542 *J. Chem. Eng. Data* **2006,** *51,* 542−544

Solubilities of Dodecylpolyoxyethylene Polyoxypropylene Ether in Supercritical Carbon Dioxide

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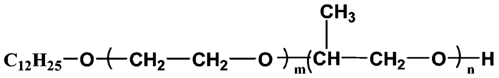
The equilibrium solubilities of two dodecylpolyoxyethylene polyoxypropylene ether nonionic surfactants (A(EO)-BmB(PO)$_n$) in supercritical carbon dioxide were measured at temperatures ranging from (308 to 328) K and pressures from (13.6 to 32.0) MPa in a stainless steel variable-volume view cell. The experimental data were correlated using a semiempirical model. The calculated results show satisfactory agreement with the experimental data.

Introduction

Carbon dioxide is an attractive alternative to certain organic solvents since it is nontoxic, nonflammable, inexpensive, and relatively nonpolluting. Examples of interesting applications based on compressed and supercritical CO_2 include polymerization[1] and particle formation by rapid expansion from supercritical solution.[2] However, a limitation is that high molecular weight or hydrophilic molecules are often insoluble in supercritical CO_2. Fortunately, hydrophilic substances, such as amino acids and hydrophilic proteins, may be solubilized in reversed micelles and microemulsions in supercritical CO_2.[3−5]

Initial studies indicate that the aggregation of surfactants to form reversed micelles in CO_2 is much more limited. Consani and Smith[6] had tested the solubility of over 130 commercially available surfactants in supercritical CO_2 at 50 °C and (10.0 to 50.0) MPa. Practically all of them were insoluble or only slightly soluble, and they did not solubilize a significant amount of water. Recently a number of research groups have subsequently investigated the design of so-called "CO_2-philic" surfactants that are soluble in CO_2 at moderate pressure. Johnston and coworkers[7] found that the surfactant with a perfluoroalkyl polyether (PFPE) tail could form micelles that can solubilize significant amounts of water. Nonetheless, there are concerns about toxicity of this class of surfactants. Silicones (polydimethyl-siloxanes) are also generally considered to be CO_2-philic. However, silicone-functional amphiphiles require higher pressure to generate a single-phase solution in supercritical CO_2 than do fluoroacrylates or fluoroether analogues. Mcfann et al.[8] found that certain nonionic surfactants solubilized excess water into CO_2 when a cosurfactant was added. So far, SC-CO_2/non-fluorous and SC-CO_2/non-silicone containing nonionic surfactants systems that can absorb a significant amounts of water have been seldom reported in the literature.

In this work, we found that A(EO)$_m$(PO)$_n$ surfactants shown in Figure 1 were soluble in SC-CO_2, although they are non-fluorous and non-silicone containing surfactants. In addition, they also have advantages of low toxicity and low price as compared with fluorous surfactants. The results of this work provide useful information for designing other low-cost CO_2-philic non-fluorous and non-silicone containing surfactants.



$C_{12}H_{25}-O-(CH_2-CH_2-O)_m-(CH(CH_3)-CH_2-O)_n-H$

Figure 1. Structures of surfactants used in this work. A(EO)$_9$(PO)$_2$: $m = 9$, $n = 2$; A(EO)$_9$(PO)$_3$: $m = 9$, $n = 3$.

Experimental Section

Carbon dioxide was commercially purchased from B.O.D. Company, Shanghai (purity 99.95%, mass fraction). A(EO)-B$_m$B(PO)$_n$ surfactants were obtained from Hangzhou Electrochemical Group and used as received.

Solubility measurement was carried out in a stainless steel variable-volume view cell with two quartz windows, which permitted visual observation of phase behavior as described previously.[9] A wrench was used to vary the pressure independently of temperature. The cell had a variable volume of (8.65 to 10.15) mL, and the whole system was placed inside the air bath in a horizontal position. A given amount of surfactants and a stirring bar were loaded into the cell, which was then sealed, and the volume of the cell was adjusted to its minimum volume. CO_2 was then injected into the cell by a syringe pump (Zhijiang Scientific Apparatus Co., Hangzhou) until a single-phase transparent solution was obtained, and the solution was stirred by a magnetic stirrer. When the temperature and pressure became constant for a period of time greater than 0.3 h, the temperature and pressure were recorded to calculate the density using the equation of state.[10] The mole fraction, x, of the solute in the supercritical CO_2 could be obtained. Then stirring was stopped, the pressure was decreased slowly until the system became cloudy, and the pressure was defined as the cloud-point pressure. The pressure was then slowly increased slightly to obtain a clear solution. This procedure was repeated again to obtain an average value for the reported cloud-point pressures at each temperature. The equilibrium temperature and cloud-point pressure were measured to accuracies of ± 0.1 °C and ± 0.5 MPa, respectively.

Results and Discussion

Solubility measurements were accomplished in a pressure range from (13.0 to 33.0) MPa and at temperatures of (308,

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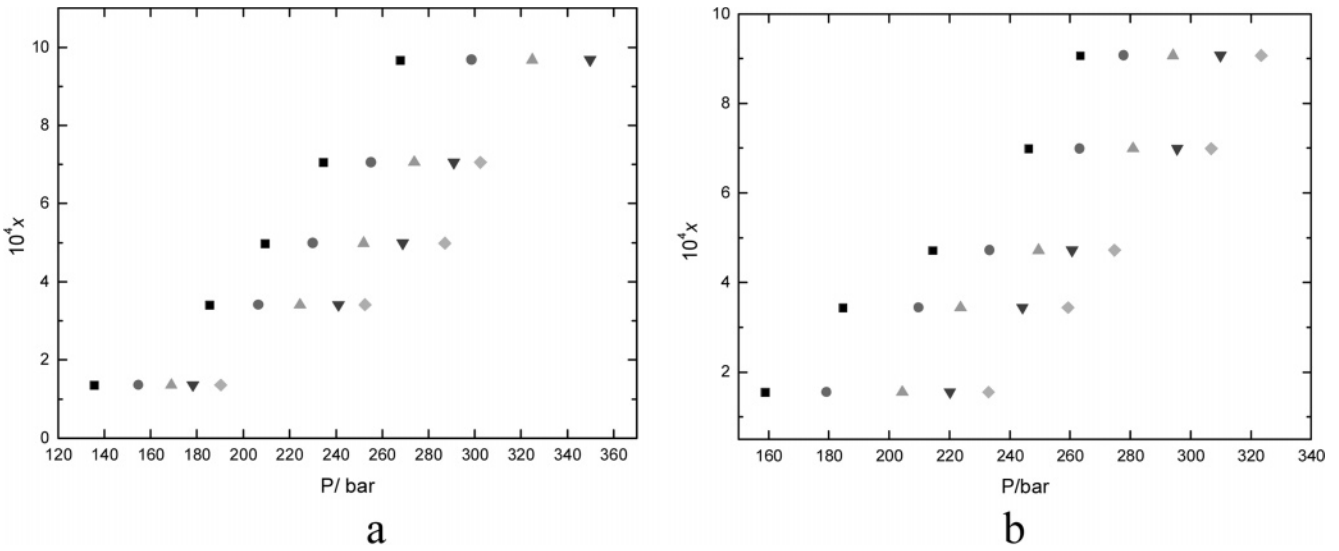

Figure 2. Solubilities of surfactants in supercritical CO_2: panel a, $A(PO)_9(EO)_2$; panel b, $A(PO)_9(EO)_3$. ■, 308 K; ●, 313 K; ▲, 318 K; ▼, 323 K; ◆, 328 K.

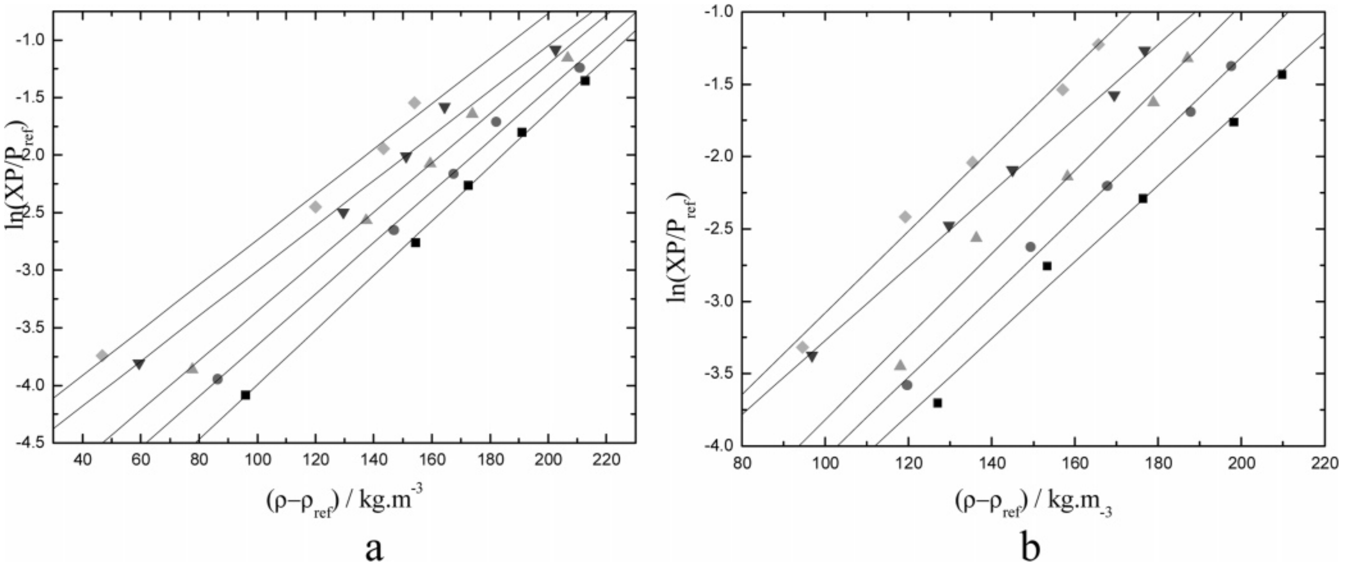

Figure 3. Plots of $\ln(xP/P_{ref})$ vs $(\rho - \rho_{ref})$ for surfactants at various temperatures: panel a, $A(PO)_9(EO)_2$; panel b, $A(PO)_9(EO)_3$. ■, 308 K; ●, 313 K; ▲, 318 K; ▼, 323 K; ◆, 328 K.

313, 318, 323, and 328) K. The resulting solubilities in terms of mole fraction, *x*, of the solute in supercritical carbon dioxide are shown in Figure 2. Each reported data point is the average of at least five replicate points. The mole fractions of solutes were reproducible within ± 3 %.

As expected, at same temperature the solubilities of solutes increase with the increase of pressure. And at same pressure, the solubilities of solutes decrease with the increase of temperature. In general, the solvent power of CO_2 increases with density of CO_2.

The experimental solubility data for these two surfactants were correlated using the following equation:[11−14]

$$\ln(xP/P_{ref}) = A + C(\rho - \rho_{ref}) \qquad (1)$$

where

$$A = a + b/T \qquad (2)$$

and

$$\ln(xP/P_{ref}) = a + b/T + C(\rho - \rho_{ref}) \qquad (3)$$

where *x* is the mole fraction of the solute (taken here to be equal to the radio of the numbers of moles of solute divided by the number of moles of carbon dioxide); *P* is the pressure; P_{ref} is 0.1 MPa; ρ is the density (taken as the density of pure carbon dioxide); ρ_{ref} is 700 kg·m^{-3}; and *A*, *C*, *a*, and *b* are constants.

In the first step, $\ln(xP/P_{ref})$ values were plotted against density (Figure 3), and the values were fitted with a straight line by least-squares regression to estimate the *C* and *A* parameters. The values of *C*, obtained from the slopes of the corresponding plots, were then averaged for each compound (Table 1).

When the *C* was held at its average values, the experimental solubility data were then used to evaluate the *A* values at various temperatures for each surfactant. The plots of *A* versus 1/*T* for each surfactant resulted in a straight line (Figure 4), from which the intercept and the slope (*a* and *b*) were obtained. The resulting

Table 1. Solubility Constants *a*, *b*, and *C* Obtained from the Data Correlation Procedure

surfactant	*a*	*B*/K	*C*/m^3·kg^{-1}
$A(EO)_9(PO)_2$	21.701	−8637.8	0.0213
$A(EO)_9(PO)_3$	9.9278	−5281.9	0.0273

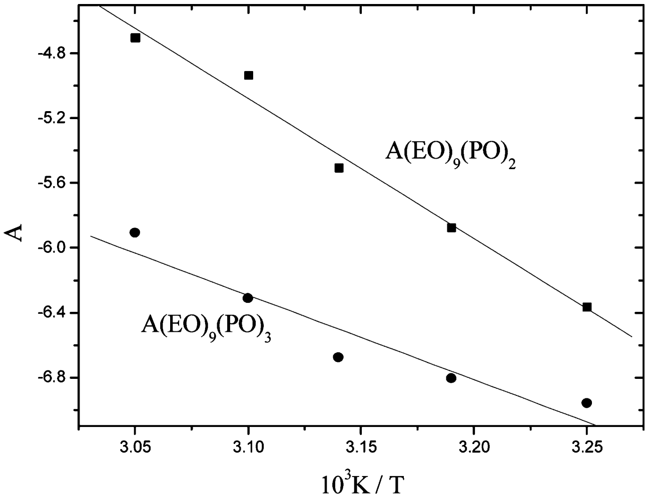

Figure 4. Plots of A vs $1/T$ for surfactants.

a and b values for surfactants are also included in Table 1. Then the values of a, b, and C were used to predict solubility from eq 3. Figure 2 compares the calculated isotherms with the experimental data. Finally, the average absolute relative deviation (AARD) was obtained with AARD $= 1/n\sum|(x_{i,\mathrm{cal}} - x_{i,\mathrm{exp}})/x_{i,\mathrm{exp}}| \times 100$ %, where n is the number of experiment point, and $x_{i,\mathrm{cal}}$ and $x_{i,\mathrm{exp}}$ are the calculated and experimental data (kg/m^3), respectively. The values of AARD are in the range (5 to 30) %.

Conclusion

The solubilities of A(EO)$_m$(PO)$_n$ surfactants, which are the non-fluorous and non-silicone containing nonionic surfactants, were measured in supercritical carbon dioxide over pressures from (13.0 to 33.0) MPa and temperatures from (308 to 328) K. As expected, the solubilites of surfactants increased with the increase of density of carbon dioxide. The solubility data were correlated using the semiempirical model (see eq 3). The solubility data agree well with the data of model in the experimental ranges.

Supporting Information Available:

One additional table. This material is available free of charge via the Internet at http://pubs.acs.org.

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