유기용매/F-AOT/sc-CO2 system의 마이크로 에멀전 형성 및 cloud point 측정

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Microemulsion formation and cloud point measurement in organic solvent/F-AOT/sc-CO_2 system

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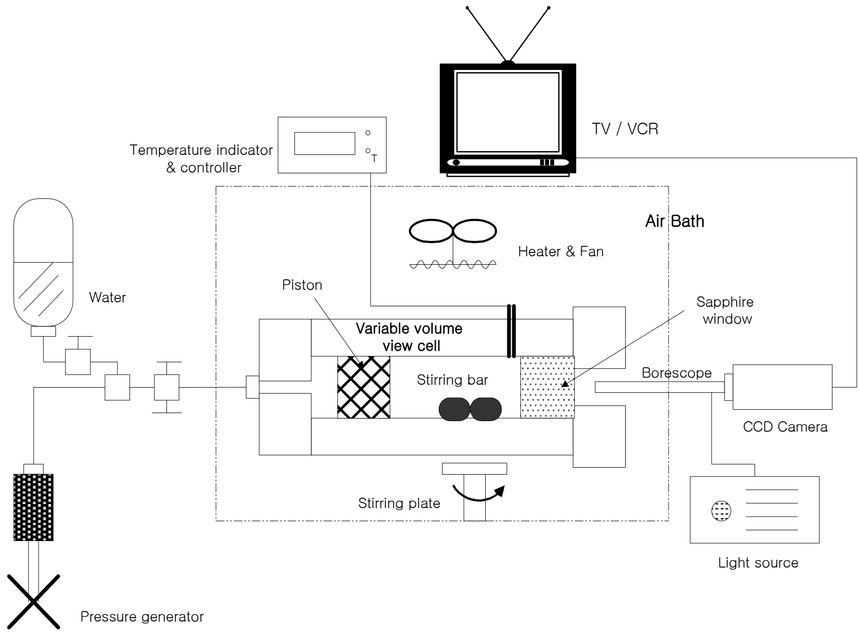
Introduction

The microemulsion is a thermodynamically stable dispersion of one liquid phase into another, stabilized by an interfacial film of surfactant and it is formed by swelling of micelle or reverse micelle. The microemulsion is typically clear solutions, as the droplet diameter is approximately 1 micrometers or less. It is consisted of at least three components; two immiscible components (generally water and oil) and a surfactant, and molecules of water are dispersed as droplets of nano or micro size surrounded by surfactant molecules into sc-CO_2. This is possible because the surfactant supports microemulsion by decreasing interfacial tension between one liquid and CO_2. To this study, first of all, we synthesized a fluorinated analogue of AOT, the sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl)-2-sulfosuccinate(di-HCF4). It was used to stabilize the microemulsion because it has bulky, a hydrophilic head group, and highly CO_2-philic side [1]. In this study, we investigated the phase behavior of microemulsion composed of organic solvent, F-AOT, and CO_2.

Experimental Section

Materials. Carbon dioxide (CO_2), 2,2,3,3,4,4,5,5-octafluoro-1-pentanol ($F_2CH(CF_2)_3CH_2OH$), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-otaol($CF_3(CF_2)_5CH_2CH_2OH$), 1,4-dioxa-ne, p-toluene-sulfonic acid monohydrate, sodium hydrogen sulfite, maleic anhydride, toluene, acetone-d_6, trifluoroacetic acid-d_6, ethanol, isopropyl alcohol, methanol, pyridine, tetrahydrofuran, aceton, acetonitrile.

Apparatus. The phase behavior of microemulsion was investigated by using a variable-volume view cell apparatus through the measurement technique of cloud point. Its schematic diagram is shown in figure 1. The high-pressure variable- volume view cell is placed on center of this system. It is hollow and equipped with sapphire window and movable piston. We can observe the phase transition inside cell through the sapphire window by using a borescope and CCD camera connected with light source and TV/VCR monitor.



Procedures. The experiment was performed by the following procedure. The piston worn by O-ring was inserted into one side window of the variable-volume view cell. After a desired amount of surfactant and magnetic stirring bar were placed inside the cell, the sapphire was inserted into the other side window and then two windows were sealed with O-rings. The assembled cell was horizontally placed inside the air bath and a position of borescope and brightness of lighting were adjusted carefully to observe the state in the cell. With low pressure CO_2 gas of less than 0.5Mpa, the cell was purged at least three times to remove the entrapped air at very slow rate to minimize the loss of surfactant. A certain amount of water was put into the cell by using the syringe. Liquefied CO_2 was charged into the cell by using high-pressure sample cylinder. The amount of liquefied CO_2 was determined by weighing the CO_2 sample cylinder before and after liquefied CO_2 was charged into the cell. The solution in the cell is pressurized above critical pressure by using the pressure generator. The solution was heated to desired temperature by heater and then the well agitated by magnetic stirring bar to form a microemulsion. Enough time was allowed to obtain the optically transparent single-phase solution (microemulsion).

Results and discussions

The cloud points were measured every 10°C at temperature ranging 30-100°C owing to weakness of O-rings at high temperature at a constant amount of CO_2(about 10g) and surfactant(0.1911g). The plots for the cloud points were described by temperature vs. pressure. Figure 2 is showing the phase behavior of isopropyl alcohol/F-AOT/sc-CO_2 microemulsion with various weight percent of isopropyl alcohol in sc-CO_2. The cloud point pressures were increased with increasing the temperature of system. The values of cloud points became low as the weight percent of isopropyl alcohol in sc-CO_2 was increased. In Figure 3, 4, and 6, the phase behavior of THF/F-AOT/sc-CO_2 and Acetonitrile /F-AOT/sc-CO_2, and ethanol/F-AOT/sc-CO_2 microemulsion is showing with various weight percent of THF, acetonitrile, and ethanol in sc-CO_2. These represented similar tendency to case of isopropyl alcohol/F-AOT/sc-CO_2 microemulsion. Figure 5 is showing the cloud points of methanol/F-AOT/CO_2 microemulsion with various weight percent of methanol in sc-CO_2. The change of cloud points is the most prominent of used organic solvents. Figure 7 is representing the cloud points of pyridine/ F-AOT/sc-CO_2 microemulsion. In case of pyridine/F-AOT/sc-CO_2 microemulsion, the all cloud points are identical at fixed temperature and pressure regardless of weight percent of pyridine in sc-CO_2. At fixed amount of organic solvent in sc-CO_2, the cloud points of isopropyl alcohol/F-AOT/CO_2 microemulsion were most positive while those of ethanol /F-AOT/CO_2 were least of all.

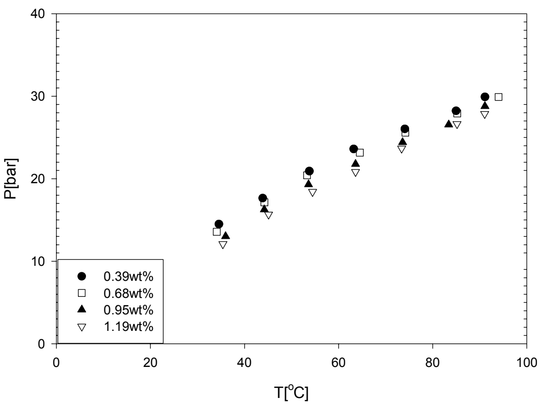


Figure 2. The cloud points of isopropyl alcohol/F−AOT/CO_2 microemulsion

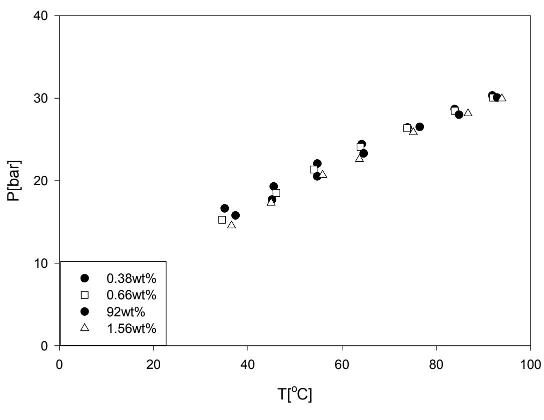


Figure 3. Cloud points of THF/F−AOT/CO_2 microemulsion

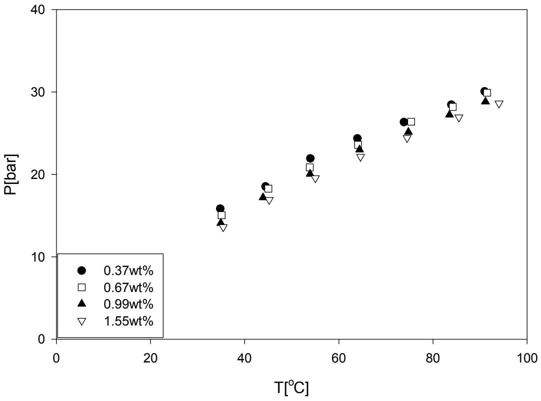


Figure 4. Cloud points of Acetonitrile/F−AOT /CO_2

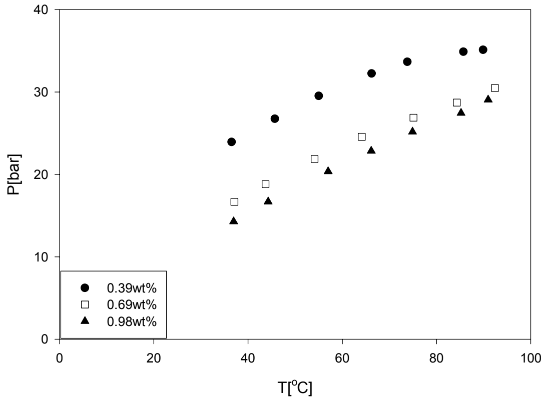


Figure 5. Cloud points of methanol/F−AOT/CO_2

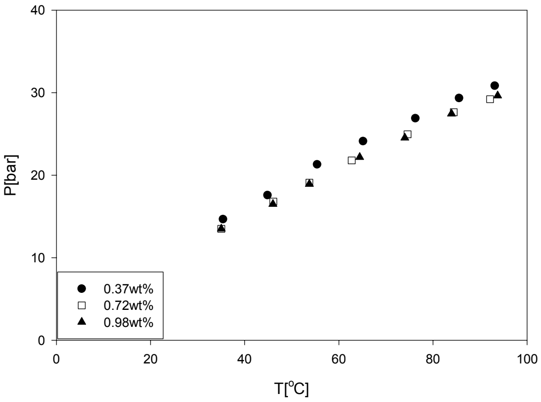


Figure 6. Cloud points of ethanol/F−AOT/CO_2 microemulsion

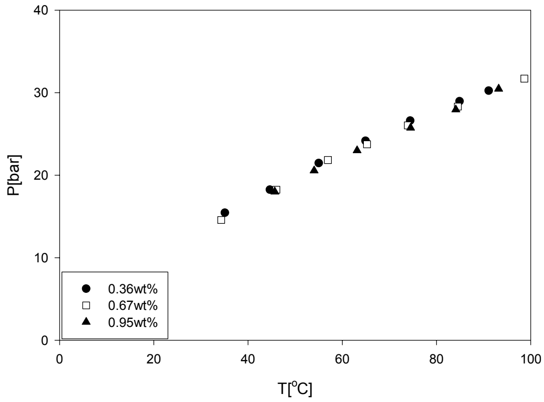


Figure 7. Cloud points of pyridine/F−AOT/CO_2 microemulsion

Conclusion

We formed various type of microemulsion composed of F-AOT, sc-CO_2, organic solvent such as methanol, ethanol, acetonitrile, pyridine, THF, isopropyl alcohol instead of water. Their cloud points were measured with various amount of organic solvents at a constant concentration of surfactant in CO_2. The behavior of F-AOT/sc-CO_2/organic solvent microemulsion represented opposite tendency in contrast to that of w/c microemulsion. The cloud points of microemulsions formed in this work were more positive than that of w/c microemulsion.

Reference

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