Preparation of Hydrogenated Surfactant/SC CO_2 Micelles and Their Micropolarity Determination

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The influence of CO_2-philicity and -phobicity of hydrogenated surfactants on preparation of reverse micelles in SC CO_2 have been investigated for the first time. To this end, we used polyethylene glycol mono *n*-alkyl ether surfactants of different polar head groups and alkyl tails. Micelles prepared were characterized by dissolving 1-ethyl-4-methoxycarbonyl pyridinium iodide probe and recording its charge-transfer band in UV absorption region. From the transition energy of charge transfer band the polarity of the aqueous core of micelles was determined in terms of solvent polarity scale E_T (30) values.

For last 25 years, much attention has been focused on supercritical fluids as an alternative to organic solvents in various chemical processes.[1–3] Supercritical carbon dioxide (SC CO_2), in particular, is of large interest because of its low cost, non toxic nature, and attractive physical properties. It has easily attainable critical temperature and pressure of 304.1 K and 7.2 MPa, respectively. Being a low critical points fluid, its physical properties can be varied widely by simply operating temperature of the system. Thus, SC CO_2 offers wider applications for extraction, separation, and as reaction medium. Because of its nonpolar nature and low dielectric constant, SC CO_2 is a poor solvent for hydrophilic molecules especially ionic species. Solvent capacity of SC CO_2 can be enhanced by preparing reverse micelles in CO_2 using suitable surfactants. Reverse micelles are composed of water droplets, stabilized by a layer of surfactant molecules, dispersed in nonpolar bulk phase. Therefore, by preparing micelles in SC CO_2 the purpose of dissolving ionic or polar solutes in CO_2 can be accomplished. Using fluorinated surfactants[4,5] water-in-CO_2 micelles were prepared. Because of high cost and difficult synthesis of fluorinated surfactants, these fluorinated micelles can not be used for commercial applications. Some commercially available hydrogenated surfactants despite being highly soluble (up to 80 wt%)[6] in CO_2 are unable to stabilize water droplets in CO_2 as the addition of water has caused the precipitation of surfactants. The solubilization of water in CO_2 using commercial hydrogenated surfactants has been achieved successfully first by adding *n*-butanol as entrainer or cosurfactant. Two types of hydrogenated surfactants have been used are polyethylene glycol mono *n*-alkyl ethers represented by a general formula $C_nH_{2n+1}(OCH_2CH_2)_mOH$ or in short $C_n(EO)_m$ and tetraethylene-pentapropylene glycol mono *n*-dodecyl ether commercially known as Ls-45. In this article, we report the preparation of hydrogenated surfactant/CO_2 micelles, the effect of CO_2-philicity and -phobicity of surfactants on water solubilization, and subsequent determination of micropolarities of micelles using 1-ethyl-4-methoxycarbonyl pyridinium iodide (EMCPI) solvatochromic probe.

For a typical measurement, a measured amount of surfactant, *n*-butanol, water, and probe stock solution prepared in *n*-butanol were loaded into the high pressure view cell, from the injection part, and then cell was closed. Pre-cooled CO_2 was introduced at a pressure until a transparent homogeneous solution was obtained. Thus for different water content (W_0, molar ratio of water-to-surfactant) of the system the transition pressures were recorded and water solubilization phase diagram were constructed. The molar ratio of *n*-butanol-to-surfactant was represented by R. Determination of $E_T(30)$ values of micelles were conducted by recording the solvatochromic charge-transfer band of the EMCPI probe observed in UV region of absorption spectrum. For UV measurements, a high pressure UV cell was used and spectra were recorded by a Jasco V-570 spectrometer. $E_T(30)$ values were calculated from the λ_{max} of charge-transfer band of EMCPI probe by using the equations described in an earlier article.[7]

Figure 1 compares the pressure dependent water solubilization capacity of $C_{12}(EO)_5$ and $C_6(EO)_5$ surfactants in presence of cosurfactant *n*-butanol. These surfactants have similar CO_2-philic pentethylene glycol head groups but different CO_2 phobocity of dodecyl and hexyl alkyl chains. The area above the plots is the region of clear homogeneous micelles solution and below is the multiphase turbid heterogeneous mixture. In multiphase turbid solution below cloud point pressure the system is composed of hydrated $C_n(EO)_m$ compounds in CO_2 gives appearance of turbid phase. When pressure of CO_2 is increased above the cloud point pressure hydrated $C_n(EO)_m$ dissolved in CO_2 and micelles are formed and system changes to clear homogeneous solution. Figure 1 shows that an amount of water W_0 =

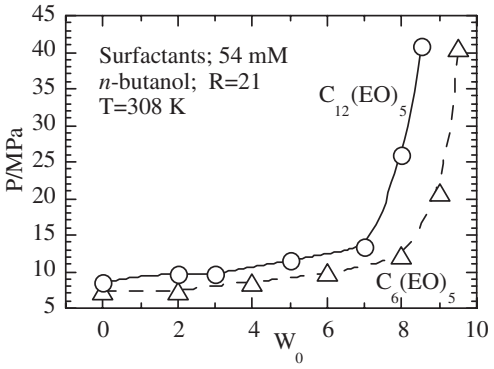

Figure 1. Comparison of water solubilization capacity of $C_{12}(EO)_5$ and $C_6(EO)_5$/SC CO_2 micelles.

8 could be dissolved at relatively low pressure of 12 MPa in $C_6(EO)_5/CO_2$ micelles and whereas a higher pressure of 26 MPa was needed to dissolved a similar amount of water ($W_0 = 8$) in $C_{12}(EO)_5/CO_2$ micelles under the similar components' concentrations and temperature. Micelles were obtained at low pressures in $C_6(EO)_5$ compared to $C_{12}(EO)_5$ because of higher CO_2-phobicity of the latter. Micelles preparation using surfactants of higher CO_2-phobicity requires high pressure of CO_2 than less CO_2-phobic surfactants.

In Figure 2, the cloud point pressures vs water solubilization plots of $C_{10}(EO)_5$ and $C_{10}(EO)_1$ have been compared. At pressure of 36 MPa, $C_{10}(EO)_5$ micelles could dissolve an mount of water $W_0 = 9$ whereas, the maximum amount of water could be solubilized at 36 MPa in $C_{10}(EO)_1$ remained as less as $W_0 = 7$. The higher water solubilization capacity in $C_{10}(EO)_5$ compared to $C_{10}(EO)_1$ has been attributed to the higher CO_2-philicity of $C_{10}(EO)_5$ compared to $C_{10}(EO)_1$. Higher is the CO_2-philicity of the surfactant larger is the water solubilization capacity of micelles.

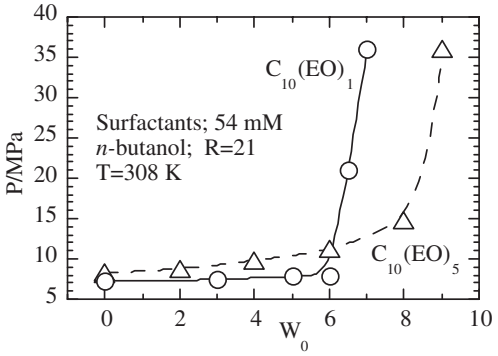

Figure 2. Comparison of water solubilization of $C_{10}(EO)_1$ and $C_{10}(EO)_5$/SC CO_2 micelles.

Micelles of tetraethylene-pentapropylene glycol mono *n*-dodecyl ether, Ls-45, and pentaethylene glycol mono *n*-octyl ether ($C_8(EO)_5$) were prepared in SC CO_2 and characterized by determining their micropolarity in terms of an empirical solvent-polarity parameter, $E_T(30)$ values, by dissolving 1-ethyl-4-methoxycarbonyl pyridinium iodide (EMCPI) solvatochromic probe. Because of the interaction between methoxycarbonyl group of EMCPI probe and polar head groups of surfactants the preferential location of the probe molecule is at the water-surfactant interface in the aqueous core of micelles. The intramolecular charge-transfer band observed in the UV region of the absorption spectrum of the probe is very sensitive to the polarity of the local environment.[7] Therefore, the quantitative changes observed in the polarity of micelles' core can be determined as a function of water content of micelles. The transition energy of the charge-transfer band of the probe should increase if the polarity of micelles' core increases. Figure 3 is the plot of $E_T(30)$ values vs the water content W_0 of Ls-45 and $C_8(EO)_5$ micelles. With increasing W_0, the value of $E_T(30)$ is increasing. There is no noticeable difference in $E_T(30)$ values for the micelles prepared using Ls-45 or $C_8(EO)_5$ surfactants as both the surfactants have glycol polar head group. Increase in the polarity of micelles with increasing the water content is attributed to the loosening of interactions between polar head group of surfactant and water at the water-surfactant interface in the aqueous core of micelles. In water/sodium bis(2-ethylhexyl) sulfosuccinate/SC ethane[8] micelles, increasing amount of water in micelles loosely bound water starts appearing in micelles' core which is more polar than tightly bound water present at low water content of micelles. The observation is supportive to our finding of increasing polarity of $C_n(EO)_m/CO_2$ micelles' core with increasing W_0 of micelles.

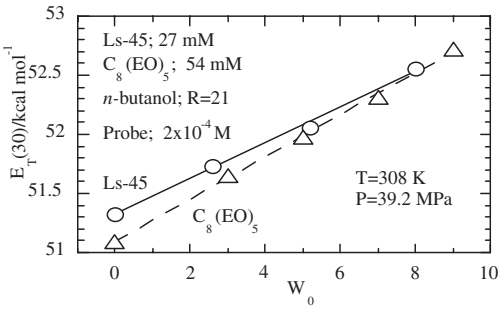

Figure 3. $E_T(30)$ values vs W_0 of Ls-45 and $C_8(EO)_5$ micelles in SC CO_2.

Solubilization of polar 1-ethyl-4-methoxycarbonyl pyridinium iodide probe inside the micelles prepared in SC CO_2 showed that polar solutes could be dissolved in nonpolar CO_2 by preparing micelles using hydrogenated surfactants. CO_2 philicity and -phobicity of hydrogenated surfactants play an important role for micelles preparation. The results obtained in this work can provide directionality to the development of low cost hydrogenated surfactants to prepare micelles in SC CO_2 and replace fluorinated and silicone surfactants, used until now, which are expensive and difficult to synthesize.

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