

Solubility and Phase Behaviors of AOT Analogue Surfactants in 1,1,1,2-Tetrafluoroethane and Supercritical Carbon Dioxide

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A series of AOT (aerosol-OT) analogue surfactants (sodium salt of dibutyl-2-sulfosuccinate, sodium salt of dipentyl-2-sulfosuccinate, sodium salt of dihexyl-2-sulfosuccinate, and sodium salt of dioctyl-2-sulfosuccinate) were synthesized and characterized by ¹H NMR and elemental analysis. A static method coupled with gravimetric analysis is developed to measure the solubility of the surfactants in 1,1,1,2-tetrafluoroethane (HFC-134a) and supercritical CO₂ (scCO₂). The solubilities of the surfactants in HFC-134a and scCO₂ are affected by the temperature, pressure, and carbon atom number of the surfactant. The solubility of the same surfactant in HFC-134a solvent is approximately two times that in the most commonly used supercritical solvent CO₂. The pressure–temperature phase diagrams for water/HFC-134a microemulsions stabilized by the surfactants were determined using cloud-point measurements for a concentration range of the surfactant from (1.85 × 10⁻³ to 5.60 × 10⁻³) M, temperature up to 338 K, and pressure up to 40 MPa in a high-pressure vessel. At a fixed temperature, the cloud-point pressure increased with increasing water-to-surfactant molar ratio (*W*₀). At a fixed *W*₀, the cloud-point pressure decreased with increasing temperature. The surfactant with the longest hydrocarbon chain has the highest cloud-point pressure even at lower surfactant concentrations.

Introduction

Supercritical carbon dioxide (scCO₂) is an attractive substitute for organic solvents since it has low toxicity, is nonflammable, and is cheap and readily available in large quantities.^{1–5} With these advantages together with its unique properties as a supercritical fluid such as its adjustable solvent power, enhanced mass transfer characteristics, and low surface tension, scCO₂ has prompted extensive research to develop scCO₂-based processes.^{6–10}

With growing interest in nanostructured materials, a number of techniques have been used for production of nanoparticles, such as gas evaporation,¹¹ sputtering,¹² coprecipitation,¹³ sol–gel method, hydrothermal,¹⁴ microemulsion,^{15–17} etc. Water-in-oil (W/O) microemulsions have received great attention. A microemulsion is a thermodynamically stable system with at least three components: two immiscible components (generally water and oil) and a surfactant. Recent experiments^{18,19} have been investigated for the use of carbon dioxide (CO₂) as a nonpolar solvent medium for formation of microemulsions.

Unfortunately, because CO₂ is a nonpolar solvent and has weak van der Waals forces, it is not suitable for dissolving polar substances, which has limited its application in the separation, reaction and material formation processes. Many supercritical fluids exhibit a low polarity, and many polar solutes are insoluble in them. Generally the more polar the fluid, the higher the critical temperature (*T*_c). Halogenated aliphatic compounds offer more polar solvation media but still have readily accessible critical constants. At present only a small number of such fluids^{20,21} have been studied, including CF₃H and CCl₃F. Owing

to their low toxicity and nonflammability, alternative hydrofluorocarbon (HFC) propellants would be desirable.²²

Olsen and Tallman^{23,24} were the first to use HFCs for electrochemical experiments in supercritical solvents. The solvent properties of 1,1,1,2-tetrafluoroethane (HFC-134a) have been investigated thoroughly as a function of temperature and pressure. This solvent was shown to be more polar than studied chlorofluorocarbons (CFCs), even though it has a relatively low critical temperature and pressure (*T*_c = 374 K, *P*_c = 4.055 MPa). Abbott et al.²⁵ also performed electrochemical measurements in HFC-134a and difluoromethane.

Tackson and Fulton²⁶ reported the properties of sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) microemulsions formed in supercritical hydrochlorofluorocarbons (HCFCs), HFC, and fluorocarbons. They also reported extensively the phase behavior of AOT and didodecyldimethylammonium bromide microemulsions formed in supercritical chlorodifluoromethane (R22). Microemulsions formed in R22 were demonstrated to have a strongly density-dependent maximum molar water-to-surfactant ratio (*W*₀).

Water-in-fluorocarbon emulsion formation in the HFCs gases 1,1,1,2,3,3,3-heptafluoropropane (R227) and HFC-134a has recently been investigated by Butz et al.²⁷ using perfluoroalkylated dimorpholinophosphate (F₈H₁₁DMP) as the surfactant. Water solubilization by anionic perfluorinated surfactants has been examined in the condensed phase of the HFC-134a in the temperature range (288 to 328) K and under a pressure of 50 MPa.²⁸

Johnston et al.²⁹ discovered that an ammonium carboxylate perfluoropolyether [CF₃O(CF₂CF(CF₃)OCF₂COONH₄, PEPF) surfactant could support a microemulsion in scCO₂. A promising recent development in this field has been the demonstration of the ability of a fluorinated analogue of AOT.³⁰

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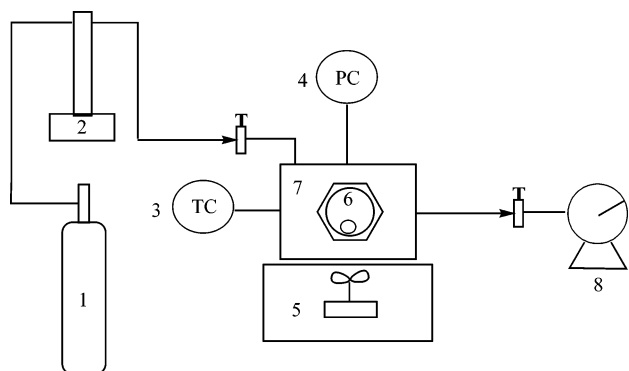


Figure 1. Schematic diagram for solubility and phase diagram measurements: 1, steel cylinder; 2, syringe pump; 3, thermocouple assembly; 4, pressure transducer; 5, magnetic stirrer; 6, glass vial; 7, high-pressure vessel; 8, wet-type gas meter.

The current work describes the solubilities and pressure-temperature phase diagrams for W/HFC-134a (water/HFC-134a) microemulsions stabilized by the surfactants using cloud-point measurements for a surfactant concentration of (1.85×10^{-3} to 5.60×10^{-3}) M, temperature up to 338 K, and pressure up to 40 MPa. These phase diagrams are important to the formation of nanoparticles in our further studies.

Experimental Section

Materials and Instruments. Maleic anhydride (99.5 %), *p*-toluenesulfonic acid monohydrate (99 %), 1,4-dioxane (99 %), sodium hydrogen sulfite (SO₂, 65.0 %) and *n*-hexanol (99.0 %) were obtained from the Sinopharm Group Chemical Reagent Co. Toluene (99.5 %), *n*-pentanone (98 %), *n*-octanol (99.5 %), and sodium hydroxide (96.0 %) were obtained from the Xi'an Chemical Reagent Factory. *n*-Butanol (99.0 %) was obtained from the Tianjin No. 3 Chemical Reagent Factory. CO₂ was obtained from the Xi'an Yatai Liquid Gas Co., and 1,1,1,2-tetrafluoroethane (HFC-134a) (99.9 %) was obtained from the Xi'an Jinzhu Modern Chemical Industry Co., Ltd. The chemical reagents used in this study were of analytical pure grade. All the chemicals were used directly without further purification.

A schematic diagram of the experimental setup for solubility measurements is given in Figure 1. The high-pressure vessel (Beijing, Sihe Chuangzhi Keji Corporation, SF-400) with a maximum pressure of 40 MPa, a maximum temperature of 353 K, and an internal volume of 60 cm³ was equipped with two sapphire windows with a diameter of 25 mm and a thickness of 20 mm. The windows were sealed on both sides with poly(ether-ether-ketone) (PEEK) seals. The high-pressure vessel was also fitted with a thermocouple assembly, a pressure transducer, and a rupture disk assembly. The vessel rests on a magnetic stirrer, and fluid is introduced into the pressure vessel using a syringe pump (model 260D, ISCO).

The ¹H NMR spectra were recorded on a superconducting Fourier digital NMR spectrometer (Bruker, AVANCF 300 MHz). The elemental analysis of the samples was performed by an elemental analyzer (Germany, Vario EL III) with a variation of ± 0.5 %.

Synthesis of Surfactants. The modified synthesis procedures of surfactants were conducted according to the methods given by Liu and Erkey.³¹ The synthesis procedure of the surfactants (sodium salt of dibutyl-2-sulfosuccinate, DBSS; sodium salt of dipentyl-2-sulfosuccinate, DPSS; sodium salt of dihexyl-2-sulfosuccinate, DHSS; and sodium salt of dioctyl-2-sulfosuccinate, DOSS) has two main steps: esterification and sulfonation reaction.

A mixture of maleic anhydride, *n*-pentanone (or *n*-octanol, *n*-butanol, *n*-hexanol), and *p*-toluenesulfonic acid monohydrate as the catalyst in a flask was refluxed under stirring at 398 K for 2 h. The water created in this reaction was collected in a trap. The yield of this esterification reaction was approximately 80 %.

Esterifiable product was neutralized to the pH of 7 using an aqueous sodium hydroxide (30 %) solution. Floc was observed in the system. Then an aqueous sodium hydrogen sulfite and ethanol as cosolvent were added into the system. The mixture was refluxed under stirring at 393 K for (3 to 4) h. A little of the product was then taken out into water and stirred to determine the reaction degree. The reaction was stopped if no oily matter floated on the water surface and the pH of the reaction system was (7 to 8). After reacting, the viscous liquid was created in the flask. This liquid was placed in a dryer to remove water in the system. The solid obtained was then dissolved in anhydrous alcohol and recrystallized. A white solid was obtained after drying at 323 K under vacuum overnight. The surfactants were characterized by ¹H NMR spectroscopy and elemental analysis as follows.

Sodium Salt of Dioctyl-2-sulfosuccinate. CH₃^a(CH₂)₅^bCH₂^c-CH₂^dOOCCH₂^eCH^f(SO₃Na)COOCH₂^gCH₂^h(CH₂)₅CH₃^j (yield, 86.6 %). ¹H NMR (CDCl₃, δ): 0.880 (a and j, t, $J = 6.75$ Hz, 6H), 1.272 (b and i, m, $J = 12.84$ Hz, 20H), 1.586 (c and h, m, $J = 5.76$ Hz, 4H), 3.135–3.166 (e, m, $J = 4.57$ Hz, 2H), 4.024 (d, t, $J = 6.87$ Hz, 2H), 4.131–4.175 (g, m, $J = 6.51$ Hz, 2H), 4.269–4.317 (f, m, $J = 4.04$, 1H). Anal. Calcd for C, 54.03; S, 7.21; H, 8.39. Found: C, 54.97; S, 6.69; H, 8.33.

Sodium Salt of Dipentyl-2-sulfosuccinate. CH₃^a(CH₂)₂^bCH₂^c-CH₂^dOOCCH₂^eCH^f(SO₃Na)COOCH₂^gCH₂^h(CH₂)₂CH₃^j (yield, 95.1 %). ¹H NMR (CDCl₃, δ): 0.908–0.873 (a and j, t, $J = 3.70$ Hz, 6H), 1.300–1.349 (b and i, m, $J = 3.09$ Hz, 8H), 1.673–1.550 (c and h, m, $J = 6.89$ Hz, 4H), 3.228–3.078 (e, m, $J = 11.76$ Hz, 2H), 4.035 (d, t, $J = 6.84$ Hz, 2H), 4.140–4.179 (g, m, $J = 5.05$ Hz, 2H), 4.262–4.311 (f, m, $J = 4.95$ Hz, 1H). Anal. Calcd for C, 46.65; S, 8.90; H, 6.99. Found: C, 46.14; S, 8.42; H, 6.71.

Sodium Salt of Dibutyl-2-sulfosuccinate. CH₃^aCH₂^bCH₂^c-CH₂^dOOCCH₂^eCH^f(SO₃Na)COOCH₂^gCH₂^hCH₂ⁱCH₃^j (yield, 90.4 %). ¹H NMR (CDCl₃, δ): 0.93 (a and j, t, $J = 2.96$ Hz, 6H), 1.36 (b and i, t, $J = 7.68$ Hz, 4H), 1.58 (c and h, t, $J = 7.55$ Hz, 4H), 3.18 (e, t, $J = 9.64$ Hz, 2H), 4.05 (d, t, $J = 6.73$ Hz, 2H), 4.18 (g, t, $J = 6.56$ Hz, 2H), 4.33 (f, t, $J = 5.12$ Hz, 1H). Anal. Calcd for C, 43.37; S, 9.65; H, 6.37. Found: C, 43.31; S, 10.07; H, 6.41.

Sodium Salt of Dihexyl-2-sulfosuccinate. CH₃^a(CH₂)₃^bCH₂^c-CH₂^dOOCCH₂^eCH^f(SO₃Na)COOCH₂^gCH₂^h(CH₂)₃CH₃^j (yield, 84.7 %). ¹H NMR (CDCl₃, δ): 0.90 (a and j, t, $J = 4.59$ Hz, 6H), 1.29 (b and i, t, $J = 1.38$ Hz, 8H), 1.59 (c and h, t, $J = 6.87$ Hz, 4H), 3.15 (e, t, $J = 9.33$ Hz, 2H), 4.05 (d, t, $J = 6.87$ Hz, 2H), 4.14 (g, t, $J = 6.60$ Hz, 2H), 4.33 (f, t, $J = 5.16$ Hz, 1H). Anal. Calcd for C, 49.47; S, 8.25; H, 7.52. Found: C, 49.57; S, 8.22; H, 7.41.

Measurements of Solubility. For each experiment, an excess amount of solute and a small magnetic stirring bar was placed in a 25 mm \times 25 mm (12 mL) glass vial that was then capped with a coarse filter paper attached to the vial with Teflon tape. The sample vial was then weighed and placed inside the pressure vessel.

The vessel was sealed and heated to the desired temperature by a heater via a machined internal heating rod. Once the test temperature was reached, stirring was initiated, and the vessel was slowly filled with fluid until the desired pressure was

Table 1. Mass of Solute Lost from the Vial at Different Time (*t*) for DPSS in HFC-134a at 308 K and under 16 MPa^a

<i>T</i> /K	<i>P</i> /MPa	<i>t</i> /h	<i>m</i> /g
308	25	5	0.0357
		9	0.0366
		13	0.0375
		16	0.0378
		20	0.0382
		24	0.0381
		28	0.0382

^a *m*, amount dissolved of surfactant.

achieved. After sufficient time (usually more than 20 h as explained in the Results and Discussion section) was allowed for equilibration of fluid/solute solution, the vessel was depressurized and opened. The vial was removed, wiped with a clean tissue, dried, and reweighed. The solubility of the solute is then given by the equation as follows:

$$\text{solubility (wt/vol)} = \frac{W_1 - W_2}{V_1 - V_2}$$

where W_1 and W_2 are the initial and final measured mass of solute in the vial, V_1 is the volume of the high-pressure vessel, and V_2 is the volume of vial. This equation incorporates a correction factor that accounts for precipitation of the solute in the fluid phase in the vial. The volume of the vessel in this equation is the volume accessible to the fluid phase, which was determined to be 48 mL.

Measurement Pressure–Temperature Phase Diagrams of Surfactants. The pressure–temperature (P – T) phase diagrams for W/HFC-134a microemulsions stabilized by the surfactants were determined using cloud-point measurements.^{31,32} The macroscopic phase behavior of the surfactant aggregates in HFC-134a was investigated using a high-pressure vessel. In a typical experiment, a certain amount of surfactant and water and a magnetic stir bar were placed in the vessel, which was then sealed. The vessel was then placed on a magnetic stirrer and heated to the desired temperature. The vessel was charged very slowly with HFC-134a from a syringe pump (ISCO, 260D) equipped with a cooling jacket. When an optically transparent single-phase solution was obtained, the pump was stopped. Subsequently, the vessel was slowly depressurized until the cloud point was reached. The temperature was controlled during each experiment with a variation of ± 0.5 °C. The pressure was measured using a pressure transducer (Beijing, Zhengkai, MCY-B) and was controlled during each experiment with a variation of ± 0.01 MPa.

Results and Discussion

Measurements of Solubility. A static method coupled with gravimetric analysis was developed for measuring the solubility of the surfactants in scCO₂ and HFC-134a.³³ In order to obtain accurate solubility of surfactant and shorten the experiment time, the first set of experiments was conducted to determine the time necessary for achieving equilibrium and the accuracy of solubility in this system. The data of the mass of solute lost from the vial at different times was listed in Table 1 for DPSS in HFC-134a at 308 K and under 16 MPa. The fluid phase became saturated with DPSS after about 20 h. The solubility of DPSS in scCO₂ was obtained at a fixed pressure with changing temperature as shown in Table 2.

Table 3 reveals that the solubility of DPSS in scCO₂ increases with an increase in pressure at a constant temperature, with the influence of pressure on the solubility being more pronounced

Table 2. Solubility of DPSS in scCO₂ with Increasing of Temperature under a Pressure of 25 MPa^a

<i>P</i> /MPa	<i>T</i> /K	<i>m</i> /g	<i>S</i> ($\times 10^{-4}$)/g·mL ⁻¹
25	308	0.0161	3.354
	318	0.0372	7.750
	328	0.0515	10.73
	338	0.0549	11.44

^a *m*, amount dissolved of surfactant; *S*, solubility.

Table 3. Solubility of DPSS in scCO₂ with Increasing of Pressure at a Temperature of 318 K^a

<i>T</i> /K	<i>P</i> /MPa	<i>m</i> /g	<i>S</i> ($\times 10^{-4}$)/g·mL ⁻¹
318	15	0.0455	9.479
	20	0.0472	9.833
	25	0.0500	10.42
	30	0.0597	12.44
	35	0.0642	13.38

^a *m*, amount dissolved of surfactant; *S*, solubility.

at higher temperature. Under lower pressure, the increasing trend of solubility with an increase in pressure is slow, while under a higher pressure, the increasing trend is fast. Pressure is the main influencing factor on the density of the supercritical fluid: when the pressure is higher, the density of the supercritical fluid is greater. The solubility of solute in the supercritical fluid is greatly related to the density and increases with an increase in density. So the solubility of the surfactant increases with an increase in pressure. This is in accord with conventional wisdom stating that the density of a supercritical fluid must increase in order to increase the solubility and extraction efficiency.³⁴ Considering the thermodynamic view, at the same temperature, on the basis of the Hildebrandt flexibility formula $\Delta H_M V(\delta_1 - \delta_2)$, if the solubility parameter of a supercritical fluid solvent δ_1 and solubility parameter of a solute δ_2 are closer, the mixture heat ΔH_M is smaller, and the two compounds can dissolve each other.

The solubility of DPSS in scCO₂ increases with an increase in temperature. The effect of temperature on solubility is complex. The crossover of solubility isotherms occurs when pressure is used as a variable. The phenomenon is a consequence of two competitive effects: the density of scCO₂ and the vapor pressure. As the temperature increases, the vapor pressure increases too, which enhances the solubility. But the density and CO₂ solvent power decrease, which results in a decrease in solubility. At pressures above the crossover region, the solubility increases with an increase in both pressure and temperature while, below this point, the solubility increases with an increase in pressure but decreases with an increase in temperature. At lower pressure, the fluid density is lowered by a small increase in temperature. Since the density effect is predominant in this region, the solubility will decrease with an increase in temperature. However, at higher pressure the fluid density is less dependent on temperature so that the observed increase in solubility with an increase in temperature could be primarily due to other factors, especially the higher vapor pressure of solid samples.^{35,36} While fixing the pressure at 25 MPa, which is above the crossover region, so an increase in solubility with an increase of temperature was observed.

The solubility results for DPSS in HFC-134a at a fixed temperature are shown in Table 4. The solubility of DPSS in HFC-134a increases with an increase in pressure. The solubility results for DPSS in HFC-134a at a fixed pressure are listed in Table 5. The solubility of DPSS in HFC-134a increases with an increase in temperature. The solubility of DPSS in HFC-

Table 4. Solubility of DPSS in HFC-134a with Increasing of Pressure at a Temperature of 318 K^a

<i>T</i> /K	<i>P</i> /MPa	<i>m</i> /g	<i>S</i> ($\times 10^{-3}$)/g·mL ⁻¹
318	16.5	0.0435	0.9063
	20.2	0.0604	1.2583
	25.0	0.0702	1.4625
	30.0	0.0898	1.8708
	33.0	0.1139	2.3729

^a *m*, amount dissolved of surfactant; *S*, solubility.**Table 5. Solubility of DPSS in HFC-134a with Increasing of Temperature under a Pressure of 25 MPa^a**

<i>P</i> /MPa	<i>T</i> /K	<i>m</i> /g	<i>S</i> ($\times 10^{-4}$)/g·mL ⁻¹
25	308	0.0341	7.104
	318	0.0702	14.63
	328	0.1124	23.42
	338	0.2467	51.40

^a *m*, amount dissolved of surfactant; *S*, solubility.**Table 6. Comparison of Solubility of DPSS in HFC-134a and scCO₂ with Increasing of Pressure and at a Temperature of 318 K^a**

<i>T</i> /K	<i>P</i> /MPa	<i>m</i> /g		<i>S</i> ($\times 10^{-4}$)/g·mL ⁻¹	
		CO ₂	HFC-134a	CO ₂	HFC-134a
318	15	0.0455	0.0435	9.479	9.062
	20	0.0472	0.0604	9.833	12.58
	25	0.0500	0.0702	10.42	14.63
	30	0.0597	0.0898	12.49	18.70
	35	0.0642	0.1139	13.38	23.73

^a *m*, amount dissolved of surfactant; *S*, solubility.**Table 7. Comparison of Solubility of DPSS in HFC-134a and scCO₂ with Increasing of Temperature and Under a Pressure of 25 MPa^a**

<i>P</i> /MPa	<i>T</i> /K	<i>m</i> /g		<i>S</i> ($\times 10^{-4}$)/g·mL ⁻¹	
		CO ₂	HFC-134a	CO ₂	HFC-134a
25	308	0.0161	0.0341	3.354	7.104
	318	0.0372	0.0702	7.750	14.63
	328	0.0515	0.1124	10.73	23.42
	338	0.0549	0.2467	11.49	51.40

^a *m*, amount dissolved of surfactant; *S*, solubility.

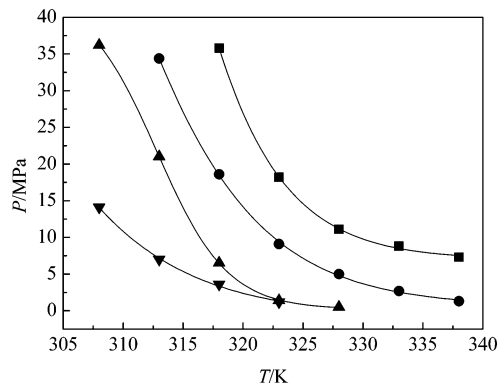
134a is affected by pressure and temperature as shown in Table 4 and Table 5, and the trend of solubility is consistent with that in scCO₂.

The theory of solubility parameters can qualitatively explain the effect of pressure and temperature on the solubility of a solute. When the solubility parameters of the solute and solvent are closer, the solubility increases. The solubility parameter of the solute is related to the property of the solute and the temperature. Generally, the solubility parameter of a solute decreases with an increase in temperature. When the pressure increases while the temperature keeps constant, the solubility parameter of solute is a constant.

The solubility of the same surfactant in HFC solvent is approximately two times that in the most commonly used scCO₂ as given in Table 6 and Table 7, because CO₂ is a nonpolar solvent and has weak van der Waals forces, so it is not suitable for dissolving polar substances in this medium. The increase in solubility in the HFC-134a medium is to some extent what would be expected for a polar solute in this more polar solvent. For these systems, a dipole–dipole interaction between the polar solute and HFC-134a exists, which would tend to enhance solubility relative to that with the dipole–quadrupole interaction present with the polar solutes and the scCO₂ system.³⁷

Table 8. Solubility of Different Surfactants in HFC-134a under 25 MPa and at 318 K^a

surfactant	<i>m</i> /g	<i>S</i> ($\times 10^{-4}$)/g·mL ⁻¹
DBSS	0.1101	22.94
DPSS	0.0702	14.63
DHSS	0.0439	9.125
DOSS	0.0270	5.625

^a *m*, amount dissolved of surfactant; *S*, solubility.**Figure 2.** Effect of *W*_o on *P*–*T* phase diagram for W/HFC-134a microemulsions supported by DPSS at [surfactant] = 0.00185 M: ■, *W*_o = 30; ●, *W*_o = 25; ▲, *W*_o = 20; ▼, *W*_o = 15.

The solubility results for different surfactants in HFC-134a at the same temperature and pressure are listed in Table 8. The solubility of sodium salt sulfosuccinate in HFC-134a decreases with an increase of the number of carbon atoms under the same conditions, which indicates the existence of hydrocarbon chain length controlling the solubility of surfactant in HCF-134a. Generally, the molecular weight of the compound is higher, its solubility in the fluid is lower. The surfactant with the longer hydrocarbon chain length has a stronger polarity. HCF-134a is a polar solvent, so the solubility of the surfactant with the longer hydrocarbon chain length is higher than that with a shorter hydrocarbon chain length.

A static method coupled with gravimetric analysis was developed for measuring the solubility of solids in scCO₂. The appealing feature of this technique is its simplicity, and it requires no specialized equipment other than a suitable pressure cell. The technique can, in principle, be easily extended to the measurement of solubilities of mixtures of solids in scCO₂ if the composition of the remaining mixture in the vial can be determined by a suitable chemical analysis such as GC, HPLC, or infrared or UV–vis spectroscopy. Preliminary mass-transfer calculations of this technique indicate that the major resistance to mass transfer was the filter paper. The time necessary for achieving equilibrium can probably be reduced by using a thinner membrane to cap the sample vial.³³

Measurement Pressure–Temperature Phase Diagrams of Surfactants. The *P*–*T* phase stability diagram for W/HFC-134a microemulsions supported by the DPSS surfactant at different *W*_o values is shown in Figure 2 and Figure 3. The cloud-point pressures increase with increasing *W*_o at a fixed temperature. This behavior is indicative of swelling of micelles with added water, which in turn strengthens attractive micelle–micelle interactions. Thus, higher pressures are required to strengthen tail–solvent interactions to prevent phase separation. While the cloud-point pressures decrease with increasing temperature at a fixed *W*_o. This result is different from that in scCO₂. Perhaps because there is a dipole–quadrupole interaction present in the polar solute and scCO₂ system, while there is a dipole–dipole interaction between the polar solute and HFC-134a. This

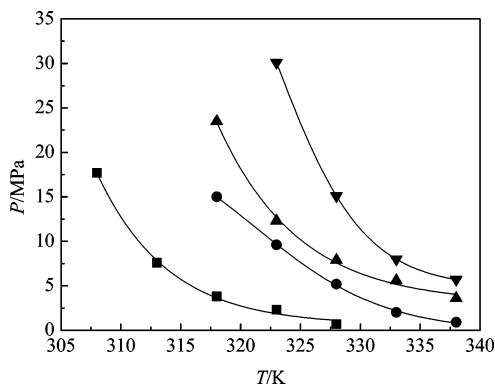


Figure 3. Effect of W_o on P - T phase diagram for W/HFC-134a microemulsions supported by DPSS at [surfactant] = 0.0037 M: ∇ , $W_o = 25$; \blacktriangle , $W_o = 20$; \bullet , $W_o = 15$; \blacksquare , $W_o = 10$.

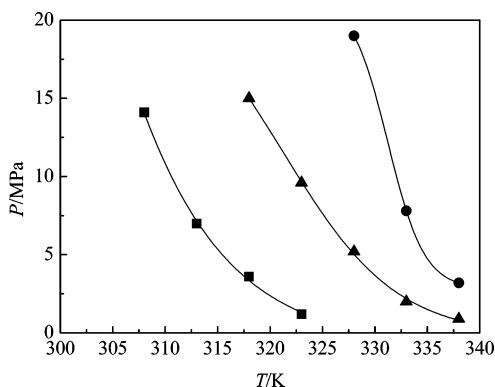


Figure 4. Effect of surfactant concentration on P - T phase diagram for W/HFC-134a microemulsions supported by DPSS at $W_o = 15$: \bullet , 0.0056 M; \blacktriangle , 0.0037 M; \blacksquare , 0.00185 M.

interaction is likely to influence the phase behaviors of the surfactant in fluids.

The P - T phase diagram at $W_o = 15$ for different DPSS concentrations is shown in Figure 4. Without any added water, the surfactant does not dissolve completely under these concentrations, resulting in a separate solid phase at the bottom of the vessel. However, a cloud point can still be reached by reducing pressure, indicating that a substantial amount of surfactant still dissolves in HFC-134a. The addition of water stabilizes the system, and an optically transparent solution can be obtained. As the surfactant concentrations increases from (1.85×10^{-3} to 5.60×10^{-3}) M, there is an appreciable increase in cloud-point pressure. When the surfactant concentrations increase from (1.85×10^{-3} to 5.60×10^{-3}) M, the amount of micelles per unit volume increases gradually, and the micelle-micelle distance decreases, which strengthens attractive micelle-micelle interactions. Thus, higher pressures are required to strengthen tail-solvent interactions to prevent phase separation.

The P - T phase diagram for W/HFC-134a microemulsions stabilized by the two surfactants (DPSS and DBSS) is given in Figure 5. The surfactant concentrations for DPSS and DBSS are 0.0037 M with $W_o = 20$. However, DHSS and DOSS cannot form microemulsions in HFC-134a because their solubilities in HFC-134a are smaller. Microemulsions cannot be formed at a significantly lower surfactant concentration, indicating that hydrocarbon chain length affects the cloud pressure greatly. The longer hydrocarbon chain, the higher cloud pressure the surfactant has, as reported by Bousquet et al.²² The fact that the surfactant with the longest hydrocarbon chain has the highest cloud-point pressure even at lower surfactant concentrations is very interesting. The HFC-134a-philicity of the tail group must

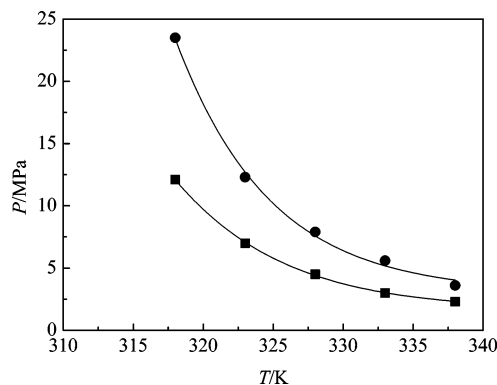


Figure 5. Comparison of P - T phase diagram for W/HFC-134a microemulsions supported by two different surfactants DBSS and DPSS at 0.0037 M and $W_o = 20$: \blacksquare , DBSS; \bullet , DPSS.

be decreasing with an increasing length of the hydrocarbon chain, and the tail-solvent interactions are too weak to compensate for attractive micelle-micelle interactions. This is in accordance with previous findings on CO_2 -philic chelating agents³⁸ and homogeneous catalysts³⁹ that small fluoroalkyl chains are as effective as long fluoroalkyl or fluoropolymer chains for solubility enhancement in scCO_2 .

Conclusion

A series of AOT analogue surfactants were synthesized and characterized. A static method coupled with gravimetric analysis was developed for measuring the solubility of surfactants in scCO_2 and HFC-134a fluids. The solubility of a particular solute was affected by pressure, temperature, solvent polarity, and the number of carbon atoms of surfactant. The solubility of polar solutes in the HFC-134a medium was found to be much higher than that in the most commonly used supercritical solvent CO_2 . The pressure-temperature phase diagrams for W/HFC-134a microemulsions stabilized by the surfactants were determined using cloud-point measurements. The phase behaviors of different surfactants as a function of temperature, pressure, and W_o are obtained in this work, which are useful in formation of nanoparticles synthesis in these microemulsions.

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