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Study on the Phase Behavior of Supercritical CO_2/Dynol-604/Water System and Solubilization of Methyl Orange in the Microemulsions

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Abstract: It was found that Dynol-604, a non-fluorous and no silicon-containing nonionic surfactant, was soluble in supercritical (SC) CO_2. The phase behavior of SC CO_2/Dynol-604/water system was studied. The results showed that one-phase water-in-CO_2 microemulsions could be formed. The solubilization of methyl orange in the microemulsions proved further the existence of water domain in the microemulsions.

Keywords: Supercritical carbon dioxide, surfactant, microemulsions, solvatochromic probe.

Instruction

Selection of CO_2-soluble surfactants is of great importance to the application of supercritical CO_2. In 1990, Consani and Smith[1] tested the solubility of over 130 commercially available surfactants in SC CO_2 at 50°C and 10-50 MPa. Practically all of them were insoluble or only slightly soluble and they did not solubilize a significant amount of water. To overcome the problem described, Hoefling *et al*. have synthesized highly CO_2-soluble surfactants[2,3], such as dimethyl siloxanes, hexafluoropropylene oxides and fluoroalkyl groups. The synthesized surfactants displayed relatively high solubility in CO_2 at moderate pressures. Poly-hexafluoropropylene oxide is the most CO_2-philic soluble polymer observed to date and surfactants with perfluoro-alkylpolyether tail exhibit very high solubility in carbon dioxide[4]. The nonionic surfactants, $C_{12}EO_3$ and $C_{12}EO_8$ formed small aggregates in CO_2 that contain approximately 2.5~5.0 surfactant molecules per aggregate[5]. So far, the formation of SC CO_2 microemulsions by non-fluorous and no silicon-containing surfactants was seldom reported in the literature[6].

In this work the phase behavior of SC CO_2/Dynol-604/water system and the solubilization of methyl orange in the microemulsions were studied.

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Experimental

The surfactant Dynol-604 was produced by Air Products and Chemicals Inc. CO_2 (99.995% purity) was supplied by Beijing Analytical Instrument Factory. Both methanol and methyl orange were A. R. Grade produced by Beijing Agent Factory. Double distilled water was used. The apparatus for phase behavior measurements and UV/vis studied was similar to those reported previously[7, 8].

Results and discussion

Phase behavior of Dynol-604 in SC CO_2 with variety of water loadings

CO_2 itself has a noticeable affinity for water, far more than that of ethane or propane[9]. The water is distributed between surfactant and CO_2 in such a way as to minimize the overall free energy of the system. In this work we determined the solubility of water in CO_2 (Wco_2) and in CO_2/Dynol-604 mixtures (Wt). **Table 1** lists the values of Wt (wt %) and Wco_2 (wt %). The corrected solubility Wc (wt %) is also given in the **Table**, which is obtained by subtracting the Wco_2 from Wt at the same temperature and pressure. Obviously, Wc is related with the quantity of the water in the reverse micelles. As shown in **Table 1**, Wc increases with the increase of pressure, and reducing temperature favors loading of water into one-phase Dynol-604 based microemulsions. The results of Wc suggest that water domain is present in the reverse micelles.

Table 1 Solubility of water in SC CO_2 Wco_2 and SC CO_2/Dynol-604 (0.016 g/mL) system Wt

Temperature °C	Pressure MPa	Density g/cm^3	Wt wt. %	Wco_2 wt. %	Wc wt. %
35	16.17	0.788	0.23	0.14	0.09
35	18.23	0.797	0.45	0.15	0.30
35	21.87	0.805	0.57	0.16	0.41
40	18.56	0.763	0.26	0.19	0.07
40	19.94	0.770	0.42	0.21	0.21

Solvatochromic probe studies

The absorbance maximum of a solvatochromic probe in UV spectrum is sensitive to the local environment about the probe. To confirm that a water domain exists and to characterize its nature, solvatochromic probe study was carried out in this work. Methyl orange (MO) was selected as solvatochromic probe, which has absorbance in the range of 400~470 nm (depending on the environment). The absorbance profiles of these experiments are illustrated in **Figures 1** and **2**. The absorption band of MO can not be observed for SC CO_2/MO, SC CO_2/MO/Dynol-604, and SC CO_2/MO/water systems, as shown in **Figure 1**. Thus, the solubility of MO in SC CO_2 and SC CO_2 / Dynol-604, and SC CO_2/water mixtures is very low. However, the absorption band can be observed for SC CO_2/MO/Dynol-604/water mixtures as shown in **Figure 2**, indicating the existence of methyl orange in water domain of the reverse micelles. **Table 2** lists the absorbance maximum ($_{max}$) at different conditions. The results in **Table 2** and **Figure 2** show that $_{max}$ increases with Wc. The $_{max}$ is in the range of 408~428 nm, while the $_{max}$ of MO in ordinary water is 464 nm. These results suggest that the polarity of the environment of the solubilized MO is in medium of bulk water and alkanes, which was also discussed by other authors[10]. As expected, the polarity of the environment increases with Wc (wt%). Thus, the formation of microemulsions is proved by the UV spectra. Water can form hydrogen bond to anionic head group such as sulfonates and sulfosuccinates to enhance the formation of reverse micelles[11]. For diblock copolymers with a poly (ethylene oxide) block, small amounts of water can cause the formation of large stable aggregates[12]. The acetylenic glycol-based Dynol-604 has hydroxy group, which can form hydrogen bond with water. Thus the water may act as a "glue" to bond the surfactant headgroups together, *i.e*. acts as a driving force for aggregation.

Figure 1 Absorbance of 1. CO_2 + Dynol-604 (0.016g/mL); 2. CO_2+H_2O + 0.1mL MO, 3. CO_2 + Dynol-604 (0.016g/mL) + 0.1mL MO systems at 21.87 MPa and 35.0°C

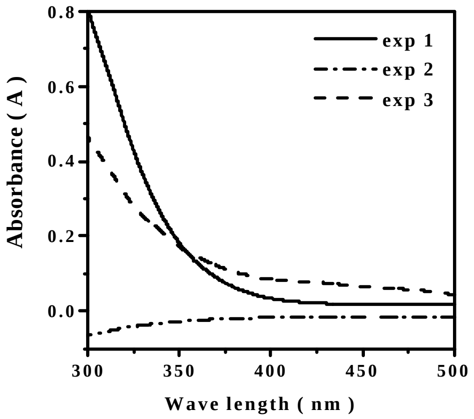


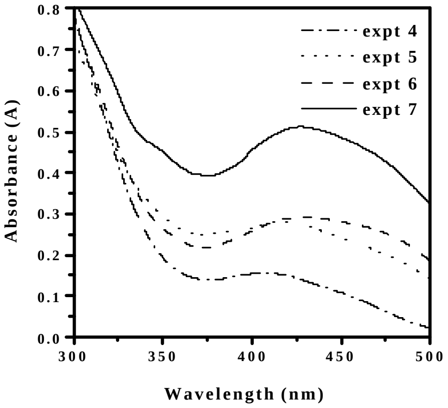
Table 2 The λ_{max} and maximum absorbance of MO in supercritical CO_2 at 35°C, 21.87 MPa and various composition*

Experiment Number	Dynol-604 (g/mL)	Wt (wt. %)	Wc (wt. %)	MO in the Cell(g×10^6)	$_{max}$ (nm)	Absorbance (A)
1	0.016	-	-	-	-	-
2	-	0.16	-	1.64	-	-
3	0.016	-	-	1.64	-	-
4	0.016	0.23	0.07	1.64	408	0.16
5	0.016	0.45	0.29	1.64	416	0.28
6	0.016	0.57	0.41	1.64	428	0.29
7	0.016	0.57	0.41	3.28	428	0.51

*Each experiment was done for three times and results averaged.

The absorbance of MO increases with the increase of Wc from experiment 4 to experiment 5, as shown in **Table 2** or **Figure 2**. The reason is that the ability of SC CO_2 microemulsions to dissolve MO increases with the increase of loading water. Moreover, absorbance values of experiment 5 and experiment 6 are approximately same although the Wc of experiment 6 is higher, because MO did not reach saturation in the microemulsions. The absorbance of experiment 7 is larger than that of experiment 6, because more MO was charged.

Figure 2 Absorbance of MO in SC CO_2 microemulsions with various added components (refer to **Table 2** for components and compositions) at 21.87 MPa and 35.0°C



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