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Solubility of solid solutes in supercritical carbon dioxide with and without cosolvents

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Abstract

The solubility of 2-naphthol and anthracene in supercritical CO_2 was determined at 308.1, 318.1 and 328.1 K, with and without cosolvent. The influence of three polar or nonpolar cosolvents, acetone, ethanol and cyclohexane, was studied at concentrations of 3.6 and 4.0 mol%. The solubility enhancement with these cosolvents is considerable, and the cosolvent effect increases in the order ethanol, acetone, and cyclohexane for 2-naphthol and for anthracene, the order is cyclohexane, ethanol, and acetone. The influence of density and cosolvent on the solid solubility was studied and discussed.

Keywords: Solubility; Supercritical fluid; Solid solute; Cosolvent

1. Introduction

Supercritical fluid extraction (SCFE) is a relatively new and promising separation technology that has a great application potential in many separation and purification processes, such as in food, pharmaceutical, polymer processing and biochemical industries, etc. Since the solubility of solids can be easily tuned with solvent density near the solvent critical point, it makes supercritical fluids (SCFs) attractive solvent candidates for separating heavy compounds, which becomes one of the main applications of SCFE technology.

In SCF technology, carbon dioxide is one of the most commonly used gases because it is an easy gas to handle, it is inert, nontoxic and nonflammable, and it has a convenient critical temperature. On the other hand, it has some limitations because of its lack of polarity and the capacity to form specific solvent–solute interactions. Therefore, there is a great incentive to improve its polarity, and it has been found that the addition of a small amount of suitable cosolvent can greatly enhance its solvent power.

A number of investigators have published equilibrium solubility data for various solids in SCFs, however, the measurements on the solubility of solids in SCFs with cosolvents are few although the concept

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of adding cosolvent to a SCF has received attention many years ago [1]. Kurnik and Reid [2] demonstrated that the solubility of a solid in a SC solvent can be enhanced in some instances by the presence of a cosolvent. Sulfur dioxide has been used as a cosolvent for benzoic acid [3]. Van Alsten et al. [4] reported solid–fluid equilibrium data for a number of systems. Dobbs et al. [5,6] measured and correlated solid–fluid equilibrium data for benzoic acid, 2-aminobenzoic acid, phthalic anhydride, and acridine in CO_2 doped with acetone or methanol. Schmitt and Reid [7] have studied solubility of monofunctional organic solids in chemically diverse supercritical fluids and the solubility of naproxen in supercritical carbon dioxide with and without cosolvents were studied by Ting et al. [8]. Joshi and Prausnitz [1] calculated the effects of cosolvents on the solubility of benzoic acid by using the Redlich–Kwong equation of state.

In this work, the flow technique coupled with gravimetric analysis was used to measure the solubility of solid solutes, anthracene and 2-naphthol, in CO_2 with and without cosolvents. Both polar (ethanol and acetone) and nonpolar (cyclohexane) substances were adopted as cosolvents to investigate the effects of cosolvent on the solubility enhancement of solid solutes in CO_2. Acetone does not self-associate and is solely hydrogen bond acceptor, while ethanol, on the other hand, is able to be both hydrogen bond donors and acceptors, which also tends to self-associate even in SCFs. Therefore, the present work can investigate the effects of both the concentration and the functionality of the cosolvents.

This work is an important step in our long-term objective to predict the solution properties of multicomponent supercritical fluid mixtures based on the molecular interactions. It will provide a basis for future attempts to demonstrate that a multicomponent supercritical solvent mixture can be highly selective for particular solutes due to specific interactions. Rational utilization of these cosolvents could improve the existing and newly proposed processes, particularly for those compounds with extremely limited solubility in pure fluids.

2. Experimental

2.1. Equipment and experimental method

The flow diagram of the equipment used is shown in Fig. 1. The syringe pump used was a Nova Model 5542121, with constant pressure operating capability for pure CO_2. The equilibrium cell consists of a 40 mm i.d., 300 mm long stainless steel tube. The pump used for cosolvents is high pressure gauging pump (BECKMAN, 100A). The system temperature was monitored by a platinum resistance thermometer accurate to ± 0.1 K, and the system pressure was measured by a pressure meter (HEISE, Newtown CONN.) with an accuracy of ± 0.5 bar. The equilibrium cell and the preheater coil were placed in a water bath which was controlled to ± 0.01 K.

The equilibrium cell was packed with solid solute, 2-naphthol or anthracene, and each end was plugged with glass wool to prevent the fine solid powder from plugging the smaller 1/6 in. i.d. interconnecting stainless steel tubing.

CO_2 and cosolvent from vessels were compressed into the mixer, then through the connecting tube heated by electricity coil, they were put into the equilibrium cell from the bottom. In the equilibrium cell, the solvent and solute reached equilibrium through mass transfer. The fluid phase reached equilibrium flowed from the top of the cell through a decompress valve into two U type tubes in turn. The solid solute was settled and weighed up by an analysis scale with an accuracy of ± 0.05 mg after drying. The volume was measured by the wet gas meter with an accuracy of $\pm 1\%$.

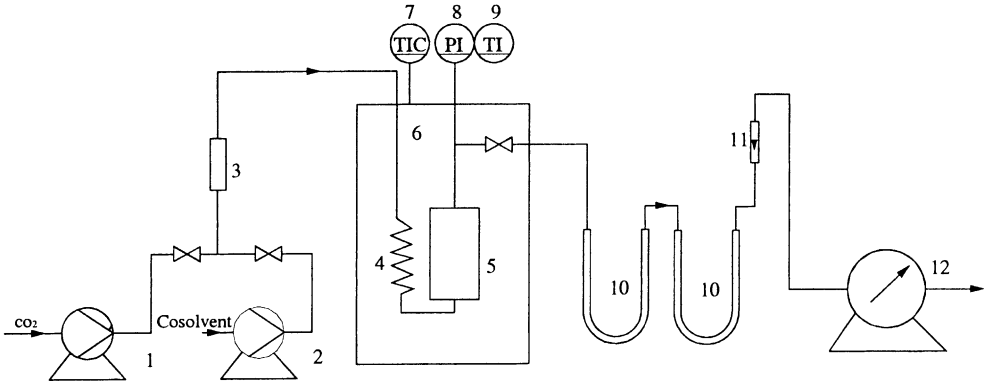

Fig. 1. Flow apparatus for solubility measurements in SCF with and without cosolvent.

Table 1
Source and purity of the materials used

Substance	Source	Purity (%)
Anthracene	Xuxing Chemcal Factory	>99.8
2-Naphthol	Imported from German	>99
Carbon dioxide	Beijing Chemical Experimental Factory	>99
Acetone	Beijing Alcohol Factory	>99.5
Ethanol	Beijing Chemical Factory	>99.5
Cyclohexane	Beijing Chemical Factory	>99

We started the measurements at a flow rate of 100 l/h, then reduced the flow rate until the solubility measured did not change with further decreasing the flow rate. By this way, we determined the suitable flow rate is 40 l/h to ensure that the solid and fluid reach equilibrium in the equilibrium cell. To make sure that all the precipitated solute was collected, two U type tubes were used in turn. From experimental observation, nearly all the solute was collected in the first U type tube, and very little precipitated in the second U type tube. The experimental error for the solute solubility is estimated to be ±2%.

3. Materials

The sources and purities of the various compounds used are given in Table 1. These materials were used without further purification.

4. Results and discussion

4.1. Solubility of solids in pure CO_2

The solubilities of 2-naphthol and anthracene in pure CO_2 were measured at 308.1, 318.1, and 328.1 K, which are listed in Table 2 and depicted in Figs. 2 and 3, respectively.

Table 2
Solubility of 2-naphthol and anthracene in pure CO_2

Pressure (MPa)	$y_2 \times 10^4$		
	308.1 (K)	318.1 (K)	328.1 (K)
2-Naphthol			
10.05	2.49	1.48	1.16
14.00	4.33	4.70	4.41
18.00	5.09	6.49	6.92
22.05	5.47	7.72	9.25
26.00	6.10	8.47	11.4
30.00	6.54	9.64	12.3
Anthracene			
10.00	0.416	0.205	0.138
15.00	0.508	0.539	0.573
20.00	0.696	0.745	0.807
25.00	0.759	0.851	1.02
30.00	0.783	0.940	1.13

In order to verify the reliability and efficiency of the solubility apparatus and the technique employed in this study, the solubility data of anthracene in CO_2 at 318.1 K and 10.0–25.0 MPa were compared in Fig. 4 with the data of Johnston et al. [9], obtained at 323.1 K and 9.0–27.6 MPa. Furthermore, our experimental data of 2-naphthol in CO_2 at 318.1 K and 10–30 MPa were compared with the data of Tan and Weng [10] in Fig. 5. As can be seen from the figures, the apparatus and the technique employed in this work give agreeable results with that of literature.

4.2. Solubility of solids in CO_2 with cosolvent

In order to investigate the effect of cosolvent on the solubility of solids in SCF, the solubility of 2-naphthol and anthracene in CO_2 with cosolvent was further measured. The cosolvents adopted are

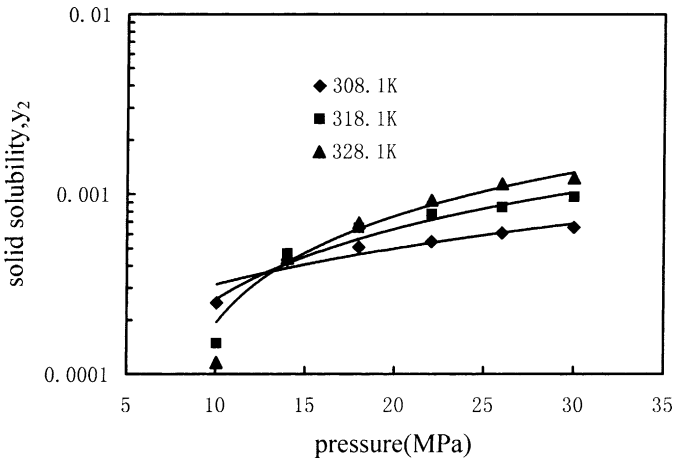

Fig. 2. Solubility of 2-naphthol in CO_2.

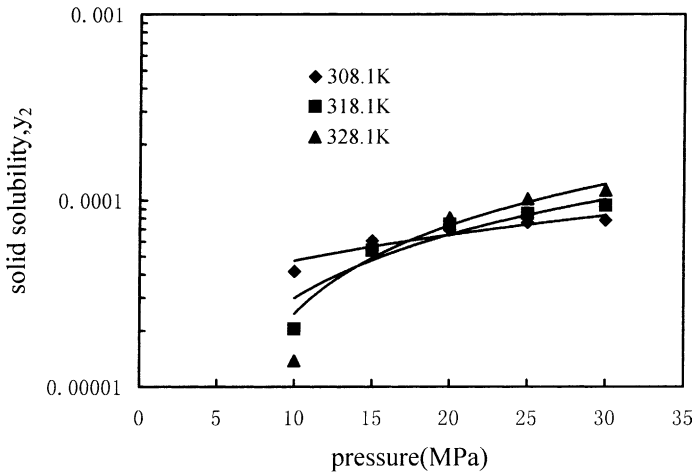

Fig. 3. Solubility of anthracene in CO_2.

acetone, ethanol and cyclohexane. Measurements for three temperatures, 308.1, 318.1 and 328.1 K, were carried out, and the experimental results are shown in Tables 3 and 4, where the corresponding densities were calculated by the Patal–Teja equation of state [11].

4.3. *Effect of density*

The addition of a cosolvent to a SCF generally can increase the bulk density of the fluid mixture which would contribute to solubility enhancement. A large variation in density would be expected close to the critical point where the isothermal compressibility is largest. However, at pressures and temperatures further away from this region, where the fluid is less compressible, the increase in bulk density is not

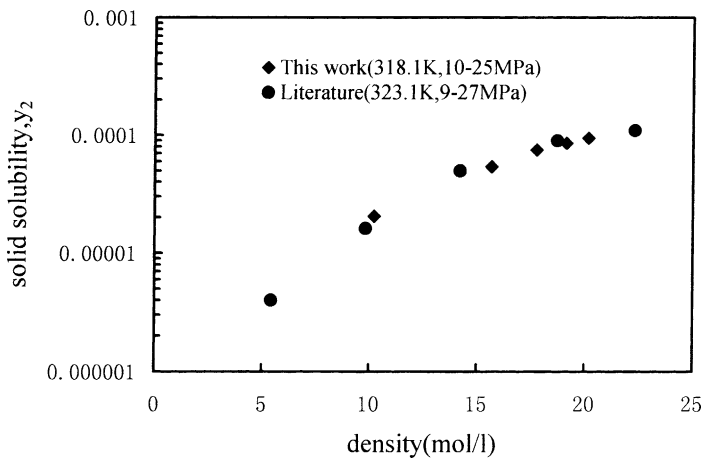

Fig. 4. Comparison of the solubility data of this work and that of Johnston et al. [9] for anthracene in CO_2.

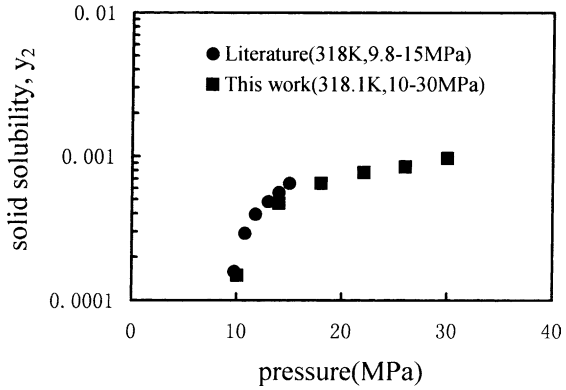

Fig. 5. Comparison of the solubility data of this work and that of Tan and Weng [10] for 2-naphthol in CO_2.

expected to be very significant and should be within a few percent (0–3% for $P > 18$ MPa) for the cosolvent concentration range between 1 and 5% [8].

The effects of density on the solubility of solids in CO_2 with cosolvent are shown in Figs. 6–9. From the figures it can be seen that the solubility of solutes increases with increasing density in general.

Table 3
Solubility of 2-naphthol in CO_2 with cosolvent of 3.6 mol%

T (K)	P (Mpa)	ρ (mol/l)	y_2 ($\times 10^4$)	T (K)	P (MPa)	ρ (mol/l)	y_2 ($\times 10^4$)	T (K)	P (MPa)	ρ (mol/l)	y_2 ($\times 10^4$)
Acetone											
308.1	10.05	16.25	4.83	318.1	10.05	13.621	4.78	328.1	10.05	9.931	3.79
308.1	14.0	17.85	5.85	318.1	14.0	16.17	7.66	328.1	14.0	14.26	10.7
308.1	18.0	18.93	6.35	318.1	18.0	17.59	9.77	328.1	18.0	16.14	15.0
308.1	22.05	19.76	7.06	318.1	22.05	18.61	11.0	328.1	22.05	17.41	18.7
308.1	26.0	20.42	8.16	318.1	26.0	19.40	12.6	328.1	26.0	18.34	22.3
308.1	30.0	20.99	9.16	318.1	30.0	20.06	15.0	328.1	30.0	19.11	19.0
Ethanol											
308.1	10.05	17.01	18.2	318.1	10.05	14.35	11.5	328.1	10.05	10.40	5.53
308.1	14.0	18.54	21.7	318.1	14.0	16.79	20.6	328.1	14.0	14.79	14.9
308.1	18.0	19.59	23.6	318.1	18.0	18.19	23.6	328.1	18.0	16.68	21.6
308.1	22.05	20.41	25.3	318.1	22.05	19.22	25.7	328.1	22.05	17.95	24.3
308.1	26.0	21.07	26.8	318.1	26.0	20.00	27.5	328.1	26.0	18.89	29.3
308.1	30.0	21.63	27.7	318.1	30.0	20.66	30.2	328.1	30.0	19.66	32.7
Cyclohexane											
308.1	10.05	16.17	7.33	318.1	10.05	13.81	5.80	328.1	10.05	10.54	3.13
308.1	14.0	17.65	8.84	318.1	14.0	16.08	8.51	328.1	14.0	14.31	8.93
308.1	18.0	18.67	9.74	318.1	18.0	17.40	10.7	328.1	18.0	16.05	12.2
308.1	22.05	19.46	10.6	318.1	22.05	18.37	13.3	328.1	22.05	17.23	14.6
308.1	26.0	20.09	11.4	318.1	26.0	19.12	13.8	328.1	26.0	18.12	17.8
308.1	30.0	20.64	12.4	318.1	30.0	19.76	15.5	328.1	30.0	18.85	18.9

Table 4
Solubility of anthracene in CO_2 with cosolvent of 4.0 mol%

T (K)	P (MPa)	ρ (mol/l)	y_2 ($\times 10^5$)	T (K)	P (MPa)	ρ (mol/l)	y_2 ($\times 10^5$)	T (K)	P (MPa)	ρ (mol/l)	y_2 ($\times 10^5$)
Acetone											
308.1	10.0	16.37	6.66	318.1	10.0	13.79	5.57	328.1	10.0	10.19	3.68
308.1	15.0	18.19	7.68	318.1	15.0	16.63	9.39	328.1	15.0	14.95	8.68
308.1	20.0	19.37	8.59	318.1	20.0	18.15	10.3	328.1	20.0	16.87	10.6
308.1	25.0	20.25	9.16	318.1	25.0	19.22	11.2	328.1	25.0	18.43	12.8
308.1	30.0	20.96	9.56	318.1	30.0	20.05	11.9	328.1	30.0	19.10	13.5
Ethanol											
308.1	10.0	17.14	8.51	318.1	10.0	14.63	7.78	328.1	10.0	10.77	5.22
308.1	15.0	18.96	9.92	318.1	15.0	17.34	9.93	328.1	15.0	15.54	9.88
308.1	20.0	20.09	10.9	318.1	20.0	18.81	11.5	328.1	20.0	17.48	12.7
308.1	25.0	20.96	11.6	318.1	25.0	19.79	12.7	328.1	25.0	18.75	14.4
308.1	30.0	21.67	12.5	318.1	30.0	20.71	13.7	328.1	30.0	19.71	15.4
Cyclohexane											
308.1	10.0	16.26	9.22	318.1	10.0	14.00	7.54	328.1	10.0	10.86	5.60
308.1	15.0	17.95	11.1	318.1	15.0	16.50	10.9	328.1	15.0	14.92	11.1
308.1	20.0	19.05	13.0	318.1	20.0	17.91	13.3	328.1	20.0	16.71	14.3
308.1	25.0	19.88	14.2	318.1	25.0	18.91	15.0	328.1	25.0	17.89	16.4
308.1	30.0	20.56	15.1	318.1	30.0	19.69	15.8	328.1	30.0	18.82	17.8

4.4. Effect of cosolvent

Both polar and nonpolar solvents were adopted as cosolvents in this work, and both polar and nonpolar solids were selected as solutes, therefore, the experimental data measured in this work are useful to study the effects of cosolvents.

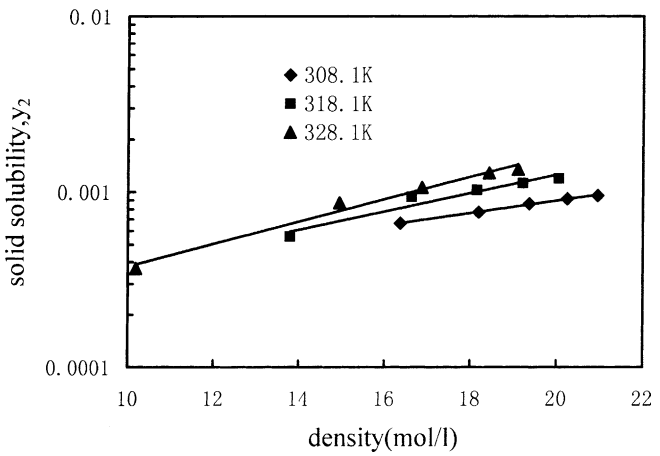

Fig. 6. Solubility of 2-naphthol in CO_2 with cosolvent of 3.6 mol% acetone.

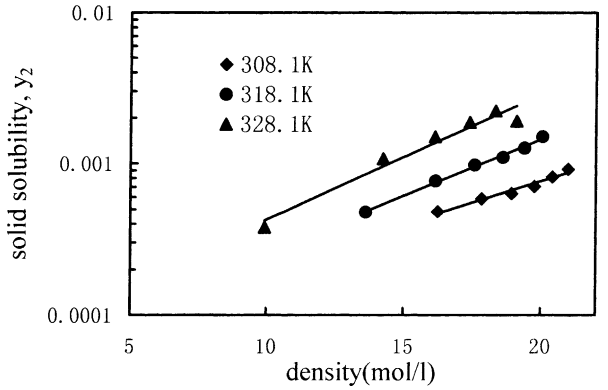

Fig. 7. Solubility of anthracene in CO_2 with cosolvent of 4.0 mol% acetone.

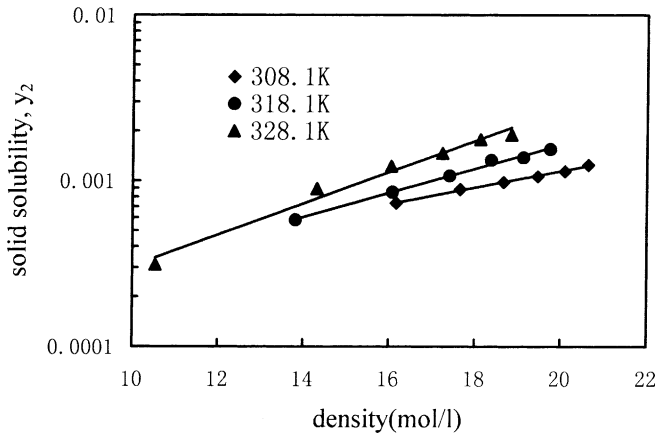

Fig. 8. Solubility of 2-naphthol in CO_2 with cosolvent of 3.6 mol% cyclohexane.

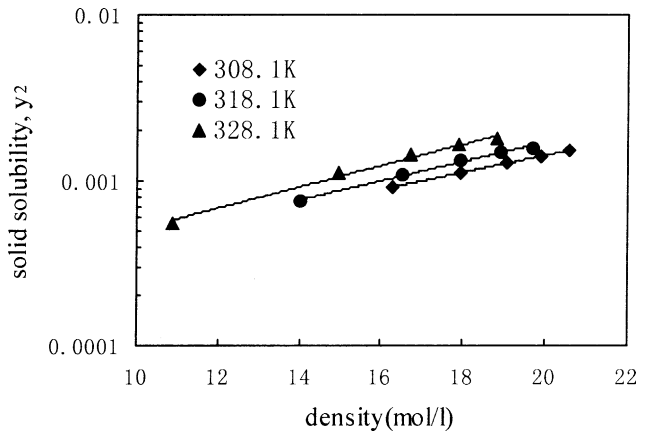

Fig. 9. Solubility of anthracene in CO_2 with cosolvent of 4.0 mol% cyclohexane.

Table 5
The average effect factors of cosolvent

Cosolvent	Temperature (K)					
	2-Naphthol			Anthracene		
	308.1	318.1	328.1	308.1	318.1	328.1
Acetone	1.43	1.81	2.37	1.31	1.69	1.59
Ethanol	5.04	4.24	3.19	1.67	2.03	1.97
Cyclohexane	2.10	2.05	1.86	1.94	2.19	2.19

The effect factor of cosolvent can be defined as [8]:

$$e = \frac{y_2^{\text{cosolvent}}}{y_2^{\text{pure}}} \tag{1}$$

where y_2^{pure} and $y_2^{\text{cosolvent}}$ denote the solubility of solids in pure SCF and in SCF with cosolvent, respectively. The average cosolvent effect factors are listed in Table 5.

Since solubility enhancement by the addition of a cosolvent is mainly caused by the formation of special interactions between the solute and cosolvent molecules, it is not surprising to find that the largest cosolvent effect on polar solute, 2-naphthol, is from ethanol, since ethanol has the strongest interactions with the solute among the three solvents used. While for the nonpolar solute, anthracene, the largest cosolvent effect comes from the nonpolar solvent, cyclohexane. In this case, the interactions between the solute and cosolvent molecules come mainly from the dispersion force.

5. Conclusion

A continuous flow apparatus was used to determine the solubility of anthracene and 2-naphthol in supercritical CO_2 in the temperature range of 308.1–328.1 K and the pressure range of 10–30 MPa, with and without cosolvent. Both polar and nonpolar solvents were adopted as cosolvents, and the cosolvent effects were studied experimentally. The experimental data are useful to the theoretical modeling research, which also provide fundamental data for SCFE process design and development.

List of symbols

e	effect factor of cosolvent
P	pressure (MPa)
T	temperature (K)
y_2	molar fraction of solid in supercritical phase (solid solubility)
$y_2^{\text{cosolvent}}$	solubility of solids in SCF with cosolvent
y_2^{pure}	solubility of solids in pure SCF

Greek letter

ρ	density (mol/l)

Acknowledgements

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