유기용매 첨가에 따른 Water in CO_2 microemulasion 의 상거동

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Phase behavior of Water-in-scCO_2 microemulsion according to addition of organic solvents

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Introduction

The microemulsions have many advantages such as low overall cost, good adhesion to vertical surfaces, better reagent performance, application to both hydrophilic and hydro-phobic contaminants, low surface tension, and good stability. The microemulsion that is formed by swelling of micelle or reverse micelle is a thermodynamically stable dispersion of one liquid phase into another, stabilized by an interfacial film of surfactant. The microemulsion is typically clear solutions, as the droplet diameter is approximately 1 micrometers or less. In case of W/C (water in CO_2) microemulsion, it is composed of at least three components; two immiscible components (water and CO_2) 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 water and CO_2. In this study, 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 W/C microemulsion because it has bulky, a water-soluble head group, and highly CO_2-philic side [1]. In this study, we investigated the phase behavior of W/C microemulsion by adding fully water-soluble organic solvents.

Theory

The Hansen's approach was used to calculate the solubility parameter of organic solvents. This theory assumes that the cohesive energy is divided into dispersion interactions, hydrogen bond and polar interactions. This is expressed by following equation [2].

$$\delta^2 = \delta_d^2 + \delta_h^2 + \delta_p^2$$

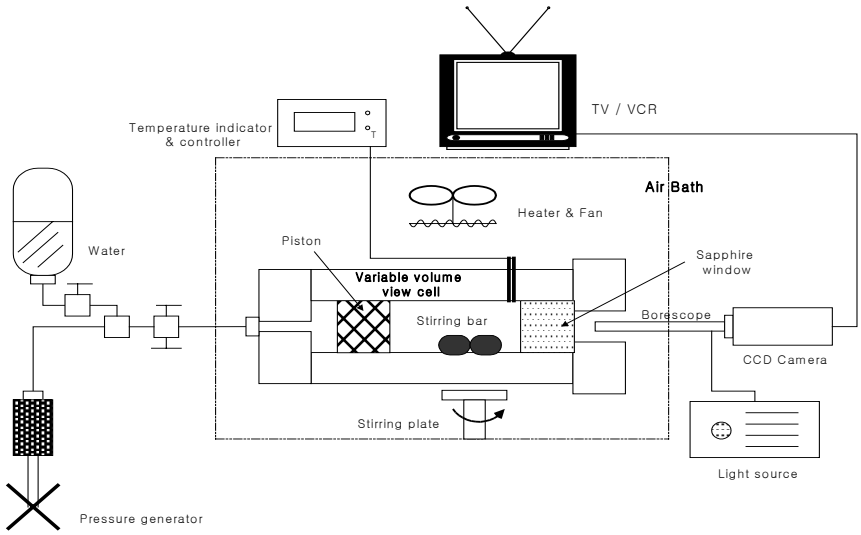
Where, δ is total solubility parameter, and $\delta_d, \delta_h, \delta_p$ are components of the solubility parameter

determined by the corresponding contributions to the cohesive energy.

Experimental Section

Materials. Carbon dioxide (CO_2), 2,2,3,3,4,4,5,5-octafluoro-1-pentanol ($F_2CH(CF_2)_3$ CH_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-dioxane ($C_4H_8O_2$), p-toluene-sulfonic acid monohydrate ($CH_3C_6H_4$ $SO_3H{\cdot}H_2O$), sodium hydrogen sulfite ($NaHSO_3$), maleic anhydride ($C_4H_2O_3$), toluene ($C_6H_5CH_3$), acetone-d_6(CD_3COCD_3), trifluoroacetic acid-d_6 (CF_3COOD), ethyl alcohol (CH_3CH_2OH), isopropyl alcohol ($CH_3CHOHCH_3$), methanol (CH_3OH), n-propyl alcohol ($CH_3CH_2CH_2OH$)), n,n-dimethylformamide ($HCON(CH_3)_2$), 2-methoxyethanol ($CH_3OCH_2CH_2OH$), pyridine (C_5H_5N), tetrahydrofuran (C_4H_8O), aceton (CH_3COCH_3), acetonitrile (CH_3CN).

Apparatus. The phase behavior of W/C 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).

Result

We used the organic solvents arranged by solvent group according to Snyder in which solvents are placed in groups of similar selectivity. The fully water-soluble solvents used by us as an additive are ethyl alcohol, isopropyl alcohol, methanol, and n-propyl alcohol which belong to the solvent group2, n,n-dimethylformamide, 2-methoxyethanol, pyridine, tetrahydrofuran which belong to the solvent group 3, and aceton, acetonitrile, 1,4-dioxane which belong to the solvent group 6. Their properties are given in table 1. The cloud points were measured every 10°C at temperature ranging 40-100°C with various organic solvents at a constant CO_2 concentration and W_0 (water to surfactant molar ratio). The plots for the cloud points were described by temperature vs. pressure. Regardless of solvent group, all cloud point curves are shown in Figure 2. Except for N,N-dimethyformamide, the other solvents showed the positive effect about W/C microemulsion formation. Particularly, isopropyl alcohol was a best additive. Figure 3, 4, 5 represent the curves of solvents group 2,3,6 respectively. As shown in this figures, the cloud point pressures of solvents group 2, 3 increased according to the solubility parameter of solvents but those of solvent group 6 decreased.

	Density [g/ml] at 25°C	Polarity index	*Solubility parameter [$(J/m^3)^{1/2}$]
Methanol	0.7866	5.1	29.1
Ethanol	0.7849	-	26.4
Isopropyl alcohol	0.7812	3.9	23.5
n-propyl alcohol	0.7997	4.0	24.4
N,N-dimethylformide	0.9439	6.4	24.8
2-methoxyethanol	0.965(at 20°C)	5.5	23.3
Tetrahydrofuran	0.881	4.0	22.5
Pyridine	0.9782	5.3	21.9
Acetonitrile	0.7766	5.8	24.3
Aceton	0.7844	5.1	19.9
1,4-dioxane	1.028	4.8	18.5

* From Handbook of solvent (1). Table 1. Properties of organic solvents

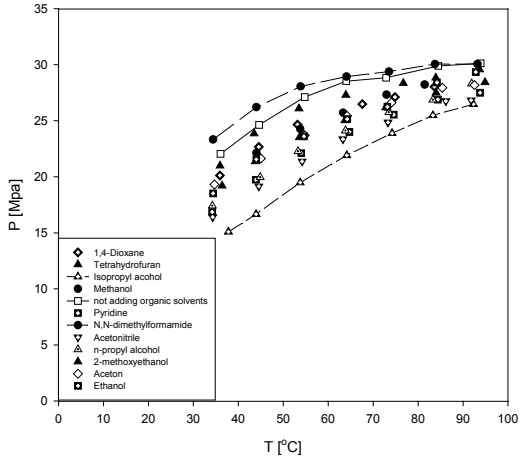


Fig 1. Cloud points of W/C microemulsion with various organic solvents.

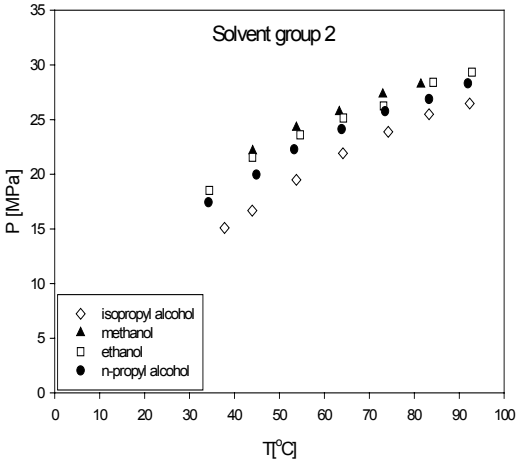


Fig 2.Cloud points of W/C microemulsion + solvent group2

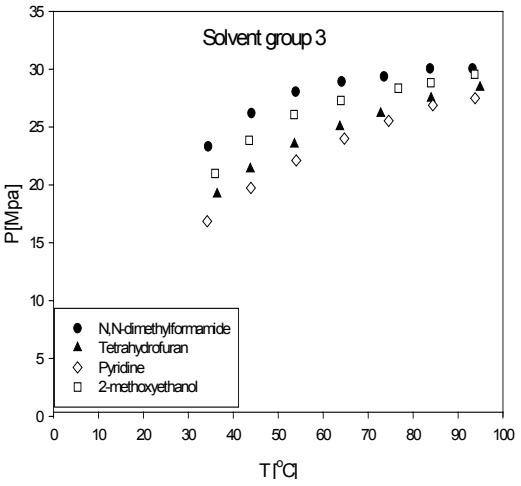


Fig3. Cloud points of W/C microeulsion + solvent group3.

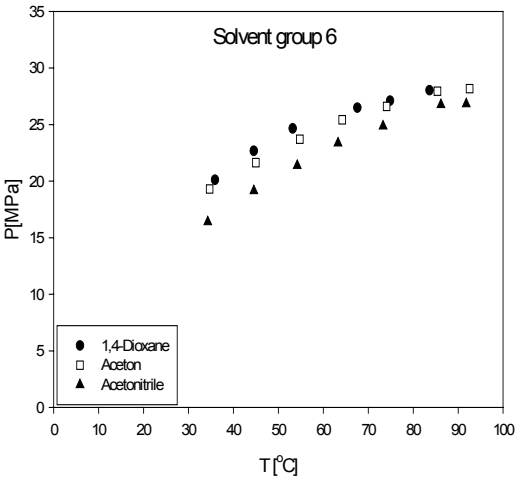


Fig4. Cloud points of W/C microemulsion + solvent group6.

Conclusion

We investigated the phase behavior of W/C microemulsion according to fully water-soluble organic solvents that is arranged by solvent group according to Synder in which solvents were classified by groups of similar selectivity. It was presented as a function of pressure and temperature. The cloud point pressures of solvents group 2, 3 increased but those of solvent group 6 decreased according to the solubility parameter of solvents.

Reference

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