



# PROPERTIES OF WATER/*N*-PROPANOL/IONIC SURFACTANT/PHENYLACETYLENE MICELLAR SYSTEMS

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Water/*n*-propanol/ionic surfactant /phenylacetylene micellar systems were formulated. The surfactants were the anionic, sodium dodecyl sulfate and the cationic cetyltrimethylammonium bromide. The ratio (w/w) of *n*-propanol/surfactant equals 2/1. The extent of the micellar region as function of temperature was determined. The particle hydrodynamic diameter of the oil-in-water micellar systems measured using dynamic light scattering and was found to decrease with temperature. In the diluted region, nanoemulsions systems were observed. Hydration of alkynes found to be highly influenced from the ionic nature of the surfactant. Cationic surfactants accelerate the addition of water to alkynes while anionic surfactants decrease the reaction rate.

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hydroformylation and carbon-carbon coupling of hydrophobic substrates in aqueous microemulsions.<sup>12-16</sup> In this study we continue our works to formulate new nanoemulsions composed of water/*n*-propanol/ionic surfactant/phenylacetylene to be used as a reaction media for the hydration of phenylacetylene. The surfactants used were the anionic sodium dodecyl sulfate (SDS) and the cationic cetyltrimethylammonium bromide (CTAB). The objective is to study the effect of the surfactants head group on the phenylacetylene hydration in oil-in-water nanoemulsions

## Introduction

Catalytic hydration of alkynes was widely investigated and reported.<sup>1</sup> Liquid-phase semi hydrogenation of phenylacetylene under mild conditions was done in the presence of organophilic Pd-montmorillonite catalysts synthesized in a micellar system based on the cationic surfactant cetyltrimethylammonium bromide.<sup>2</sup> Palladium nanoparticles incorporated in a hydrotalcite proved to be efficient catalysts for the liquid-phase semi hydrogenations phenylacetylene.<sup>3</sup> Palladium nanoparticles also proved to be active and selective catalysts for the liquid-phase semi hydrogenations of phenylacetylene, 3-butyne-1-ol, 4-octyne and 1-phenyl-1-butyne.<sup>4,5</sup> Phase transfer catalyzed reaction of phenylacetylene occurring under mild conditions with carbon monoxide, aqueous base, toluene as the organic phase, and catalytic amounts of nickel cyanide as the metal catalyst and cetyltrimethylammonium bromide as the surfactant affords unsaturated acids in reasonable yields.<sup>6</sup> Brønsted acidic ionic liquids have been successfully developed as task specific ionic liquids for hydration of alkynes (e.g. phenylacetylene) under mild conditions to give high yields of ketones as a selective product.<sup>7</sup> Gold nanoparticles exhibit high activity and stability in the hydrogenation of phenylacetylene into styrene in the phenylacetylene-styrene mixture.<sup>8,9</sup> A new simple protocol for the hydration of alkynes that is expected to reduce the hazards associated with industrially important processes was recently reported.<sup>10</sup> A possible mechanism of hydration of phenylacetylene in near-critical water was proposed.<sup>11</sup> A three-phase emulsion-solid state-transport method (EST) system can be applied successfully for catalytic hydrogenation, cyclotrimerization, decarbonylation,

## Experimental

### Materials

Phenylacetylene (PAC), cetyltrimethylammonium bromide (CTAB) and *n*-propanol were purchased from Sigma-Aldrich Chemical Company. Sodium dodecyl sulfate (SDS) was purchased from Ridel de Haën. All the components were used as supplied without further purification. Triply distilled water was used for all experiments.

### Methods

#### Phase behavior at constant temperature

A four-component system behavior is described in pseudo ternary phase diagrams in which the weight ratio of surfactant/cosurfactant is fixed. The determination of the phase behavior was performed in a thermostated bath ( $T \pm 0.1$  K). Ten weighted samples composed of mixtures of (surfactant + cosurfactant) and oil were prepared in culture tubes sealed with Viton -lined screw caps at predetermined weight ratios of oil/ surfactant/cosurfactant. The mixtures were titrated with water and were equilibrated during a time interval of up to 24 h. The different phases were determined visually and optically using crossed polarizer's method. Appearance of turbidity was considered as an indication for phase separation. The phase behavior was determined only after sharp interfaces had become visible. The completion of

this process was hastened by centrifuging the samples. Every sample that remained transparent and homogeneous after vigorous vortexing was considered as belonging to the one phase region.<sup>17-19</sup>

### Particle size determination

Particle size measurements were performed using Zetasizer Nano S (ZEN 1600, Malvern Instruments Ltd., Worcestershire, United Kingdom) for the measurements of size of dispersed particles in solution. The equipment includes a 4 mW, 633 nm He-Ne laser. Size measurement range between 0.6nm to 6 nm, size measurement angle equals 173°, concentration range for size measurement was between 0.1ppm (0.00001 vol%) – 40 wt% and temperature measurement range between 275 K to 363 K. 1.5 ml micellar samples was introduced in a disposable polystyrene cuvettes and measured at temperatures range between 298 and 323 K by steps of 5 K. The particle hydrodynamic diameter is calculated from the translational diffusion coefficient ( $d_H$ ) using the Stokes-Einstein relationship:

$$d_H = \frac{k_B T}{6\pi\eta D} \quad (1)$$

where

$d_H$  is the hydrodynamic diameter,  
 $k_B$  is Boltzmann's constant,  
 $T$  is the absolute temperature and  
 $\eta$  is the solvent viscosity.

The results are averages of three experiments.

### Emulsification of the substrates

Typically, a mixture of triply distilled water (TDW, 89.3 wt.%), and a suitable surfactant (3.3 wt.%) was stirred at room temperature. Then, the substrate (0.8 wt.%) was added drop wise under vigorous stirring. The emulsion, so formed, was titrated with *n*-propanol until a clear transparent mixture was obtained (usually 6.6 wt.%). A calculated amount of the desired acid was added to the microemulsion in order to obtain a 0.33 M microemulsion.

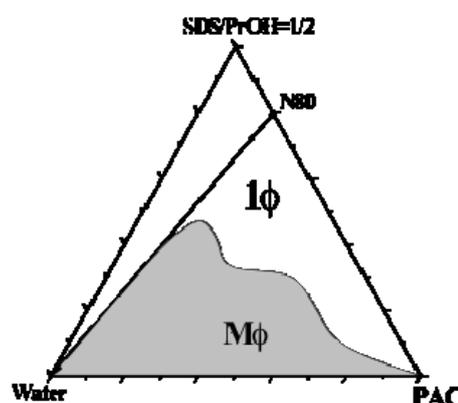
### General procedure for the hydration of alkynes

The above microemulsion of the substrate was placed in either an autoclave or in a pressure vessel and heated with stirring to the desired temperature for the required length of time. The reaction vessel was cooled to room temperature and the microemulsion was treated with NaCl (2 g), which caused phase separation. The aqueous phase was extracted with Et<sub>2</sub>O (2×15 mL) and the combined organic phases were neutralized with aqueous NaHCO<sub>3</sub>, dried (MgSO<sub>4</sub>), concentrated and chromatographed on silica gel. The products were then analyzed by <sup>1</sup>H NMR, MS, and GC in the usual manner and compared with authentic samples.

## Results and Discussion

### Phase behavior

Figures 1 and 2 present the phase behaviors of water/sodium dodecylsulfate/*n*-propanol/ phenylacetylene and water / cetyltrimethylammonium bromide / *n*-propanol/ phenylacetylene systems at 298 K, respectively. The ratio (w/w) of *n*-propanol/ surfactant equals 2/1. As shown in the Figures, the one phase micellar system appears from the first addition of water and continues to appear until 40 wt.% water in the case of sodium dodecyl sulfate based system. In the case of cetyltrimethylammonium bromide based system, the one phase continues until 25 wt.% water for high surfactant+cosurfactant contents (above 50 wt%), while for low surfactant+cosurfactant contents (below 50 wt%) the one phase continues until 10 wt.% water.



**Figure 1.** Pseudo ternary phase diagram of the water/*n*-propanol/ sodium dodecyl sulfate /phenylacetylene system at 298 K. The mixing ratio (w/w) of *n*-propanol/surfactant equals 2/1. The one phase region is designated by 1 $\phi$ , and the multiple phase regions are designated by (M $\phi$ ). N80 is the dilution line where the weight ratio of (surfactant + propanol)/ phenylacetylene equals 4/1.

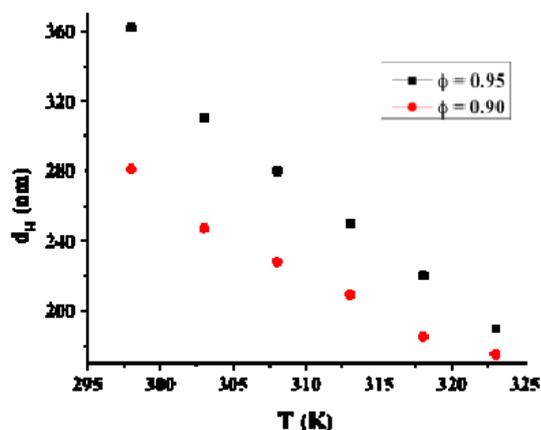


**Figure 2.** Pseudo ternary phase diagram of the water/*n*-propanol/ cetyltrimethylammonium bromide /phenylacetylene system at 298 K. The mixing ratio (w/w) of *n*-propanol/surfactant equals 2/1. The one phase region is designated by 1 $\phi$ , and the multiple phase regions are designated by (M $\phi$ ). N80 is the dilution line where the weight ratio of (surfactant + propanol)/ phenylacetylene equals 4/1.

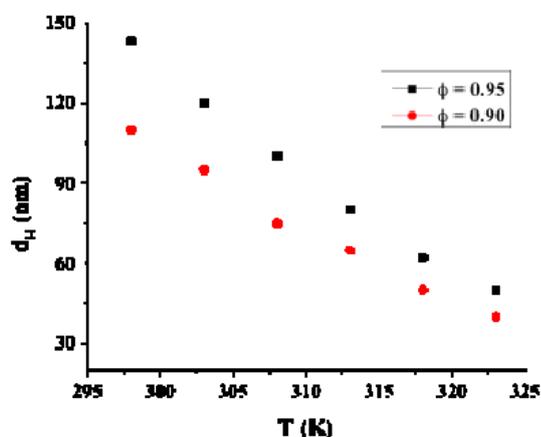
Similar findings on the behavior of sodium dodecyl sulfate in the presence of other aromatic oils were reported.<sup>18,19</sup> The area of the one phase region,  $A_T$  (%), varies slightly with temperature. Similar behavior of the dependence of the phase behavior on temperature of ionic surfactants was reported elsewhere.<sup>18,19</sup>

### Diffusion properties

We estimated the hydrodynamic diameter ( $d_H$ ) of the micellar system in the water-rich region at water volume fraction equals 0.90 and above using equation 1. The variation in the values of the hydrodynamic diameter ( $d_H$ ) at water volume fractions of 0.90 and 0.95 for the studied system as function of temperature is shown in Figures 3 and 4. As shown in Figures, the hydrodynamic diameter decreases with temperature. The values of the hydrodynamic diameter indicate that the micellar systems formed are nanoemulsions. These systems will be used as alternative reaction media for the hydration of phenylacetylene.



**Figure 3.** Variation of the particle hydrodynamic diameter as function of temperature for water/n-propanol/ sodium dodecyl sulfate / phenylacetylene oil-in-water nanoemulsions along N80 dilution line.



**Figure 4.** Variation of the particle hydrodynamic diameter as function of temperature for water/n-propanol/ cetyltrimethylammonium bromide/phenylacetylene oil-in-water nanoemulsions along N80 dilution line.

### Hydration of phenylacetylene

Highly efficient hydration of alkynes has been performed in water upon addition of a suitable surfactant that solubilizes the substrate. From previous studies, it had been showed that hydration of alkynes depends on the ionic nature of the surfactants.<sup>10</sup> In this report we introduced two different types of surfactants, anionic and cationic surfactants. Some representative results summarized in Table 1 indicate that hydration of phenylacetylene is more efficient upon the addition of cetyltrimethylammonium bromide.

**Table 1.** Dependence of the hydration of phenylacetylene on the nature of the surfactants<sup>[a]</sup>



Entry	Surfactant	Isolated PhCOMe [%] <sup>[b]</sup>
1	SDS	72
2	CTAB	87

[a] Reaction conditions as described in section 2 except that all experiments were performed for only 3 h at 140 °C [b] Average of at least two experiments that did not differ by more than  $\pm 3\%$ .

### Conclusions

New nanoemulsions were developed for performing hydration reactions of phenylacetylene that will lead to a significant reduction in the vast amount of organic solvents used currently, and consequently increase the safety and diminish the cost of chemical processes. Since the particle size of the micellar system is an important parameter in determining the yield of hydration reaction of phenylacetylene, the results presented in this study recommend performing these reactions at water volume fractions above 0.90 or at surfactant contents slightly above the critical micelle concentration and at high temperatures. The influence of the nature of the surfactant was investigated in the alkynes hydration process. It was found that the cationic surfactants increase the reaction rate.

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