CHARACTERIZATION OF WATER/n-PROPANOL/NONIONIC SURFACTANT/PHENYLACETYLENE MICROEMULSIONS

Monzer Fanun[a]*, Ahmad Shakarnah[a], Michael Schwarze[b], Reinhard Schomäcker[b], Zackaria Nairoukh[c], Jochanan Blum[c]

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Water/*n*-propanol/nonionic surfactant /phenylacetylene micellar systems were formulated and used for the hydration of phenylacetylene. The ratio (w/w) of *n*-propanol/surfactant equals 2/1. The surfactants were sucrose laurate (L1695) and Marlipal 24/70 (M2470). The extent of the micellar region as function of temperature was determined. The particle hydrodynamic diameters of the oil-in-water micellar systems measured using dynamic light scattering and were found to decrease with temperature for sucrose laureate and to increase for Marlipal 24/70 based systems. In the diluted region microemulsion systems were observed. Highly efficient hydration of phenylacetylene was performed in these microemulsions. The reaction results indicate that hydration of phenylacetylene is more efficient when sucrose laurate was used for the formulation of the microemulsions.

Corresponding Authors
Tel: + 972522406061;
Fax: + 972 22 79 69 60
E-Mail: Fanunm@gmail.com; mfanun@science.alquds.edu
[a] Colloids and Surfaces Research Center, Al-Quds University, East Jerusalem 51000, Palestine
[b] Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 124, D-10623 Berlin, Germany
[c] Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Introduction

In our previous studies, we have demonstrated that applying a three phase emulsion (or microemulsion)-solid state-transport method (EST) system can be applied successfully for catalytic hydrogenation, hydroformylation and carbon-carbon coupling of hydrophobic substrates in aqueous microemulsions.[1-5] Hydration of alkynes usually still involve either toxic mercury derivatives or some other environmentally disfavoured late metal compounds.[6] Ultra-low palladium catalysts was used for phenylacetylene semi hydrogenation.[7] Hydration of phenylacetylene using Brönsted acidic ionic liquids in the absence of Nobel metal catalyst/sulphuric acid was reported.[8] A possible mechanism of hydration of phenylacetylene in near-critical water was also proposed.[9] A new method for the hydration of alkynes that is expected to reduce the hazards associated with industrially important processes and to convert the conventional methods into environmentally favoured syntheses was reported.[10] Internal and aliphatic acetylenes were hydrated by treatment of their microemulsions with 0.33 M mineral acid between 80 and 140 °C. The products are easily isolated from the reaction mixtures by phase separation.[10] In this study we continue our efforts to formulate new microemulsions composed of water/*n*-propanol/nonionic surfactant /phenylacetylene to be used as a reaction media for the hydration of phenylacetylene. The nonionic surfactants used were sucrose laurate (L1695) with a hydroxylated head group and Marlipal 24/70 (M2470) with an ethoxylated head group. The objective is to study the effect of the surfactants head group on the phenylacetylene hydration in oil-in-water microemulsions.

Experimental

Phenylacetylene (PAC), Sucrose laurate (L1695) was obtained from Mitsubishi-Kasei Food Corp. (Mie, Japan). Marlipal 24/70 (M2470) was obtained from Sasol Company (Hamburg, Germany). All the components were used as supplied without further purification. Triply distilled water was used for all experiments.

Sample preparation for pseudo ternary phase diagram at constant temperature

The phase behaviour of a four-component system is described in pseudo ternary phase diagrams in which the weight ratio of surfactant/cosurfactant is fixed. The determination of the phase behaviour was performed in a thermo stated 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 behaviour was determined only after sharp interfaces had become visible. Every sample that remained transparent and homogeneous after vigorous vortexing was considered as belonging to the one phase region in the phase diagram.[11,12]

Dynamic light scattering

Particle size measurements were performed using Zetasizer Nano S (ZEN 1600) for the measurements of size and molecular weight of dispersed particles and molecules in solution by Malvern Instruments Ltd. (Worcestershire, United Kingdom). The equipment includes a 4 mW, 633 nm He-Ne laser. Size measurement range between 0.6 nm to 6 μm, size measurement angle equals 173º, concentration range for size measurement was between 0.1 ppm (0.00001 vol %) – 40 wt %, molecular weight range between 10^3 to 10^7 Da and temperature measurement range between 275 K to 363 K. 1.5 ml micellar sample was introduced in a disposable polystyrene cuvettes and measured at temperatures range between 273 and 323 K by steps of 5 K. The particle hydrodynamic diameter is calculated from the translational diffusion coefficient (D) using the Stokes-Einstein relationship:

$$d_H = k_B T/6\pi\eta D \qquad (1)$$

where d_H is the hydrodynamic diameter, k_B is Boltzmann's constant, T is the absolute temperature and η is the solvent viscosity. The results are averages of 3 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_2O (2×15 mL) and the combined organic phases were neutralized with aqueous $NaHCO_3$, dried ($MgSO_4$), concentrated and chromatographed on silica gel. The products were then analyzed by ^1H 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 behaviours of water/ sucrose laurate /*n*-propanol/ phenylacetylene and water/ Marlipal 24/70 /*n*-propanol/ phenylacetylene systems at 298 K. The ratio (w/w) of *n*-propanol/ surfactant equals 2/1. As shown in the Figure, the phase behaviour indicates the appearance of transparent micellar region after the first addition of water. Similar findings on the behaviour of sucrose ester surfactants in the presence of other cyclic oils were reported.[12-14] The area of the one phase region A_T (%), varies slightly with temperature for Marlipal 24/70. The phase behaviour of the system based on sucrose laurate shows temperature independency. Similar behaviours of the dependence of the phase behaviour on temperature of nonionic surfactants were reported elsewhere.[14-17]

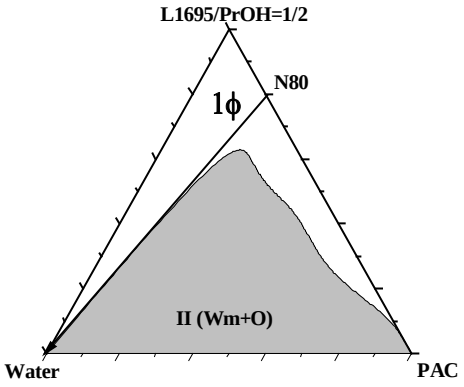


Figure 1. Pseudoternary phase diagram of the water/*n*-propanol/ sucrose laurate/phenylacetylene system at 298 K. The mixing ratio (w/w) of *n*-propanol/ sucrose laurate equals 2/1. The one phase region is designated by 1Φ, and the multiple phase regions are designated by (MΦ). N80 is the dilution line where the weight ratio of (sucrose laurate + propanol)/ phenylacetylene equals 4/1.

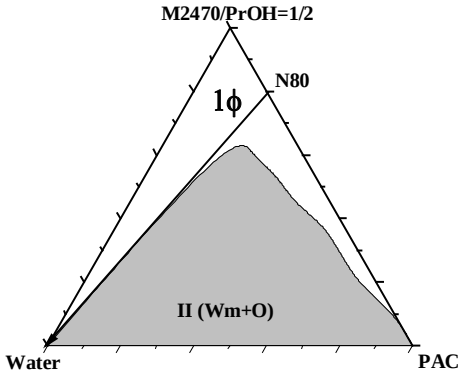


Figure 2. Pseudoternary phase diagram of the water/*n*-propanol/ Marlipal 24/70 /phenylacetylene system at 298 K. The mixing ratio (w/w) of *n*-propanol/ Marlipal 24/70 equals 2/1. The one phase region is designated by 1Φ, and the multiple phase regions are designated by (MΦ). N80 is the dilution line where the weight ratio of (Marlipal 24/70 + propanol)/ phenylacetylene equals 4/1.

Diffusion properties

The hydrodynamic diameter (d_H) of the oil-in-water micellar systems were measured for water volume fractions equal 0.90 and 0.95. The variation in the values of the (d_H) for the sucrose laurate based system decreased as function of temperature (from 298 to 323 K) as shown in Figure 3. Similar behaviour of the hydrodynamic radius of sucrose laurate based systems was reported elsewhere.[14,18,19]

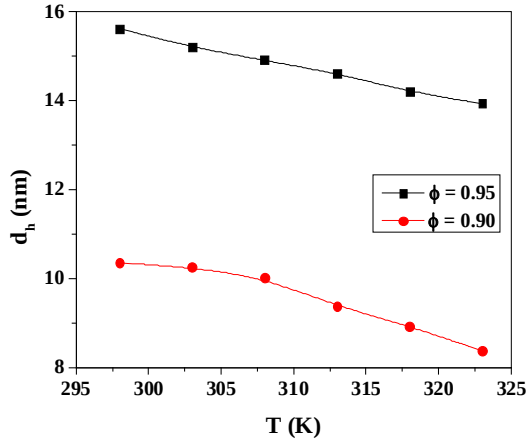


Figure 3. Variation of the particle hydrodynamic diameter as function of temperature for water/*n*-propanol/ sucrose laurate/phenylacetylene oil-in-water nanoemulsions along N80 dilution line.

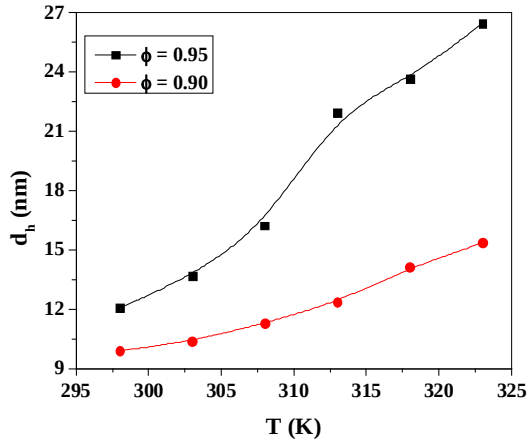


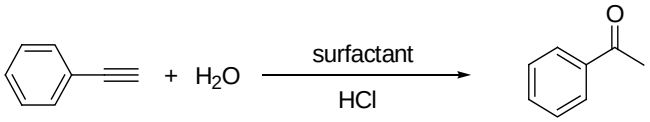
Figure 4. Variation of the particle hydrodynamic diameter as function of temperature for water/*n*-propanol/ Marlipal 24/70 / phenylacetylene oil-in-water nanoemulsions along N80 dilution line.

Figure 4 presents the variation of the hydrodynamic diameter of the oil-in-water micellar system as function of temperature for the ethoxylated Marlipal based system at 0.9 and 0.95 water volume fractions. The hydrodynamic diameters increase with increasing temperature. The values of the hydrodynamic diameter indicates that the micellar systems formed are microemulsions. These systems will be used as alternative reaction media for the hydration of phenylacetylene.

Hydration of phenylacetylene

Highly efficient hydration of alkynes have been performed in water upon addition of a suitable surfactant that solubilises the substrate. From previous studies, it had been showed that hydration of alkynes depends on the ionic nature of the surfactants.[10] In this report we introduced two different types of surfactants, both are non-ionic but they are different in structures. Some representative results summarized in Table 1 indicate that hydration of phenylacetylene is more efficient upon the addition of sucrose laurate.

Table 1. Dependence of the hydration of phenylacetylene on the nature of the surfactants. [a]



Entry	Surfactant	Isolated PhCOMe [%][b]
1	Marlipal	83
2	Sucrose laurate	97

[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 ± 3 %.

Conclusion

New microemulsions were developed for performing hydration reactions of phenylacetylene that will lead to a significant reduction in the vast amount of organic solvents and toxic agents used currently in organic syntheses, and consequently increase the safety and diminish the cost of chemical processes. Determination of the particle size diameters of the diluted oil-in-water micellar systems enables the distinction of the diluted micellar systems as microemulsions. 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.

Acknowledgment

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