Published in final edited form as:

Fluid Phase Equilib. 2010 November 25; 298(2): 212–218. doi:10.1016/j.fluid.2010.07.020.

Phase equilibrium for surfactant Ls-54 in liquid CO₂ with water and solubility estimation using the Peng-Robinson equation of state

Pedro J. Tarafa^a and Michael A. Matthews^{b,*}

^aDepartment of Engineering Sciences and Materials, University of Puerto Rico, Mayagüez PR 00681 USA

^bDepartment of Chemical Engineering, University of South Carolina, Columbia SC 29208 USA

Abstract

It is known that the commercial surfactant Dehypon® Ls-54 is soluble in supercritical CO₂ and that it enables formation of water-in-CO₂ microemulsions. In this work we observed phase equilibrium for the Ls-54/CO₂ and Ls-54/water/CO₂ systems in the liquid CO₂ region, from 278.15 - 298.15 K. In addition, the Peng-Robinson equation of state (PREOS) was used to model the phase behavior of Ls-54/CO₂ binary system as well as to estimate water solubilities in CO₂. Ls-54 in CO₂ can have solubilities as high as 0.086 M at 278.15 K and 15.2 MPa. The stability of the microemulsion decreases with increasing concentration of water, and lower temperatures favor increased solubility of water into the one-phase microemulsion. The PREOS model showed satisfactory agreement with the experimental data for both Ls-54/CO₂ and water/CO₂ systems.

Keywords

carbon dioxide; surfactant Ls-54; Peng-Robinson; solubility; microemulsion

1. Introduction

Compressed carbon dioxide (CO₂), both in the subcritical and supercritical (SC) state, may be a promising alternative for decontamination of biomaterials and medical devices. In its compressed state, CO₂ has excellent physical properties that enable rapid penetration into structures for the removal of contaminants [1-7]. However, CO₂ does not have the solvation power needed to solubilize large or polar compounds, such as proteins and biomolecules. Certain surfactants can significantly increase the solubility of heavy organics and polar compounds in compressed CO₂ [8,9]. The strategy is to create a water-in-CO₂ microemulsion phase structure to enhance the water content in CO₂, and therefore, make it available for dissolving large or polar compounds. In these systems, the polar heads of the surfactant orient inwards to the micelle core, forming tiny aqueous domains (between 5 - 100 nm in diameter), as seen in Figure1. Such micelles are also known as reverse micelles.

© 2010 Elsevier B.V. All rights reserved.

*Corresponding author. Swearingen Engineering Center, 301 Main St, Columbia SC 29208 Tel. 803-777-0556. Fax: 803-777-8265 matthews@cec.sc.edu .

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

The formation of stable water-in-CO₂ microemulsions is challenging due to the unusually strong attractive interdroplet interactions, which results from the weak solvation of the surfactant tails by CO₂ [10-12]. This weak solvation is due primarily to the low polarizability of CO₂ compared to organic solvents [13]. A great deal of effort has been directed in designing surfactants with an effective “CO₂-philic” tail since relatively few conventional surfactants are soluble in supercritical CO₂ [14].

Early attempts by Consani and Smith to disperse water into SC CO₂ phase showed that most conventional surfactants are insoluble in CO₂ [14]. Later, Hoeffling *et al.* designed effective fluorosurfactants for compatibility with CO₂ [15]. The fluorinated chains provide low cohesive energy density groups, thereby promoting low solubility parameters and low polarizability. Many papers on the design of CO₂-compatible surfactants and formation of water-in-CO₂ microemulsions have since emerged. The most effective compounds reported to stabilize water-in-CO₂ microemulsions are the partially or fully fluorinated surfactants [16-18], especially the fluorinated sodium bis(2-ethylhexyl)sulfosuccinate (AOT) analogue [19,20].

Although high CO₂ compatibility can be achieved by fluorinated surfactants, their cost high and toxicity is a concern. Therefore, efforts have been directed toward hydrocarbon surfactants [21-23], hybrid fluorocarbon-hydrocarbon surfactants [24-26], and O-surfactants by incorporating oxygen into the surfactant tails [27]. Different techniques have been used to characterize the water-in-CO₂ microemulsions, including nuclear magnetic resonance (NMR) [28-29], small angle x-ray scattering (SAXS) [30], and UV-vis spectrophotometry [30,31].

The ability to dissolve highly polar or ionic species in the polar microdomains of the microemulsion is, to a large part, dependent upon the amount of water incorporated into the microemulsion. Thus, the molar water-to-surfactant ratio (W_0) is a convenient measure of the polar solvent strength of the microemulsion. For ionic surfactants, the microemulsion will have a solvent power for polar species approaching that of bulk water when W_0 is above 10. The W_0 value can be adjusted through controlled addition of water to the solution or through the manipulation of the pressure or temperature of the solution. Nonionic surfactant systems are much less susceptible to this effect. The curvature of the interfacial film of the microemulsion droplet is determined by a balance between the electrostatic interactions of the head groups and repulsive interactions of the surfactant tail group.

Whereas most of the early work utilized fluorinated surfactants, recent advancements have been made with hydrocarbon surfactants, although with somewhat limited W_0 and thus small polar water domains. Ryoo *et al.* [21] demonstrated a highly branched nonionic hydrocarbon surfactant, octa(ethylene glycol) 2,6,8-trimethyl-4-nonyl ether, that could form a with up to 2% water, capable of solubilizing proteins such as lysozyme. Recently, it has been shown that ethoxylated surfactants are highly soluble in CO₂ and can produce low interfacial tensions between water and CO₂ [13]. One such surfactant is Dehypon® Ls-54 (a non-fluorinated and non-ionic surfactant), which forms hydrated reverse micelles in SC CO₂ with water uptake up to 0.5 wt % with 1.5 wt % LS-54 [30]. Ls-54 is an ethoxylated alcohol with five ethylene oxide (EO) and four propylene oxide (PO) groups; its chemical structure is H-(CH₂)₁₂-(O-CH₂-CH₂)₅-O-(CH-(CH₃)-CH₂-O)₄-H. The reason for high solubility may be that Ls-54 surfactant has a low molecular weight and four PO groups, which are CO₂-philic [32,33].

Hence, it is the purpose of this study to determine solubilities of surfactant Ls-54 in liquid CO₂ by extending Liu *et al.* work [30] to a temperature range of 278.15 - 298.15 K. Also, we extended measurements on the phase behavior of Ls-54/water/CO₂ ternary mixture to the

liquid CO₂ regime. The experimental evaluation was carried out using the static synthetic method, as described elsewhere [34].

In addition, the Peng-Robinson (PR) equation of state (EOS) [35] with van der Waals mixing rules were used to formulate a mathematical model to predict and estimate solubilities of Ls-54 and water in CO₂. PREOS is selected because of its good performance in predicting liquid densities, especially for non-polar materials [36], and for reasonable accuracy near the critical point [37]. This method has one interaction parameter for binary mixtures, k_{ij} , which is sensitive in predicting solubilities and is generally determined by fitting experimental data.

2. Materials and Methods

2.1 Materials

Dehypon® Ls-54 surfactant was donated by Cognis Corporation, Ambler, PA. Bonded grade CO₂ (99.8% purity) was supplied by National Welders Supply Co., Durham, NC. Deionized (DI) water was also used throughout the experiments.

2.2 Apparatus

The static synthetic method was used for the phase equilibrium measurements on the binary Ls-54/CO₂ and ternary Ls-54/water/CO₂ mixtures. A schematic of the apparatus is shown in Figure 2. The major components are a phase monitor system (SPM 20, Thar Technologies, Inc.), and an environmental chamber (Model LU-113, Espec Corp.). The phase monitor system includes a high-pressure stainless steel variable volume view cell equipped with a video camera and sapphire windows (not shown) to allow visualization of the contents under pressure. A thermocouple (dual 'J' type, Omega Engineering Inc.) and a pressure transducer (Sensotec transducer, model TJE/743-11) located on the side of the cell allow measurement of the vessel temperature and pressure. All electronic measurements are displayed on a monitor and computer. The cell can be pressurized by either a hand pump (manually movable piston) or a high pressure syringe pump (ISCO Pumps, model 500 HP Custom). The view cell was placed inside an environmental chamber to control the temperature. The mixtures in the view cell were stirred using a magnetic bar and a stirring plate.

2.3 Experimental

Solubility data were obtained by cloud point measurements. Phase separation was observed through the sapphire window using the video monitor.

CO₂ densities at a given pressure and temperature were computed from the modified Benedict-Webb-Rubin EOS software (designed by Dr. David Bush, Georgia Institute of Technology) that calculates the thermo-physical properties of CO₂. The syringe pump accurately registered the total volume of CO₂ supplied to the view cell. The mass of CO₂ in the solvent mixture was thus determined from the CO₂ volume and density at the loading conditions.

The procedure to obtain the cloud point pressures for the Ls-54/water/CO₂ ternary mixture is described; the procedure for Ls-54/CO₂ is analogous. A suitable amount of the surfactant and the desired amount of DI water were initially charged into the high-pressure view cell. Air in the cell was replaced by CO₂ purging five times at 0.21 MPa. The cell was sealed and placed in the environmental chamber. At a fixed temperature, CO₂ was slowly pumped into the cell with the syringe pump. The fluids were simultaneously stirred. After reaching thermal equilibrium, the pressure was increased with the hand pump until a homogeneous, transparent single-phase solution was observed. At that point the stirring was stopped and

the cell pressure was slowly decreased at a rate of approximately 0.007 MPa per second until the solution became cloudy. The cloud point pressure was recorded, and the pressurization/depressurization process was repeated three times at each condition. The system temperature was then either raised or lowered and the entire procedure was repeated to obtain additional data without having to reload the cell. In this manner isopleths were obtained. Each set of measurements for a specific composition was done at temperatures ranging from 278.15 to 298.15 K.

3. Model

The standard PREOS is given by

$$P = \frac{RT}{V-b} - \frac{a}{V^2+2bV-b^2} \quad (1)$$

For pure substances, a and b are computed from critical properties;

$$a = (0.457235 R^2 T_c^2 / P_c) \alpha \quad (2)$$

$$b = 0.0778 RT_c / P_c \quad (3)$$

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) (1 - \sqrt{T/T_c}) \right]^2 \quad (4)$$

P_c , T_c , and ω are critical pressure, critical temperature, and acentric factor, respectively.

For binary mixtures, the van der Waals mixing rules for the attraction and repulsive parameters (a and b) are given by the following equations

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$b = \sum_i x_i b_i \quad (6)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (7)$$

where k_{ij} is the binary interaction parameter. For purpose of this work the subscript i will represent the solvent (CO₂) and j the solute.

For dilute solutions, the solute fugacity coefficient can be calculated as [35,36]

$$\ln \phi_j = \ln \left(\frac{RT}{P(V-b_i)} \right) + \frac{b_j}{b_i} \left(\frac{PV}{RT} - 1 \right) - \frac{a_{ij}}{2\sqrt{2}RTb_i} \times \left(\frac{2a_{ij}}{a_{ii}} - \frac{b_j}{b_i} \right) \ln \left(\frac{V + (1+\sqrt{2})b_i}{V + (1-\sqrt{2})b_i} \right) \quad (8)$$

where ϕ is the fugacity coefficient expressed as

$$\phi_j = \frac{f_j}{x_j P} \quad (9)$$

f_j is the fugacity of the solute at equilibrium in the mixture and x_j represents its molar fraction.

The saturation value or solubility (x_j) for a solute of low volatility (as in the case of water and Ls-54) is computed as

$$\ln x_j = \ln \left(\frac{P_v}{P} \right) - \ln \phi_j + \frac{\bar{V}_j P}{RT} \quad (10)$$

where P_v is the vapor pressure of the solute at T and $\bar{V}_j$ is the partial molar volume of the solute, which can be considered equal to its molar volume at room conditions. This equation was previously suggested [36] and tested [36,38] to describe the solubility of low-volatile and incompressible substances in compressed fluids. In this study, Eq. (10) is employed to calculate the solubility of either water or Ls-54 in compressed CO_2 fitting the experimental data by finding the binary interaction parameter (k_{ij}) that best adjusts at each temperature. Maple™ was used to solve the equations and predict the isotherm solubilities.

4. Results and Discussions

4.1 Solubility of Ls-54 surfactant in liquid CO_2

The phase behavior of Ls-54/ CO_2 system was investigated at different compositions in the pressure-temperature domain as shown in Figure 3. The surfactant mole fraction was varied from 1.73×10^{-3} to 3.48×10^{-3} . A clear one-phase solution was observed above the solid line for each Ls-54 mole fraction. As seen in Fig. 3, at higher temperatures the pressure necessary to retain Ls-54 in the liquid CO_2 increases. Because an increase in temperature causes a reduction in the continuous phase density, a corresponding increase in pressure is necessary to maintain Ls-54 solubility. Also as temperature increases, CO_2 energetic interactions with the surfactant decrease, reducing stability of the structure. At constant temperature, the pressure required to dissolve the surfactant increases with the mole fraction of the surfactant.

The pressure dependence of the solubility of Ls-54 between 278.15 - 298.15 K is shown in Figure 4. As expected, the solubility increases with pressure (or density) at a given temperature. Also, for a given pressure the solubility is higher at lower temperatures. This is because the effect of temperature on the solvent power of CO_2 is dominant and, thus, the solubility is reduced by increasing temperature. In summary, these results indicate that the solubility of surfactant Ls-54 in liquid CO_2 can be as high as 0.086 M at 278.15 K and 15.2 MPa.

4.2 Solubility prediction for the Ls-54/ CO_2 binary system with the PREOS

The PREOS was evaluated fitting solubilities for the binary mixture of surfactant Ls-54 in liquid CO_2 . Critical parameters (T_c and P_c), the acentric factor (ω) and vapor pressure (P_v) for Ls-54 are not available in the literature and were estimated as follows. T_c and P_c were estimated with the group-contribution based method reported by Marrero and Gani [39] for organic compounds, while the acentric factor was determined from a correlation proposed

by Han and Peng [40]. The vapor pressure was estimated by using an additive rule over the partial vapor pressure for each constituent in this compound (i.e. dodecane, ethylene oxide, and propylene oxide). Table 1 lists the estimated parameters for Ls-54.

The experimental solubilities, given as mole fraction of Ls-54 in CO₂, were compared to the predicted solubilities from the PREOS. Figure 5 shows two plots (5a and 5b), represented by isotherms, that compare the calculated and experimental solubilities at 288.15 and 298.15 K, respectively. The experimental mole fractions of Ls-54 in the CO₂-rich phase represent the mean and standard deviation for each value. In general the agreement between the predicted and the experimental data for all temperatures is satisfactory. The large majority of the data are within 10% or less of the predicted values, but differences between 20 – 30% are observed at the lower pressure in each isotherm. As temperature is decreased, the difference between the experimental and the predicted data becomes larger at the lowest solubility point (i.e. at very dilute mixtures), probably due to larger experimental uncertainty. Apart from this, good predictions are obtained for the entire temperature range evaluated in this work. Table 2 summarizes the solubility data (experimental and predicted) and the fitted binary interaction parameters by temperature. A t-test of difference of means at a 95% of confidence level was used to judge the significance of the difference between the predicted and experimental data. No significant difference was found.

The fitted PR binary interaction parameters (k_{ij}) were dependent on temperature. According to Eq. (7), the magnitude of a_{ij} is reduced by an increase in k_{ij} . Thus, molecular interactions would be expected to decrease with a temperature rise. As seen in Table 2, k_{ij} values increase as the temperature is increased. It needs to be pointed out that important contributing factors in obtaining these results were the estimates obtained for the unknown parameters of surfactant Ls-54. Since the equations used to predict the phase behavior are strongly dependent on these properties (i.e. T_c , P_c and P_v), the availability of measured data for Ls-54 would allow higher level of accuracy for predicting the solubility, as well as for the binary interaction parameter.

4.3 Ls-54/water/CO₂ ternary mixture

Cloud point pressures for the CO₂/Ls-54/water ternary system were also measured at temperatures from 288.15 to 298.15 K. The compositions of water were varied (0.55, 0.70, 0.84, and 1 wt %), keeping the mole fraction of Ls-54 at about 1.75×10^{-3} (2.5 wt % Ls-54). Figure 6 shows the dependence of the dissolution or cloud point pressure on the mole fraction of water at a fixed mole fraction of Ls-54. As shown in this figure, the cloud point pressure increases with water mole fraction. This behavior may indicate that the stability of the emulsion decreases with increasing concentration of water. For all experiments, the cloudy phase was stable and did not precipitate over prolonged periods of time even when agitation was stopped. Turbidity increased with decreasing pressure.

CO₂ itself has some affinity for water [33,41]. This is because water molecules will organize themselves in polyhedral cavities with CO₂ [42-44] through specific hydrogen bondings between the oxygen atoms in CO₂ and water molecules [45,46]. Hence, it is expected that water is distributed between the surfactant aggregates and CO₂ in such a way as to minimize the overall free energy of the system. Then as more water is added, a second phase appears. An important parameter used to describe the water content in the microemulsion system is the W_0 . In this study the corrected molar ratio of water-to-surfactant, expressed by W_0^c , was estimated using the following equation [47]:

$$W_0^c = W_0^t - W_0^{CO_2} \quad (11)$$

where W_0^t represent the ratio of total amount of water loaded into the system per surfactant and $W_0^{CO_2}$ indicates the ratio of the solubility (mole fraction) of water in pure CO_2 at each condition per surfactant. W_0^c can be considered as the quantity of water in the reverse micelles (i.e. the number of water molecules held by a surfactant molecule in emulsion) if all of the surfactant molecules and excess water molecules over solubility in the system are used to form the microemulsions.

$W_0^{CO_2}$ values were estimated using the PREOS approach because the available experimental data were limited for the experimental conditions. Hence, the same procedure taken for the Ls-54/ CO_2 binary system (employing Eqs. 1 – 10) was used again, but to fit published isotherms of experimental solubilities of water in CO_2 , taken from King *et al.* [48]. Critical parameters, molar volumes, and acentric factors for water were found in the literature. The fugacity coefficient for water (ϕ_w) was calculated with Eq. (8) assuming infinite dilution of water. In this limit, water/water interactions and complications from hydrogen bonding are not expected. Figure 7 compares the solubility (in mole fraction) of water in CO_2 as a function of pressure at constant temperature obtained from the PREOS with the available experimental data. Solid lines represent the calculated results using the model whereas points indicate the experimental data from King *et al.* [48]. The agreement between the calculated and experimental phase boundaries is satisfactory for all the isotherms. The percent differences between the solubilities calculated at 288.15 K from the experimental data fall below 3.4%. For 293.15 K, the highest difference is found at 12.7 MPa where the predicted solubility is 8.7% higher than the experimental datum. At 298.15 K, all the predicted solubilities agree for no more than 2% of difference except for the first three points where the predicted solubilities are 5, 8 and 11% higher than the experimental data, respectively. The binary interaction parameter is strongly dependent on temperature. As seen in Figure 7, the k_{ij} values fall from 0.1990 to 0.1925 as the temperature rises from 288.15 to 298.15 K.

Table 3 shows W_0^t , the calculated W_0^c , and the dissolution pressures for the CO_2 /Ls-54/water ternary system at the evaluated temperatures. As observed in Table 3, the W_0^c increases as the dissolution pressure of the ternary system increases. Also, W_0^c values increased with decreasing temperature, suggesting that reducing temperature favors more solubility of water into the one-phase microemulsion. This is due to the decrease in water solubility in pure CO_2 when temperature is increased. For nonionic surfactants, a decrease in temperature favors interaction of the surfactant with water due to a greater degree of hydrogen bonding with the EO head groups. Consequently, the natural curvature about the water core should increase, providing a greater water uptake capacity. The ability to form a dilute microemulsion with dispersed water when the surfactant prefers the water phase is well-known for water-oil systems. In this case, the microemulsion is formed by the favorable entropy of mixing a small amount of water in a large amount of continuous phase [49].

The results for W_0^c imply that water domains are present in the reverse micelles, which has been previously demonstrated by solubilization of biomacromolecule lysozyme and methyl orange [30]. The calculated water uptake by the reverse micelle under the tested conditions oscillated from 0.47 to 0.87 wt %. According to Ryoo *et al.* [21], two water molecules are required to solvate the two pairs of non-bonded electrons on the ether group (EO) of surfactant Ls-54. In our study, it is observed that the $W_0^c / [EO] \geq 2$ for the conditions having water-to-surfactant loads (W_0^t) above 12. Thus, it appears that the core contains free water molecules with properties like bulk water for $W_0^t \geq 12$ in the liquid CO_2 region. Further

analysis using dynamic light scattering, FTIR spectroscopy or a solvatochromic probe could confirm this hypothesis.

In the other hand, the values of W_0^c may not represent the correct ratios of water and Ls-54 molecules in the microemulsion. For instance, the solubility of Ls-54 in CO₂ is neglected in Eq. (11). If this solubility is considered, then the W_0^c values will become larger. In addition, the solubility of water and Ls-54 in CO₂ phase for the ternary system will be different from that in pure CO₂ due to entrainer effect of each component. If water has higher solubility in CO₂ in the presence of Ls-54, then the W_0^c values will decrease.

5. Conclusions

This study revealed that Ls-54 in CO₂ can have solubilities as high as 0.086 M at 278.15 K and 15.2 MPa. More surfactant Ls-54 can be dissolved by CO₂ at the liquid state than in the supercritical region reported by Liu *et al.* [30]. Hence, more Ls-54 can be dissolved by CO₂ as temperature decreases.

For the ternary mixture, the cloud point pressure increases as the water mole fraction increases. Hence, the stability of the microemulsion decreases with increasing concentration of water. The corrected water-to-surfactant ratios increase as the dissolution pressure of the ternary system increases. At a given pressure the corrected water-to-surfactant ratio increases with decreasing temperature. Hence, lower temperature favors more solubility of water into the one-phase microemulsion.

The PREOS model showed satisfactory agreements with the experimental data for both Ls-54/CO₂ and water/CO₂ systems. Therefore, it could be successfully implemented to predict reliable solubilities for the conditions and parameters employed in this work.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors acknowledge the Alfred P. Sloan Foundation and the South East Alliance for Graduate Education and the Professoriate (SEAGEP) for providing financial assistance for Pedro J. Tarafa. Special thanks are also given to Angel E. Mercado (USC graduate student) for his help and suggestions with the mathematical model.

7. References

- [1]. Bok E, Kelch D, Schumacher KS. Solid State Technol. 1992; 35:117–120.
- [2]. Fukushima Y, Wakayama H. J. Phys. Chem. B. 1999; 103:3062–3064.
- [3]. Zhang X, Han B. Clean Soil Air Water. 2007; 35:223–229.
- [4]. Jessop, PG.; Leitner, W. Chemical Synthesis Using Supercritical Fluids. Jessop, PG.; Leitner, W., editors. Wiley; Weinheim: 1999. p. 213
- [5]. Jung JM, Ganapathy HS, Yuvaraj H, Johnston KP, Lim KT. Microelectronic Eng. 2009; 86:165–170.
- [6]. Mukhopadhyay M. J. Chem. Technol. Biotechnol. 2009; 84:6–12.
- [7]. Weber DC, McGovern WE, Moses JM. Met. Finish. 1995; 93:22–26.
- [8]. Li QS, Zhang ZT, Zhong CL, Liu YC, Zhou QR. Fluid Phase Equilib. 2003; 207:183–192.
- [9]. Li QS, Zhong CL, Zhang ZT, Zhou QR. Korean J. Chem. Eng. 2004; 21:1173–1177.
- [10]. Peck DG, Johnston KP. Macromolecules. 1993; 26:1537–1545.
- [11]. Meredith JC, Johnston KP. Langmuir. 1999; 15:8037–8044.

- [12]. Lee CT, Johnston KP, Dai HJ, Cochran HD, Melnichenko YB, Wignall GD. *J. Phys. Chem. B.* 2001; 105:3540–3548.
- [13]. O'Neill ML, Cao Q, Fang M, Johnston KP, Wilkinson SP, Smith CD, Kerschner JL, Juveller SH. *Ind. Eng. Chem. Res.* 1998; 37:3067–3079.
- [14]. Cosani KA, Smith RD. *J. Supercrit. Fluids.* 1990; 3:51–65.
- [15]. Hoefling TA, Enick RM, Beckman EJ. *J. Phys. Chem.* 1991; 95:7127–7129.
- [16]. Nagai T, Fujii K, Otake K, Abe M. *Chem. Letters.* 2003; 32:384–385.
- [17]. Sagisaka M, Fujii T, Ozaki Y, Yoda S, Takebayashi Y, Kondo Y, Yoshino N, Sakai H, Abe M, Otake K. *Langmuir.* 2004; 20:2560–2566. [PubMed: 15835124]
- [18]. Keiper JS, Behles JA, Bucholz TL, Simhan R, DeSimone JM, Lynn GW, Wignall GD, Melnichenko YB, Frielinghaus H. *Langmuir.* 2004; 20:1065–1072. [PubMed: 15803679]
- [19]. Nagai T, Fujii K, Otake K, Abe M. *Chem. Letters.* 2007; 36:92–93.
- [20]. Liu ZT, Wu J, Liu L, Sun CA, Song LP, Gao ZW, Dong WS, Lu J. *J. Chem. Eng. Data.* 2006; 51:1761–1768.
- [21]. Ryoo W, Webber SE, Johnston KP. *Ind. Eng. Chem. Res.* 2003; 42:6348–6358.
- [22]. Eastoe J, Dupont A, Steytler DC, Thorpe M, Gurgel A, Heenan RK. *J. Colloid Interface Sci.* 2003; 258:367–373. [PubMed: 12618107]
- [23]. Liu JC, Han BX, Wang ZW, Zhang JL, Li GZ, Yang GY. *Langmuir.* 2002; 18:3086–3089.
- [24]. Dupont A, Eastoe J, Martin L. *Langmuir.* 2004; 20:9960–9967. [PubMed: 15518481]
- [25]. Sagisaka M, Fujii T, Koike D, Yoda S, Takebayashi Y, Furuya T, Yoshizawa A, Sakai H, Abe M, Otake K. *Langmuir.* 2007; 23:2369–2375. [PubMed: 17309200]
- [26]. Harrison K, Goveas J, Johnston KP, Orear EA. *Langmuir.* 1994; 10:3536–3541.
- [27]. Eastoe J, Gold S, Rogers S, Wyatt P, Steytler DC, Gurgel A, Heenan RK, Fan X, Beckman EJ, Enick RM. *Angew. Chem. Int. Ed.* 2006; 45:3675–3677.
- [28]. Thurecht KJ, Hill DJT, Whittaker AK. *J Supercrit. Fluids.* 2006; 38:111–118.
- [29]. Fremgen DE, Smotkin ES, Gerald RE, Klingler RJ, Rathke JW. *J. Supercrit. Fluids.* 2001; 19:287–298.
- [30]. Liu JC, Han BX, Zhang HL, Li GZ, Zhang XG, Wang J, Dong BZ. *Chem. Eur. J.* 2002; 8:1356–1360.
- [31]. Holmes JD, Ziegler KJ, Audriani M, Lee CT, Bhargava PA, Steytler DC, Johnston KP. *J. Phys. Chem. B.* 1999; 103:5703–5711.
- [32]. Chen QL, Beckman EJ. *Green Chem.* 2008; 10:934–938.
- [33]. Mawson S, Yates MZ, O'Neill ML, Johnston KP. *Langmuir.* 1997; 13:1519–1528.
- [34]. Gupta, RB.; Shim, JJ. *Solubility in Supercritical Carbon Dioxide.* Gupta, RB.; Shim, JJ., editors. CRC Press; Boca Raton, FL: 2007. p. 5-11.
- [35]. Peng D, Robinson DB. *Ind. Eng. Chem. Fundam.* 1976; 15:59–64.
- [36]. Bartle KD, Clifford AA, Shilstone GF. *J. Supercrit. Fluids.* 1992; 5:220–225.
- [37]. Valderrama JO. *Ind. Eng. Chem. Res.* 2003; 42:1603–1618.
- [38]. Sabirzyanov AN, Il'in AP, Akhunov AR, Gumerov FM. *High Temp.* 2002; 40:203–206.
- [39]. Marrero J, Gani R. *Fluid Phase Equilib.* 2001; 183:183–208.
- [40]. Han BX, Peng DY. *Can. J. Chem. Eng.* 1993; 71:332–334.
- [41]. Wiebe R. *Chem. Rev.* 1941; 29:475–481.
- [42]. Mori YH. *Energy Conversion and Management.* 1998; 39:1537–1557.
- [43]. Sloan, ED.; Carolyn, AK. *Clathrate hydrates of natural gases.* third ed. CRC Press; New York: 2007.
- [44]. Teng H, Yamasaki A. *Int. J. Heat Mass Transfer.* 1998; 41:4315–4325.
- [45]. Ludwig R. *Angew Chem. Int. Ed.* 2001; 40:1808–1827.
- [46]. Sato H, Matubayasi N, Nakahara M, Hirata F. *Chem. Phys. Lett.* 2000; 323:257–262.
- [47]. Sagisaka M, Yoda S, Takebayashi Y, Otake K, Kondo Y, Yoshino N, Sakai H, Abe M. *Langmuir.* 2003; 19:8161–8167.
- [48]. King MB, Mubarak A, Kim JD, Bott TR. *J. Supercrit. Fluids.* 1992; 5:296–302.

- [49]. Johnston KP, Cho D, DaRocha SRP, Psathas PA, Ryoo W, Webber SE, Eastoe J, Dupont A, Steytler DC. *Langmuir*. 2001; 17:7191–7193.

Figure 1.
Structure of a water-in-CO₂ microemulsion droplet.

Figure 2. Schematic diagram of the phase monitor system and its components. (1) CO₂ gas cylinder; (2) syringe pump; (3) pump control; (4) hand pump; (5) environmental chamber; (6) variable volume view cell; (7) stirrer plate; (8) video camera; (9) TV or monitor; (10) controller.

Figure 3.

Cloud point profile for Ls-54/CO₂ binary mixture at different compositions. (◆) Ls-54 mole fraction = 3.48×10^{-3} ; (■) Ls-54 mole fraction = 3.03×10^{-3} ; (▲) Ls-54 mole fraction = 2.61×10^{-3} ; (●) Ls-54 mole fraction = 1.73×10^{-3} .

Figure 4. Solubility of Ls-54 in liquid CO₂ at different conditions. (◆) 278.15 K; (■) 283.15 K; (▲) 288.15 K; (○) 293.15 K; (×) 298.15 K.

Figure 5.

Phase diagrams for Ls-54 in CO₂: (a) T = 288.15 K and $k_{ij} = 0.863$; (b) T = 298.15 K and $k_{ij} = 0.9$. Solid lines represent the solubility from the PREOS model and points the experimental data (x denotes the mole fraction solubility of Ls-54 in CO₂).

Figure 6. Effect of temperature and water fraction on cloud point pressure of Ls-54 in CO₂: (◆) 288.15 K; (■) 293.15 K; (▲) 298.15 K. [Ls-54] = 1.75×10^{-3} mol/mol CO₂ (2.5% wt).

Figure 7.

Experimental and predicted solubility of water in CO₂ as a function of pressure. Solid lines represent the solubility from the PREOS model whereas points indicate the experimental data from King *et al.* [48]. (●) 288.15 K and $k_{ij} = 0.1990$; (×) 293.15 K and $k_{ij} = 0.1906$; (■) 298.15 K and $k_{ij} = 0.1925$.

Table 1

Estimated physical properties and parameters for Dehypon® Ls-54.

T_c (K) ^a	P_c (MPa) ^a	ω	b	$P_v \times 10^3$ (MPa) at 288.15 K	$P_v \times 10^3$ (MPa) at 293.15 K	$P_v \times 10^3$ (MPa) at 298.15 K
889.5	9.54	1.937		2.91	4.24	6.3

^aCalculated from Marrero and Gani [39]

^bCalculated from Han and Peng [40]

Table 2Solubilities and PR binary interaction parameters for Ls-54 in CO₂ at different temperatures.

T (K)	k_{ij}	P (MPa)	Solubility (mol Ls-54/mol CO ₂) $\times 10^3$	
			PR model	Experimental
298.15	0.900	16.53	1.37	1.73
		19.38	2.32	2.50
		20.71	2.99	3.00
		22.02	3.87	3.70
293.15	0.878	14.05	1.28	1.73
		16.91	2.20	2.50
		18.53	3.04	3.00
		20.09	4.17	3.70
288.15	0.863	13.25	1.40	1.73
		15.89	2.39	2.50
		16.89	2.94	3.00
		18.42	4.06	3.90
283.15	0.849	11.33	1.23	1.73
		14.16	2.22	2.50
		15.56	3.00	3.00
		17.21	4.29	3.90
278.15	0.830	9.67	1.32	1.73
		12.46	2.42	2.50
		13.51	3.06	3.00
		15.24	4.50	3.90

Table 3

Cloud point pressure for Ls-54 in CO₂ with different water concentrations and W_0^c values for the CO₂/Ls-54/water system.

		288.15 K			293.15 K			298.15 K		
[Ls-54] × 10 ³ (mol/mol CO ₂)	wt % H ₂ O	W_0^t	P (MPa)	ρ_{CO_2} (mol/L)	W_0^c	P (MPa)	ρ_{CO_2} (mol/L)	W_0^c	P (MPa)	ρ_{CO_2} (mol/L)
1.75	0.55	8	17.84	21.54	6.45	20.18	21.33	6.07	20.90	20.92
1.75	0.70	10	20.25	21.84	8.42	21.94	21.55	8.04	22.31	21.11
1.75	0.84	12	20.51	21.92	10.42	21.60	21.65	10.04	23.69	21.29
1.75	1.00	14	22.90	22.13	12.41	24.06	21.80	12.04	25.35	21.49
										12.46