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Study on phase behaviors of supercritical CO_2 including surfactant and water

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Abstract

Phase behaviors for the supercritical CO_2 ($scCO_2$) + surfactant binary system and the $scCO_2$ + surfactant + water ternary system were investigated at temperatures from 308.2 to 343.2 K by using a synthetic-type apparatus. Polyethylene oxide-2,6,8-trimethyl-4-nonyl ethers (TMN) was used as the surfactant. For the binary system, vapor–liquid phase-transition pressures increased with increasing temperature and the critical points (maximum pressures on the phase-boundary curves) were observed at TMN composition around 1.5 wt%. On the other hand, for the ternary system including 1 wt% of TMN, two phase-transition pressures were obtained at each temperature and composition. A transparent phase was observed above the upper phase-transition pressure and a cloudy phase including emulsions appeared between the upper and the lower phase-transition pressures. Vapor and liquid phases were clearly separated below the lower phase-transition pressure. The upper phase-boundary curves had a minimum pressure around water composition about 1 wt% on *P*–*w* phase diagram. On the other hand, the lower phase-transition pressures decreased monotonously with increasing water composition.

Keywords: Emulsion; Phase behavior; Supercritical carbon dioxide; Water; Synthetic method

1. Introduction

Supercritical carbon dioxide ($scCO_2$) has been expected as a representative green solvent and a lot of processes for the extraction of flavors and medicinal properties from natural products have been in a practical realization [1]. In the processes, however, nonpolar or weakly polar substances having low molecular weight are mainly treated as target substances because highly polar substances and high molecular weight substances are less soluble in $scCO_2$, and which restricts the application fields of $scCO_2$. Among the methods to improve the weak solvent power of $scCO_2$, water in $scCO_2$ (W/CO_2) emulsions have been received much attention as one of the most effective methods. W/CO_2 emulsions are expected to be applied to the extraction of heavy metals from polluted soils, the cleaning of micro- or nano-space of materials, such as semiconductors, and the dispersion polymerization for manufacturing nano-particles [2]. Particularly, the application to the cleaning process in the production of semiconductors is considered to be effective because the high diffusivity and low viscosity of $scCO_2$ are of great advantage to the removal of residues in the microscopic clearances of high-aspect-ratio structures [3–5].

In the research of W/CO_2 emulsions, some experimental investigations have been reported on the formation and the size distribution of W/CO_2 emulsions by observing phase behaviors or using a dynamic light scattering technique [6–14]. The stability of emulsions has also been discussed in terms of the interfacial properties of the water–CO_2 interface with some surfactants [15–20]. The results of these studies have represented that the necessary properties of the surfactants to form stable W/CO_2 emulsions are a good affinity with $scCO_2$ and a large steric volume of CO_2-philic groups. The hydrophilic–CO_2-philic balance (HCB) value is frequently used as an index for the stability of emulsions. HCB is defined as the ratio of inter-

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action energies between CO_2-philic groups and CO_2 molecules to between hydrophilic groups and water molecules as follows:

$$1/\mathrm{HCB} = \frac{A_{\mathrm{TC}} - A_{\mathrm{TT}} - A_{\mathrm{CC}}}{A_{\mathrm{HW}} - A_{\mathrm{HH}} - A_{\mathrm{WW}}} \quad (1)$$

where A is the interaction energy between CO_2 (C) , CO_2-philic tail group of surfactant (T), water (W) and hydrophilic head group of surfactant (H). $1/\mathrm{HCB} > 1$ in Eq. (1) is required to obtain stable W/CO_2 emulsions, so, strong attractive interactions between CO_2-philic groups and CO_2 molecules are necessary condition. Relatively weak interactions between hydrophilic groups and water molecules are also required for W/CO_2 emulsions [13]. Therefore, non-ionic surfactants are better for this purpose than ionic surfactants.

On the other hand, in the theoretical research, the behaviors of W/CO_2 emulsions were analyzed with equations of state and molecular simulations. Meredith and Johnston [21,22] used lattice-fluid self-consistent field theory to predict stability and flocculation of block copolymer stabilizers in $scCO_2$. The predicted results of the upper critical solution densities and the critical flocculation densities were in good agreement with the experimental results for the binary systems of $scCO_2$ + block copolymer of polystyrene-*b*-poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) and poly(vinyl acetate)-*b*-PFOA. The mechanism for the formation of W/CO_2 emulsions has also been studied by using molecular dynamic simulations. However, it takes a long time to obtain the simulation results even for a single emulsion.

It has been reported in previous researches that the surfactants having fluorinated hydrocarbon CO_2-philic groups exhibit an outstanding ability to form stabilized W/CO_2 emulsions. However, such surfactants are more harmful to a human health and expensive, compared with common chemical substances. In this situation, the surfactants composed of CO_2-philic groups of branched hydrocarbons attract much attention because they are less harmful and inexpensive. Among them, polyethylene oxide-2,6,8-trimethyl-4-nonyl ether (TMN) has excellent properties to form a stable emulsions. Ryoo et al. [13] investigated phase behaviors for the $scCO_2$ + TMN and $scCO_2$ + TMN + water systems and diameters of W/CO_2 microemulsions by a dynamic light scattering technique. The results show high availability of TMN to form stable microemulsions. However, the experimental data on the phase behaviors for $scCO_2$ + non-ionic surfactant + water systems, especially for the surfactants including CO_2-philic hydrocarbon tails, have not been accumulated enough to design surfactant structures and to develop new processes. Moreover, more useful theoretical models are required to predict the phase equilibria for such systems from the standpoint of engineering. Therefore, in this work, the phase-transition pressures of the $scCO_2$ + TMN and the $scCO_2$ + TMN + water systems were measured at pressures from 20 to 50 MPa and temperatures from 308.2 to 343.2 K to accumulate new experimental data and new knowledge in a wider range of water composition.

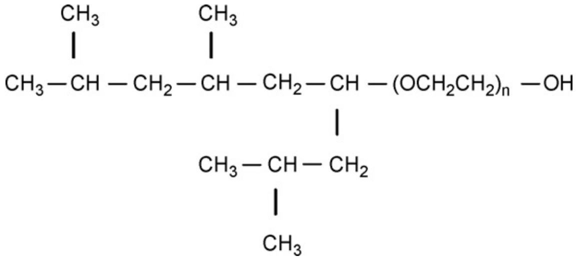

Fig. 1. Chemical structure of polyethylene oxide-2,6,8-trimethyl-4-nonyl ether (TMN).

2. Experimental

2.1. Materials

Carbon dioxide was purchased from Iwatani Industrial Gases and had a purity greater than 99.95 mol%. Water of A.C.S. regency grade was purchased from Sigma–Aldrich. Tergitol(R) TMN-3 (TMN) purchased from FLUKA was used as a surfactant in this work. The chemical structure of TMN is shown in Fig. 1. TMN has a highly branched CO_2-philic hydrocarbon group and hydrophilic ethylene oxide (EO) groups as well as a hydroxyl group. Content of water in TMN measured with Karl-Fischer titration (DIA Instruments, KF-21 type) was 1.08 wt%. The molecular weight distribution of TMN used in this work was estimated from the analytical results with the mass spectrometer of MALDI-TOF/TOF/MS/MS spectroscopy (BRUKER DALTONICS, Ultra flex I) and is shown in Fig. 2. The molecular weight was distributed from 242 to 604 g/mol at 44 g/mol intervals. The interval of 44 g/mol corresponds to the molecular weight of EO. Therefore, TMN including from 1 to 9 EO groups was used in this work. The number-average molecular weight was 419.6 g/mol and the average number of EO groups ($\bar{n}$) was 4.81. All compounds were used as received in the present work. Therefore, in the CO_2 + TMN binary mixtures, small amounts of water (0.0045 to 0.033 wt%) were involved. In the ternary mixtures, however, the existence of water in TMN was within the uncertainty in the composition determination.

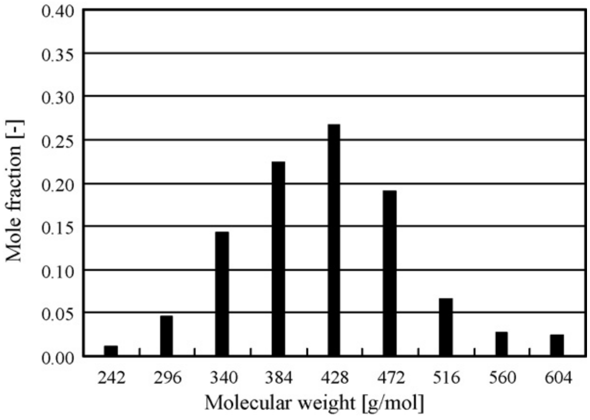

Fig. 2. Molecular weight distribution of TMN used in this work.