Chinese Chemical Letters Vol. 11, No. 9, pp. 823–826, 2000 

# Enhancement of Solubility of Troeger's Base in Supercritical Carbon Dioxide by Methanol

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**Abstract:** The solubility of Troeger's base (TB) in SC-$CO_2$/$CH_3OH$ was measured at 308K in the pressure range of 8 to 13 MPa, and methanol concentration ranges from 0 to 20 mol%. The solubility increases dramatically with methanol concentration. Comparison of solubility in supercritical $CO_2$ with and without 10 mol% $CH_3OH$ in the pressure of 8 MPa at 308K implies that both curves are steep in the lower pressure range but become smooth as the pressure increases.

**Keywords:** Solubility, supercritical $CO_2$, methanol, Troeger's base.

## Introduction

The most commonly used mobile phase in supercritical-fluid chromatography (SFC) is carbon dioxide, which is a nonpolar solvent. Nonpolar compounds of low molecular weight are well dissolved and eluted, but the solubility decreases as the polarity or the molecular weight increases. Investigators found that by adding a small amount of polar cosolvent to nonpolar SCFs the solubility of a polar substance increases significantly[1,2]. Since the mechanism of the solubility enhancement and the selectivity improvement by a cosolvent are complex, solubility data over a wide temperature and pressure range are desirable for engineering as well as for thermodynamic considerations.

TB is one of the classical racemates with many features. It has been used in many fields, such as chiral solvating agents, DNA-binding ligands and for the construction of biomimetic molecular receptors and clathrate hosts[3]. In order to separate TB racemate by supercritical chromatography, its solubility in supercritical fluid becomes important. In our previous work[4], the solubility of TB in SC-$CO_2$ was determined. In the present work, methanol was used as a cosolvent to increase the solubility of TB. And satisfactory results were obtained (typical solubility enhancement of 1 order of magnitude).

## Experimental

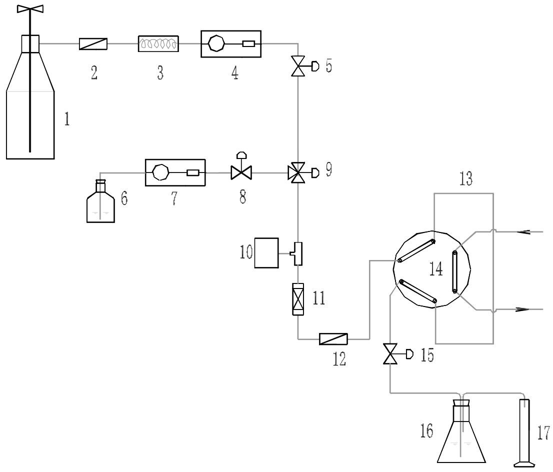
### *Materials*

$CO_2$ (purity 99.99%) was obtained from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. A racemic mixture of Troeger's base with a purity 98% was purchased from Aldrich Chemical Company Inc. Methanol was AR grade, and supplied by Hangzhou Chemical Plant (purity >99.5%).

*Apparatus and procedure*

The apparatus used was described in detail elsewhere[4]. Briefly, it consisted of a gas cylinder, a cooling bath, two HPLC-pumps, a saturator(50 × 4.6 mm empty HPLC-column), a digital pressure gauge, and a constant temperature bath (**Figure 1**).

**Figure 1** Scheme of the apparatus for determination of solubility in SCF




1. gas cylinder; 2. fliter; 3. condenser; 4. HPLC-pump; 5. valve; 6. cosolvent tank; 7. HPLC-pump; 8. valve; 9. three way valve; 10. pressure transducer; 11. saturator; 12. filter; 13. injection loop; 14. sampling valve; 15. valve; 16. Erlenmeyer flask; 17. graduated cylinder

The procedure was also similar to that employed in previous work[4]. The main difference was the method to prepare mobile phases of mixture. $CO_2$ and methanol were pumped with two independent pumps and then mixed before entering the chromatographic column. The flow rate of each pump was calibrated by the volume of SCF or methanol pumped within definite time interval. Therefore the composition of the mobile phase was reproducible.

**Results and Discussion**

In the previous work[4], solubility isotherms for TB in SC-$CO_2$ were obtained at 308, 318 and 328K over 8-15 MPa range. Although the solubility changes with temperature and pressure, all the solubility data are within $10^{-4}$ mole fraction.

In the present study, the solubility of TB in $CO_2$ with methanol was determined at 308K and 8 MPa, and the methanol concentration ranges from 0 to 20 mol%. The data represent an average of at least five determinations. As the result shown in **Figure 2**, the solubility increases dramatically with the concentration of methanol (typical 1 order of magnitude). This implies that the interaction between TB and methanol is quite strong.

**Figure 2** Solubility of TB in supercritical carbon dioxide with methanol cosolvent

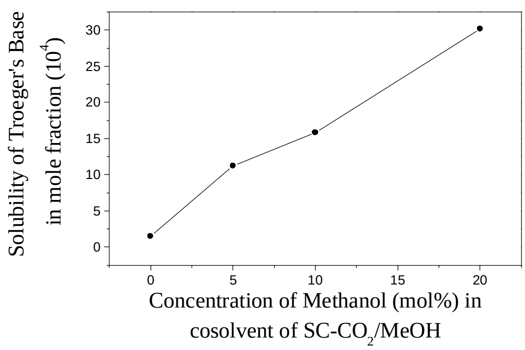



**Figure 3** Solubility of TB in supercritical carbon dioxide with and without methanol cosolvent

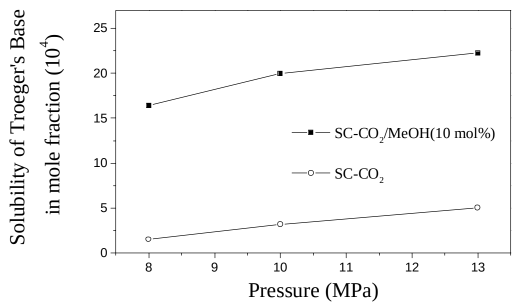



**Table 1.** Comparison of solubility in SC-$CO_2$ with and without $CH_3OH$

| Pressure (MPa) | TB solubility(mole/L) $CO_2/CH_3OH$ | $CO_2$ | Absolute difference of solubility with and without $CH_3OH$ | Ratio of solubility with $CH_3OH$ to that without $CH_3OH$ |
|---|---|---|---|---|
| 8 | 0.00164 | 0.000150 | 0.00149 | 10.93 |
| 10 | 0.00200 | 0.000316 | 0.00168 | 6.32 |
| 13 | 0.00223 | 0.000501 | 0.00172 | 4.44 |

The solubility of TB in SC-$CO_2$ with 10 mol% methanol cosolvent was measured at 308K in the pressure range from 8 to 13 MPa. The results are compared with the data without the cosolvent in **Figure 3**. It can be seen that both curves with and without the cosolvent are steep in the lower pressure range but become smooth as pressure increases. The absolute difference between the solubilities with and without the cosolvent keeps almost constant in the pressure range, but the ratio of the solubility with methanol to that without the cosolvent is greater at the lower pressure (**Table 1**).

## Acknowledgment

The authors are grateful to the National Natural Science Foundation of China for the financial support (Project no. 29776040).

## References

1. M. Zhong, B. Han, H. Yan, *J. Supercritical Fluids*, **1997**, *10*, 113.
2. B. Guan, Z. Liu, B. Han, H. Yan, *J. Supercritical Fluids*, **1999**, *14*, 213.
3. Bag, Braja Gopal, *Curri. Sci.*, **1995**, *68*(3), 279.
4. Q. L. Ren, B. G. Su, M. Huang, P. D. Wu, *J. Chemical and Engineering Data*, **2000**, *45*(3) (in press).

Received 8 March 2000