like methyl orange and cobalt chloride. The unique advantage of these kind of reverse micelles is that the formation and breaking of them could be repeated easily by controlling the pressure. We are very interested in the applications of these kinds of microemulsions. In this work, we study the hydrolysis of benzoyl chloride (BzCl) (Scheme 1a), *p*-nitrophenyl chloroformate (NPhCl) (Scheme 1b), and explore the possibility to prepare Au nanoparticles in the CO_2-induced microemulsion. The results indicate that the microemulsion can be used to carry out the reactions and to prepare nanoparticles with potential advantages. These studies in turn give some information on the properties of the reverse micellar solution.
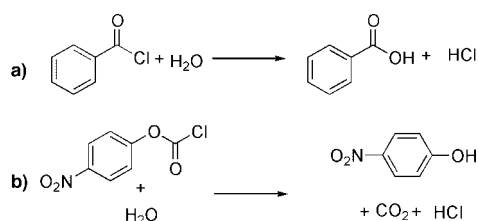
Scheme 1. Hydrolysis reaction.

Experimental Section

Materials: P104 was provided by BASF Corporation with a composition of $(EO)_{27}(PO)_{61}(EO)_{27}$. BzCl, *p*-xylene, hydrogen tetrachloroaurate ($HAuCl_4$), and potassium borohydride (KBH_4) were AR Grade, and were supplied by Beijing Chemical Reagent Factory. NPhCl, ≥ 97 % purity, was obtained from Aldrich and used as received. CO_2 (99.995 % purity) was supplied by Beijing Analytical Instrument Factory. Double distilled water was used throughout the experiments.

Apparatus and procedures to study the phase behavior: The apparatus for studying the phase behavior of $KBH_4/H_2O/P104/p$-xylene/CO_2 and $HAuCl_4/H_2O/P104/p$-xylene/CO_2 microemulsions was the same as that previously used to investigate the phase behavior of $P104/H_2O/p$-xylene/CO_2 system.[41] Briefly, it consisted of a high-pressure view cell with a volume of 40 cm³, a constant temperature water bath, a high-pressure syringe pump (DB-80), a pressure gauge, a magnetic stirrer, and a gas cylinder. The temperature of the water bath was controlled by HAA-KE D8 temperature controller, and the temperature fluctuation of the water bath was less than ± 0.03 °C. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, Model 93) and an indicator, which was accurate to ± 0.025 MPa in the range of 0 – 20 MPa. There were graduations on the high-pressure view cell so that the volume of the liquid-phase in the cell could be known easily. The experiment was based on the fact that the solution is clear and transparent if the water is all solubilized, otherwise, the solution is hazy or milky.[42–43] In a typical experiment, the air in the view cell was replaced by CO_2, P104 (5 g) in *p*-xylene (15 wt %), and the desired amount of aqueous KBH_4 or $HAuCl_4$ solution was loaded into the high-pressure view cell. The cell was placed into the constant temperature water bath. After thermal equilibrium had been reached,

the stirrer was started, the solution became hazy and milky, and CO_2 was charged into the cell slowly. With the addition of CO_2, the hazy and milky solution gradually became transparent. The pressure at which the solution became completely clear was recorded. Generally, one experiment required about two hours. W_0 was calculated easily on the basis of the masses of the polymer and water added.[41]

Apparatus and procedures used for the hydrolysis reaction: The apparatus used in the hydrolysis reaction was similar to that for determining the phase behavior described above. The difference being, the usage of a six-port valve, equipped with a sample loop, which was used to charge the hydrophobic reactants. In a typical reaction, the air in the high-pressure view cell was replaced by CO_2. P104 (5 g) in *p*-xylene (15 wt %) and a known amount of water were loaded into the reaction cell. The cell was then placed into the constant temperature (40.0 °C) water bath. After thermal equilibrium had been reached, the magnetic stirrer was started and CO_2 was compressed into the cell to the desired pressure. After the addition of CO_2, the hazy and milky solution became homogeneous and transparent; this indicated the formation of the microemulsion. The hydrophobic reactant (BzCl or NPhCl dissolved in *p*-xylene) was injected into the high-pressure view cell through the sample loop of the six-port valve and the reaction was then started. After stirring for 10 hours, the reaction mixture was subjected to column chromatography to remove the surfactant P104. The products were then analyzed by HPLC (DuPont instrument, model 8800).

Apparatus and procedures used to synthesize and recover Au nano-particles: The schematic diagram of the apparatus used for the synthesis of the Au nanoparticles in microemulsion is shown in Figure 1. The constant temperature water bath, high-pressure syringe pump (DB-80), pressure
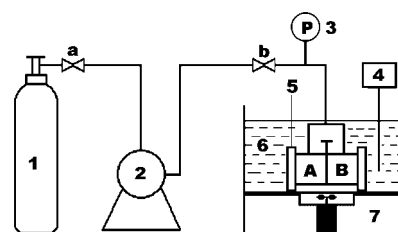

Figure 1. Schematic diagram of the apparatus for the reaction and phase behavior study. 1) gas cylinder, 2) high-pressure syringe pump, 3) pressure gauge, 4) temperature controller, 5) high-pressure cell, 6) water bath, 7) magnetic stirrer, a and b. valves.

gauge, and magnetic stirrer were the same as those used for the phase behavior study, but the high-pressure cell was different. The key function of the cell was that it could mix the two solutions under pressure if necessary. It consisted mainly of a stainless steel body, a stainless steel baffle with a teflon seal on the edge, and a handle. The baffle could divide the cell into two chambers (Chamber A and Chamber B shown in Figure 1). The solutions in the two chambers could be mixed by adjusting the position of the handle under pressure. In the experiment, the aqueous solutions of $HAuCl_4$ and KBH_4 of desired concentrations were freshly prepared separately. The cell was flushed with CO_2 to remove the air. Chamber A and Chamber B of the cell were charged with the solution of P104 in *p*-xylene. Desired amounts of $HAuCl_4$ and KBH_4 aqueous solutions were loaded into Chamber A and Chamber B, respectively. The cell was placed in a water bath at constant temperature. After thermal equilibrium had been reached, CO_2 was compressed into the cell to the desired pressure and the stirrers in the two chambers were started to accelerate the formation of microemulsions. The two micellar solutions, containing $HAuCl_4$ and KBH_4 were mixed by turning the baffle using the handle. Au nanoparticles were then synthesized by reducing $HAuCl_4$ with KBH_4 in the reverse micelles. After the reaction, CO_2 was slowly vented for about half an hour, and the Au nanoparticles were collected as a precipitate, as the reverse micelles began to break after releasing CO_2. The organic solution was decanted and the precipitated Au particles were collected and washed with water. The size and shape of the obtained Au particles were determined by TEM with a HITACHI H-600A electron microscope. The maximum resolution of the

microscope was 0.5 nm. Particles were sonicated for 1 minute in ethanol and then directly deposited on the copper grid before the measurement.

Apparatus and procedures for the UV study: UV-visible spectroscopy was used to monitor the synthesis of Au nanoparticles in the microemulsion. The UV-visible apparatus was similar to that reported previously.[44] It consisted of a gas cylinder, a high-pressure pump, a pressure gauge, a UV-visible spectrometer, a temperature-controlled high-pressure UV sample cell, valves, and fittings. The UV-visible spectrophotometer was produced by Beijing General Instrument Company (model TU-1201, resolution: 0.1 nm). The sample cell was composed mainly of a stainless steel body, two quartz windows, a stirrer, and a temperature controlling system. The optical path length and the inner volume of the sample cell were 1.32 cm and 1.74 cm³, respectively.

In the experiment, a UV sample cell was connected to the two-chamber cell (see Figure 1, the connecting tube and the valve are not shown in the Figure). The air in the UV sample cell was removed by a vacuum pump. The temperature of the cell was maintained at 40 °C. The microemulsion with Au nanoparticles was then synthesized and transferred into the UV sample cell at constant temperature and pressure. The UV spectrum of the solution was then recorded every ten minutes until it was unchanged.

Results and discussion

The phase behavior of a system with and without HAuCl₄ and KBH₄: Au nanoparticles can be synthesized in the water core of microemulsions by the reduction of $HAuCl_4$ with KBH_4.[45] We have studied the phase behavior of P104/p-xylene/CO_2/H_2O microemulsion (Figure 1).[41] The results indicate that at 40 °C and at an ambient pressure of CO_2, the P104/p-xylene/CO_2 cannot solubilize water. As the pressure of CO_2 increases to a certain value, the water solubilization capability of P104/p-xylene/CO_2 solution increases abruptly. This indicates the formation of reverse micelles.

The addition of inorganic salts may affect the phase behavior of the microemulsion.[7] Therefore, in this work we first investigate the phase behavior in the presence of $HAuCl_4$ and KBH_4; results of which are illustrated in Figure 2. At a
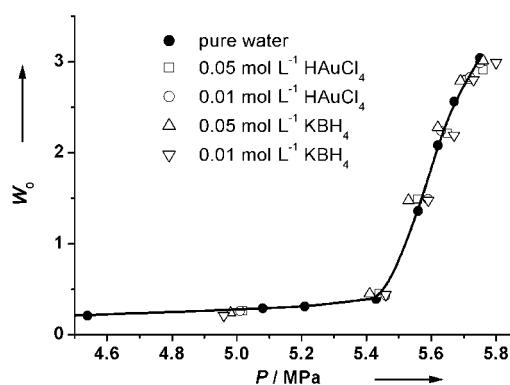
Figure 2. The effect of the salt concentration and pressure of CO_2 on the maximum W_0 for the solution of P104 in p-xylene (15 wt%) at 40.0 °C.

given temperature and pressure, p-xylene/CO_2 mixed solvent can dissolve small amounts of water, which have been subtracted from the total amount of water when calculating W_0 (molar ratio of water to EO segments).[41] Figure 2 shows that $HAuCl_4$ and KBH_4 have no considerable effect on the phase behavior in the salt concentration range in which we are interested. This maybe ascribed to the fact that the surfactant

is nonionic, and the microemulsion is not sensitive to the ionic strength. Figure 2 also shows that the reverse micelles can be formed as the pressure of CO_2 reaches over 5.5 MPa, because W_0 increases sharply with increasing pressure. The data in Figure 2 allow us to select suitable conditions to prepare Au nanoparticles. In all the following sections, the results are obtained at 40.0 °C, and the concentration of the polymer in the solution is 15 wt% (based on p-xylene).

Synthesis and recovery of Au nanoparticles

UV-visible spectroscopy of the Au nanoparticles: Colloidal dispersions of Au exhibit absorption bands in the UV-visible range, that are due to the resonant excitation of surface plasmons. Therefore, the Au nanoparticles, stabilized in the reverse micelles, can be analyzed in situ by their UV-visible spectra.[45–47] It is well known that the plasmon absorption peak at 525 nm is characteristic of Au particles larger than ∼3 nm. This peak is red-shifted and is substantially broadened upon particle aggregation.[45] In this work, the spectrum of a ruby-colored solution of Au nanoparticles in the P104/p-xylene/CO_2 microemulsion system shows an absorption peak at 525 nm (Figure 3).
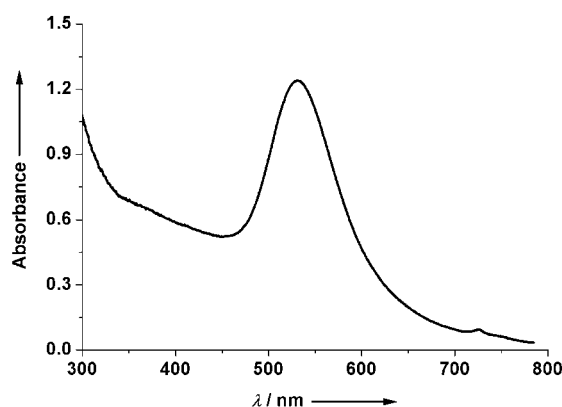
Figure 3. The UV-visible spectrum of Au nanoparticles in P104/p-xylene/CO_2/H_2O microemulsion. $P = 5.75$ MPa, $W_0 = 2.9$, [KBH_4] = [$HAuCl_4$] = 0.05 mol L⁻¹.

The recovery of nanoparticles: The conventional techniques to recover nanoparticles from the reverse micelles, such as superrate centrifugation and filtration, are generally to precipitate nanoparticles together with the surfactants. It is difficult to remove the surfactant completely as the obtained particles are always embedded in the surfactant.[48] Without a doubt, the best way to recover the nanoparticles from the reverse micelles is by precipitation of the particles, while the surfactants remain in the solvent. In this work, the reverse micelle formation is induced by compressed CO_2. The breaking of the reverse micelles can be accomplished simply by the venting of CO_2. Therefore, solubilized Au nanoparticles in reverse micelles can be precipitated after releasing the CO_2. Our experiment shows that the upper organic phase has no UV absorbance band for Au after CO_2 is released; this indicates the precipitation of the Au particles. The reversibility of the reverse micelle system is a unique feature and it is

advantageous for the recovery of the nanoparticles synthesized in the reverse micelles.

The effect of operating conditions on particle size and distribution: The particle size and distribution data are obtained by measuring the diameter of the particles in the transmission electron microscopy (TEM) photographs. The operating conditions such as W_0, the molar ratio of reductant to HAuCl$_4$, have large influences on the nucleation and growth of the nanoparticles, and consequently on the size and shape of the particles.[49–50] To study the effect of operating conditions on the particle size and distribution, the synthesis of Au nanoparticles was carried out by changing the following experimental conditions: W_0 of the microemulsion, molar ratio of KBH$_4$ to HAuCl$_4$, and the concentration of both reactants. Figure 4 illustrates the TEM photographs of Au
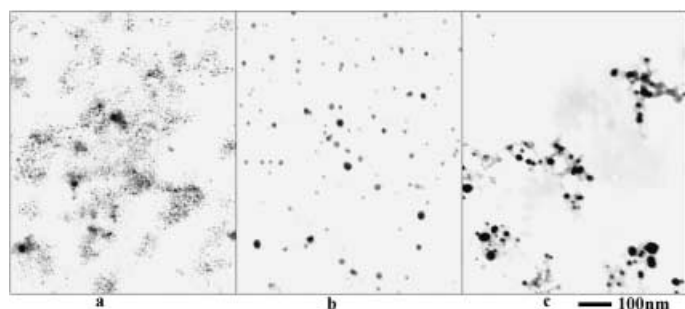

Figure 4. TEM photographs of Au particles synthesized in P104/*p*-xylene/CO$_2$/H$_2$O microemulsion with different W_0. a) $W_0 = 0.9$; b) $W_0 = 1.5$; c) $W_0 = 2.5$. The concentration of KBH$_4$ and HAuCl$_4$ are both 0.05 mol L^{-1} in aqueous solution.

nanoparticles synthesized in the microemulsion of P104/*p*-xylene/CO$_2$/H$_2$O with different W_0. The diameter of the Au particle increases with increasing W_0. As the W_0 increases from 0.9–2.5, Au particle size increases from 6–30 nm. This may be ascribed mainly to the fact that the average number of reactant ions per droplet increases with increasing W_0.[50] Also, the number of nuclei decreases with increasing W_0, because the rearrangement rate of the microemulsion decreases with the amount of water; [17] hence, less nuclei result in larger particles.

The synthesis of Au particles has been performed at various molar ratios of KBH$_4$ to HAuCl$_4$ (R). The concentration of HAuCl$_4$ was fixed at 0.05 mol L^{-1} and R was changed from 0.2–2.5 (Figure 5a, $R = 0.2$, Figure 4b, $R = 1$, Figure 5b, $R = 2.5$). With increasing R, the particle size decreases from 23–5 nm. This is mainly due to the fact that increasing the amount of reducing agent per droplet will accelerate the nucleation process.[49–51] Therefore, smaller particles are formed in the microemulsion with a larger R value. Figure 5b also shows that the particles have a bimodal size distribution. The larger particles have a diameter of about 14 nm. The bimodal distribution of particle diameter also appears in other microemulsion systems.[17] The presence of bigger particles shows particle aggregation.

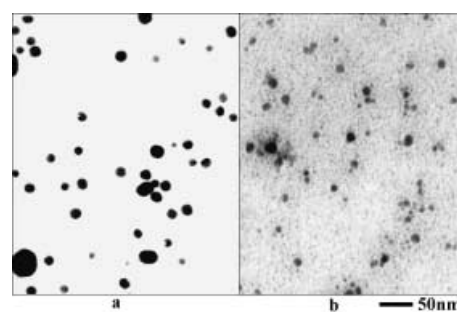The particle size decreases with the concentration of the reactants, while W_0 and R are kept constant. When the

Figure 5. Effect of the molar ratio of KBH$_4$ to HAuCl$_4$ on the size of Au nanoparticles. W_0 is 1.5. The concentration of HAuCl$_4$ is 0.05 mol L^{-1} in aqueous solution. The concentration of KBH$_4$ is: a) 0.01 mol L^{-1} and b) 0.125 mol L^{-1} in aqueous solution.

concentration of the reactants increased from 0.05–0.12 mol L^{-1}, the particle size decreased from 20–6.5 nm (Figure 4b, Figure 6). Figure 6 also shows a distinct bimodal size distribution. The larger particles have a diameter of about 17 nm. The smaller particles, at a higher concentration of HAuCl$_4$, can be attributed to more nuclei forming at the very beginning of the reduction. To form a stable nucleus a minimum number of atoms are required.[18, 52–53] For nucleation, several atoms must collide at the same time.[17] N_n (Number of nuclei formed) is expected to increase with the reactant concentration so that at larger concentrations of HAuCl$_4$, N_n will be larger; therefore smaller particles are formed.
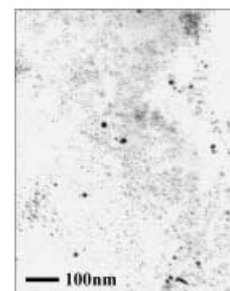
Hydrolysis reactions: The hydrolysis of BzCl and NPhCl (Scheme 1) is performed in the P104/H$_2$O/*p*-xylene/CO$_2$ microemulsions. Both of these substrates are water-insoluble

Figure 6. TEM photographs of Au particles synthesized in P104/*p*-xylene/CO$_2$/H$_2$O microemulsion with higher concentration of reactant. W_0 is 1.5. The concentration of HAuCl$_4$ and KBH$_4$ is 0.12 mol l^{-1} in aqueous solution.

and known to be sensitive to the physical properties of the reaction medium.[22] The water is in large excess relative to the substrate; hence, the hydrolysis can be treated with pseudo-first-order kinetics. The observed pseudo-first-order rate constants $k_{obs} = k[H_2O]$, determined for the hydrolysis reactions at different W_0 values, are listed in Tables 1 and 2, and Figure 7 illustrates the dependence of k_{obs} on W_0. The data in Tables 1 and 2, and Figure 7 indicate that k_{obs} increases with the increase of W_0 for both substrates. For example, the k_{obs} at

Table 1. Hydrolysis of benzoyl chloride (BzCl) in P104/*p*-xylene/CO$_2$/H$_2$O microemulsions.[a]

Entry	W_0	Mol H$_2$O/Mol^{-1} BzCl	$k_{obs} \times 10^5$ [s^{-1}]
1	1.03	9.9	1.12
2	1.62	15.5	2.16
3	2.25	21.5	6.06
4	3.08	29.5	10.6

[a] The concentration of BzCl is 0.096 mol L^{-1} based on the volume of the CO$_2$ expanded solution.

Table 2. Hydrolysis of *p*-nitrophenyl chloroformate (NPhCl) in P104/*p*-xylene/CO$_2$/H$_2$O microemulsions.[a]

Entry	W_0	Mol H$_2$O/Mol^{-1} NPhCl	$k_{obs} \times 10^5$ [s^{-1}]
1	0.61	10.1	2.61
2	1.01	16.7	3.26
3	1.66	27.6	4.21
4	2.21	36.7	5.32
5	3.02	50.1	6.98

[a] The concentration of NPhCl is 0.055 mol L^{-1} based on the volume of the CO$_2$-expanded solution.
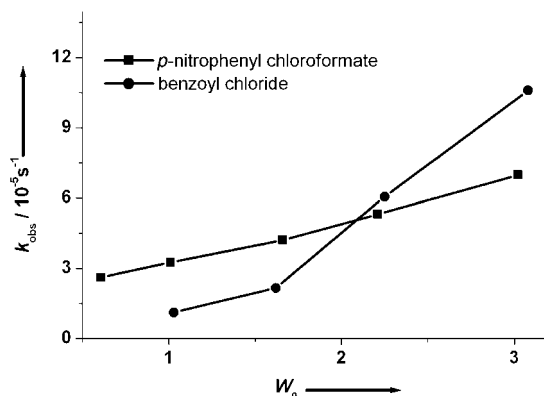
Figure 7. The dependence of k_{obs} on W_0.

$W_0 = 3.08$ is almost ten times faster than that at $W_0 = 1.03$ for the hydrolysis of BzCl. It can also be seen from Figure 7 that the effect of W_0 on the rate constant of NPhCl is smaller than that of BzCl. The k_{obs} of NPhCl hydrolysis is larger than that of BzCl at $W_0 < 2.2$, and becomes smaller at $W_0 > 2.2$. This is consistent with earlier published results by other authors,[21] who conducted the reactions in other microemulsions. This can be explained by the difference in mechanism of the two substrates. Both substrates are poorly soluble in water; therefore, they preferentially solubilize in the hydrophobic phase (*p*-xylene/CO$_2$) and interphase of the microemulsions.[21–22, 54] As a result, the reactions only occur in the interphase where the substrates and water can meet. The structure of the interfacial water in reverse micelles changes with the increase of W_0.[55] In the case of a surfactant, such as P104, added water initially hydrates the EO segments. Further addition of water is incorporated into the micellar cores and causes the reverse micelles to swell. Water in the periphery is more structured and has different physical properties, such as lower polarity, as compared to the bulk water. Only in large water droplets do the physical properties resemble those of bulk water.[56] The polarity of water in the micelles increases with W_0. On the other hand, an increase in the droplet size (W_0) leads to a decrease in interaction between water molecules and hydrophilic EO segments in the polymer surfactant,[57] thereby reducing the nucleophilicity of the interfacial water. As the hydrolysis of the substrates is sensitive to the polarity and nucleophilicity of the water, the variation of W_0 will affect the kinetics of the hydrolysis. The acyl transfer reactions are commonly classified into three groups:[54, 58]a) dissociative mechanism (S$_N$1), with an acylium ion intermediate (Scheme 2a); b) concerted displacement, which can have an
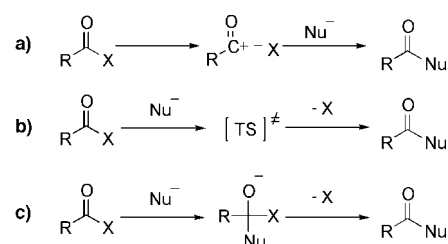
Scheme 2. Mechanism of hydrolysis reaction.

associative or dissociative character (Scheme 2b), and c) associative (S$_N$2) or addition–elimination, with a tetrahedral addition intermediate (Scheme 2c). The dissociative pathway will be favored by a polar solvent and a conjugative electron release effect that will stabilize the carbocationic intermediate. The associative pathway is more sensitive to the nucleophilicity of the nucleophilic agent and is favored by an electron attractive substitute. The hydrolysis of BzCl takes place predominately through a dissociative (S$_N$1) path at larger W_0, and the reaction takes place fundamentally through an associative (S$_N$2) pathway at small W_0 in the sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane/water microemulsion.[54] Due to conjugative electron release by the aryl group which assists the C–Cl bond breaking, in the transition state of BzCl hydrolysis, the C–Cl bond breaking progresses further relative to that found in the hydrolysis of NPhCl.[21, 22] In other words, the hydrolysis of BzCl proceeds by a mechanism more like S$_N$1, which involves the formation of acylium$^+$ and Cl$^-$ ions.[22, 23]Therefore, the k_{obs} of BzCl hydrolysis increases with increasing W_0 as a result of the increased polarity of the water. Furthermore, the k_{obs} increases slowly when the W_0 is very small, and in this case the reaction may take place through an associative pathway in which decreased nucleophilicity is unfavorable to the reaction. In the case of NPhCl, the hydrolysis takes place through a S$_N$2 path, owing to the inductive electron attraction effect of *p*-nitrophenoxy group. The nucleophilic attack is the rate-determining step, and the reaction is sensitive to the nucleophilicity of water. As the W_0 increases, the nucleophilicity of the interfacial water decreases; this is unfavorable for hydrolysis, even though the increase of water polarity is favorable. Therefore, there are two opposite factors that affect the reaction rate with increasing W_0. As a result, the rate constant is less sensitive to W_0.

Conclusion

In conclusion, the CO$_2$-induced microemulsion (P104/*p*-xylene/CO$_2$/H$_2$O can be used to carry out the hydrolysis reactions of BzCl and NPhCl, and to prepare Au nanoparticles by the reduction of HAuCl$_4$ with KBH$_4$ in the reverse micelles. The observed rate constants k_{obs} of both hydrolysis reactions increase with W_0, and W_0 has a larger influence on the hydrolysis of BzCl. The Au nanoparticles can be precipitated and recovered after the venting of CO$_2$, while the copolymer remains in the organic phase.

Acknowledgement

[1] R. Schomäcker, *Prog. Colloid Polym. Sci.* **1990**, *81*, 131.

[2] J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, **1982**.

[3] J. K. Thomas, *Chem. Rev.* **1980**, *80*, 283.

[4] D. Langevin in *Reverse Micelles* (Eds.: P. L. Luisi, B. E. Straub), Plenum, New York, **1984**, pp. 287–303.

[5] K. A. Bartscherer, M. Minier, H. Renon, *Fluid Phase Equilib.* **1995**, *107*, 93.

[6] C. A. Bunton, L. S. Romsted in *Handbook of Microoemulsion Science and Technology* (Eds.: P. Kumar, K. L. Mittal), Marcel Dekker, New York, **1999**, pp. 457–482.

[7] F. Candau in *Handbook of Microoemulsion Science and Technology* (Eds.: P. Kumar, K. L. Mittal), Marcel Dekker, New York, **1999**, pp. 679–712.

[8] Y. L. Khmelnitsky, I. N. Neverova, V. I. Polyakov, V. Y. Grinberg, A. V. Levashov, K. Martinek, *Eur. J. Biochem.* **1990**, *190*, 155–159.

[9] K. Holmberg in *Handbook of Microoemulsion Science and Technology* (Eds.: P. Kumar, K. L. Mittal), Marcel Dekker, New York, **1999**, pp. 713–742.

[10] M. A. Hernandez-Torres, J. S. Landy, J. G. Dorsey, *Anal. Chem.* **1986**, *58*, 744.

[11] R. W. Gale, R. D. Smith, J. L. Fulton, *Anal. Chem.* **1987**, *59*, 1977.

[12] M. P. Pileni, *J. Phys. Chem.* **1993**, *97*, 6961.

[13] V. Pillai, P. Kumar, M. J. Hou, P. Ayyub, D. O. Shah, *Adv. Colloid Interface Sci.* **1995**, *55*, 241.

[14] V. Pillai, D. O. Shah in *Industrial Applications of Microemulsions* (Eds.: C. Solans, H. Kunieda), Marcel Dekker, New York, **1997**, pp. 227.

[15] M. A. López-Quintela, J. Quibén-Solla, J. Rivas in *Industrial Applications of Microemulsions* (Eds.: C. Solans, H. Kunieda), Marcel Dekker, New York, **1997**.

[16] L. Jeunieau, F. Debuigne, J. B. Nagy in *Reactions and Synthesis in Surfactant Systems* (Ed.: J. Texter), Marcel Dekker, New York, **2001**.

[17] J. B. Nagy in *Handbook of Microoemulsion Science and Technology* (Eds.: P. Kumar, K. L. Mittal), Marcel Dekker, New York, **1999**, pp. 499–548.

[18] K. Osseo-Asare in *Handbook of Microoemulsion Science and Technology* (Eds.: P. Kumar, K. L. Mittal), Marcel Dekker, New York, **1999**, pp. 549–604.

[19] C. C.Wang, D. H. Chen, T. C. Huang, *Colloids Surf. A.* **2001**, *189*, 145.

[20] M. P. Pileni, *Structure and Reactivity in Reverse Micelles*, Elsevier, Amsterdam, **1989**.

[21] G. B. Jacobson, C. T. Lee, K. P. Johnston, *J. Org. Chem.* **1999**, *64*, 1201.

[22] L. García-Río, J. R. Leis, E. Iglesias, *J. Phys. Chem.* **1995**, *99*, 12318.

[23] H. Al-Lohedan, C. A. Bunton, M. M. Mhala, *J. Am. Chem. Soc.* **1982**, *104*, 6654.

[24] M. J. Schwuger, K. Stickdorn, R. Schomäcker, *Chem. Rev.* **1995**, *95*, 849–864.

[25] G. A. Ozin, *Science* **1996**, *271*, 920.

[26] G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612.

[27] R. W. Cahn, *Nature* **1992**, *359*, 591.

[28] A. Henglein, *Chem. Rev.* **1989**, *89*, 1861.

[29] V. L. Colvin, M. C. Schlamp, A. P. Alivisatos, *Nature* **1994**, *370*, 354.

[30] B. C. Gates, *Chem. Rev.* **1995**, *95*, 511.

[31] L. L. Beecroft, C. K. Ober, *Chem. Mater.* **1997**, *9*, 1302.

[32] A. F. Lee, C. J. Baddeley, C. Hardacre, R. M. Ormerod, R. M. Lambert, G. Schmid, H. West, *J. Phys. Chem.* **1995**, *99*, 6096.

[33] B. Fegley, Jr., P.White, H. K. Bowen, *Am. Ceram. Soc. Bull.* **1985**, *64*, 1115.

[34] Z. X. Tang, C. M. Sorensen, K. J. Klabunde, G. C. Hadjipanayis, *J. Colloid Interface. Sci.* **1991**, *146*, 38.

[35] S. Komarneni, R. Roy, E. Breval, M. Ollinen, Y. Suwa, *Adv. Ceram. Mater.* **1986**, *1*, 87.

[36] R. W. Siegel, S. Ramasamy, H. Hahn, Z. Q. Li, T. Lu, R. Gronsky, *J. Mater. Res.* **1988**, *3*, 1367.

[37] P. Fayet, L. Z. Woste, *Phys. D* **1986**, *3*, 177.

[38] M. A. McHugh, V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed., Butterworth-Heinemann, Boston, **1994**.

[39] C. A. Eckert, L. K. Barbara, P. G. Debenedetti, *Nature* **1996**, *383*, 313.

[40] G. Musie, M. Wei, B. Subramaniam, D. H. Busch, *Coord. Chem. Rev.* **2001**, *219–221*, 789.

[41] R. Zhang, J. Liu, J. He, B. X. Han, X. G. Zhang, Z. M. Liu, T. Jiang, G. H. Hu, *Macromolecules*, **2002**, *35*, 7869.

[42] P. Alexandridis, K. Andersson, *J. Phys. Chem. B* **1997**, *101*, 8103.

[43] P. Alexandridis, K. Andersson, *J. Colloid Interface Sci.* **1997**, *194*, 166.

[44] J. Lu, B. X. Han, H. K. Yan, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3269.

[45] M. Brust, D. Bethell, C. J. Kiely, D. J. Schiffrin, *Langmuir* **1998**, *14*, 5425.

[46] Y. Mizukoshi, K. Okitsu, Y. Maeda, T. A. Yamamoto, R. Oshima, Y. Nagata, *J. Phys. Chem. B* **1997**, *101*, 7033.

[47] T. Fujimoto, Y. Mizukoshi, Y. Nagate, Y. Maeda, R. Oshima, *Scr. Mater.* **2001**, *44*, 2183.

[48] M. L. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglas, L. E. Brus, *J. Am. Chem. Soc.* **1988**, *110*, 3046.

[49] C. L. Chiang, *J. Colloid Interface Sci.* **2001**, *239*, 334.

[50] C. L. Chiang, *J. Colloid Interface Sci.* **2000**, *230*, 60.

[51] J. L. Zhang, B. X. Han, J. C. Liu, X. G. Zhang, J. He, Z. M. Liu, T. Jiang, G. Y. Yang, *Chem. Eur. J.* **2002**, 8, 3879.

[52] P. C. Hiemenz, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1977, p. 234.

[53] J. A. Dirksen, T. A. Ring, *Chem. Eng. Sci.* **1991**, *46*, 2389.

[54] L. García-Rio, J. R. Leis, J. A. Moreira, *J. Am. Chem. Soc.* **2000**, *122*, 10325.

[55] S. L. Regen, *J. Org. Chem.* **1977**, *42*, 875.

[56] P. Mukerjee in *Solution Chemistry of Surfactants, Vol 1* (Ed.:K. L. Mittal), Plenum, New York, **1979**, pp. 153.

[57] C. Guo, H. Z. Liu, J. Y. Chen, *Colloids Surf. A* **2000**, *175*, 193.

[58] B. D. Song, W. P. Jencks, *J. Am. Chem. Soc.* **1989**, *111*, 8470.