# Why Do Co-solvents Enhance the Solubility of Solutes in Supercritical Fluids? New Evidence and Opinion

**Xiaogang Zhang, Buxing Han,* Zhenshan Hou, Jianling Zhang, Zhimin Liu, Tao Jiang, Jun He, and Hongping Li[a]**

**Abstract:** The effects of two polar co-solvents, chlorodifluoromethane and acetone, on the solubility and enthalpy of a solution of 1,4-naphthoquinone in supercritical (SC) $CO_2$ were studied. We found that the dissolution process becomes less exothermic in the presence of the co-solvents relative to that in pure $CO_2$, although the solubility is enhanced significantly by the co-solvents. This indicates that the increase in the solubility by adding co-solvents results from the increase of the entropy of solution. On the basis of the unexpected results we propose a new mechanism for the solubility enhancement of the solute by the co-solvents in supercritical fluids (SCF); this should be applicable to cases in which the local density of the SC solvent around the solute and the co-solvent is larger, and the co-solvent associates preferentially with the solute. The results are also very important for the understanding of other fundamental questions of SCF science, such as the effect of co-solvents on the thermodynamic and kinetic properties of the reactions in SCFs.

**Keywords:** calorimetry · co-solvent · solution enthalpy · solvent effects · supercritical fluids

## Introduction

Supercritical fluid (SCF) science and technology has rapidly developed in the past decade and will be one of the most important topics in the coming decades with respect to clean and environmentally benign chemistry and technology.[1] Utilization of supercritical (SC) $CO_2$, which is non-toxic, non-flammable, and environmentally benign, is most attractive because it can provide the opportunity for replacing conventional organic solvents and solving some challenging technique problems in a variety of applications; [2] it also has a relatively mild critical temperature and pressure (31.1° C and 7.38 MPa). However, $CO_2$ is a poor solvent for high molecular-weight or hydrophilic molecules because of its very low dielectric constant and polarizability per volume; this limits wider application. It is well known that small amount of polar co-solvent can enhance the solubility of a polar solute in SC $CO_2$ significantly.[3] A general explanation is that the interaction between the co-solvent and solute is very strong; this explanation is based on the results of spectroscopic studies,[4] integral equation methods,[5] and molecular simulation.[6] However, the mechanism for the solubility enhancement by co-solvents is still unclear. It is no doubt that an insight into the mechanism would be of great importance to the development of SC science and technology.

The effect of co-solvents on the thermodynamic properties of a solute in solution is a key for understanding the mechanism of the solubility enhancement by co-solvents. In this work, we conduct the first direct measurement for the solution enthalpy of solute in SCFs in the presence of co-solvents. The effects of two polar co-solvents, chlorodifluoromethane and acetone, on the solubility and enthalpy of solution of 1,4-naphthoquinone in SC $CO_2$ are studied. We find that the enthalpy of solution increases significantly by the addition of co-solvents, that is, the dissolution process becomes less exothermic in the presence of the co-solvents, although the solubility is enhanced significantly. Detailed analysis allows us to get the real mechanism of the solubility enhancement by the co-solvents.

## Experimental Section

**Materials:** $CO_2$ (99.995%) and chlorodifluoromethane (99.9%) were supplied by the Beijing Analytical Instrument Factory. Acetone (99.5%) was produced by the Beijing Chemical Reagent Factory. 1,4-Naphthoquinone (99%) was purchased from Aldrich. The chemicals were used as received.

**Apparatus and procedures:** The calorimeter was a constant temperature environment type, which was recently constructed in our laboratory. It can be used to determine the enthalpy of solution and the solubility of solute in

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[a] Prof. B. Han, Dr. X. Zhang, Dr. Z. Hou, J. Zhang, Dr. Z. Liu,
Dr. T. Jiang, Dr. J. He, H. Li
Center for Molecular Science, Institute of Chemistry
Chinese Academy of Sciences, Beijing 100080 (China)
Fax: (+86) 10-62559373
E-mail: hanbx@infoc3.icas.ac.cn

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SCFs. The principle of the calorimeter is simple. At constant pressure, SC solvent that contains the co-solvent of interest flows through a calorimeter vessel, which contains a solid solute that is then dissolves. The temperature of the calorimeter vessel changes if the dissolution process absorbs or releases heat. The enthalpy of solution is obtained by the mass of the solute dissolved, the energy equivalent, and the temperature change of calorimeter vessel after correction by using graphical extrapolation based on Dickinson's method.[7] The schematic diagram of the calorimeter is shown in Figure 1. It consists mainly of a calorimeter vessel, an equilibrium cell (for the measuring of solubility), a sample collector, a gas cylinder containing a pure or mixed solvent, thermostats, an electric calibrator, a precision thermistor thermometer, and a data collection and processing system. The accuracy of the pressure gauge, which was composed of a transducer (FOXBORO/ICT) and an indicator, was ±0.025 MPa in the pressure range of 0–20 MPa. Temperature fluctuation of the water bath was less than ±0.001 K in 24 h, and the sensitivity of the temperature measurement was ±0.00005 K. The stability of pressure during the experiments was very important. To do this, we used an 8 L gas cylinder submerged into a constant temperature water bath (shown in Figure 1). The pressure of the gas in the cylinder was easily controlled by the temperature of the water bath. Experiments showed that this method was very effective because the pressure change was less than ±0.01 MPa during an experiment. A detailed description of the calorimeter and experimental procedure used to determine the enthalpy of solution naphthalene in SC $CO_2$ was reported previously.[8] The main difference in the set up was that the gas cylinder in Figure 1 contained a SC $CO_2$/co-solvent mixture, as the enthalpy and solubility of the solute in a SC $CO_2$/co-solvent was under investigation in this work, while that used in the previous work[8] contained pure $CO_2$, because the enthalpy and solubility of naphthalene in pure SC $CO_2$ was studied.

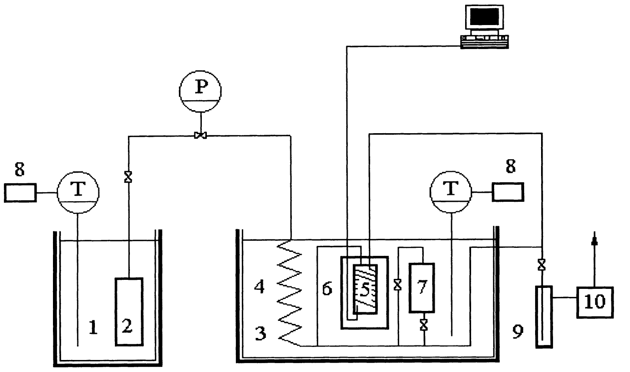


Figure 1. Schematic representation of calorimeter for measuring solution enthalpy of solids in supercritical fluids: 1 and 3: constant-temperature bath, 2: gas cylinder, 4: preheating coil, 5: calorimeter vessel, 6: outer can, 7: equilibrium cell, 8: temperature controller, 9: sample trap, 10: flow gas meter.

All the experiments were performed at 308.15 K. The calorimeter vessel and equilibrium cell were thoroughly cleaned before experiment and then tightly packed with mixtures of solid solute and copper scraps, which enhanced the heat conduction, reduced the possibility of the solvent channeling, and prevented the solute material from lump formation under pressure. Before each experiment, the system was stabilized for at least 8 h to reach thermal equilibrium. The solubility was determined by opening the needle valve slightly to allow SC fluid to pass through the equilibrium cell. The solubility of the solute could be easily calculated by the masses of the solute collected and solvent passing through the flow meter. These data were used to calculate the mole fraction of the solute in the vapor phase at the specified temperature and pressure. At each condition, the experiment was repeated at least three times and the reproducibility was better than ±2.5%.

The procedure for the enthalpy measurement was similar to that of the solubility measurement. SC fluid was allowed to pass through the calorimeter vessel, and the temperature change was monitored by using a computer. The mass of the solute dissolved in this process was known by the solubility at the experimental conditions and the mass of the fluid passing through the calorimeter vessel. The energy equivalent was measured by an electric calibrator under the experimental conditions; the repeatability of the measurement was better than ±0.2%.

## Results and Discussion

The solubility and solution enthalpy of 1,4-naphthoquinone in pure $CO_2$, $CO_2$/$CHClF_2$ (1.1 mol%), $CO_2$/acetone (0.5 mol%), and $CO_2$/acetone (1.1 mol%) were measured at 308.15 K and different pressures. To confirm that the mixed solvents are in the single-phase region, we first determined the phase behavior of the $CO_2$/co-solvent mixtures at 308.15 K by using the optical cell reported previously.[9] The results show that $CO_2$/acetone (0.5 mol%) and $CO_2$/acetone (1.1 mol%) mixture are a single phase when the pressure is higher than 7.30 MPa, and $CO_2$/$CHClF_2$ (1.1 mol%) mixture is homogeneous at any pressure. All the experiments to determine the solubility and enthalpy of solution were conducted at pressures higher than 7.3 MPa. The results are listed in Table 1. The densities of the mixed solvents were also

Table 1. Solubility and enthalpy of solution of1,4-naphthoquinone in pure $CO_2$, $CO_2$-$CHClF_2$ (R22) and $CO_2$-acetone at 308.15 K and different pressures.

| 1,4-naphthoquinone in pure $CO_2$ | | | 1,4-naphthoquinone in $CO_2$-$CHClF_2$ (1.1 mol%) | | | 1,4-naphthoquinone in $CO_2$-acetone (1.1 mol% | | | 1,4-naphthoquinone in $CO_2$-acetone (0.5 mol%) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Density mol $L^{-1}$ | Solubility ($\times 10^3$) mole frac | Solution enthalpy kJ $mol^{-1}$ | Density mo $L^{-1}$ | Solubility ($\times 10^3$) mole frac | Solution enthalpy kJ $mol^{-1}$ | Density mol $L^{-1}$ | Solubility ($\times 10^3$) mole frac | Solution enthalpy kJ $mol^{-1}$ | Density mol $L^{-1}$ | Solubility ($\times 10^3$) mole frac | Solution enthalpy kJ $mol^{-1}$ |
| 8.76 | 0.173 | 1018.50 | 8.18 | 0.516 | 237.94 | 10.18 | 4.601 | 0.53 | 6.80 | 0.564 | 233.22 |
| 9.06 | 0.193 | 1173.25 | 8.55 | 0.566 | 415.02 | 11.29 | 5.150 | 2.74 | 7.21 | 0.607 | 239.42 |
| 9.95 | 0.266 | 695.40 | 9.41 | 0.676 | 576.16 | 12.99 | 5.992 | 20.92 | 7.67 | 0.679 | 236.69 |
| 10.33 | 0.306 | 430.23 | 10.40 | 0.824 | 260.32 | 13.71 | 6.222 | 22.08 | 8.20 | 0.776 | 277.51 |
| 12.48 | 0.661 | 156.38 | 11.21 | 0.978 | 224.60 | 14.17 | 6.581 | 38.73 | 9.24 | 0.910 | 327.18 |
| 13.25 | 0.872 | 86.05 | 12.28 | 1.230 | 72.84 | 14.75 | 6.740 | 15.99 | 9.75 | 0.985 | 257.67 |
| 14.41 | 1.310 | 83.81 | 13.74 | 1.810 | 40.84 | 15.15 | 7.209 | 13.51 | 10.66 | 1.180 | 227.19 |
| 15.00 | 1.680 | 74.34 | 14.22 | 2.060 | 31.94 | 15.41 | 7.578 | 11.96 | 11.55 | 1.310 | 181.87 |
| | | | 14.65 | 2.180 | 18.21 | 15.61 | 7.602 | 8.61 | 12.21 | 1.470 | 151.57 |
| | | | | | | | | | 13.05 | 1.600 | 76.36 |
| | | | | | | | | | 13.54 | 1.740 | 54.68 |
| | | | | | | | | | 14.20 | 1.860 | 39.39 |
| | | | | | | | | | 15.04 | 2.090 | 17.74 |

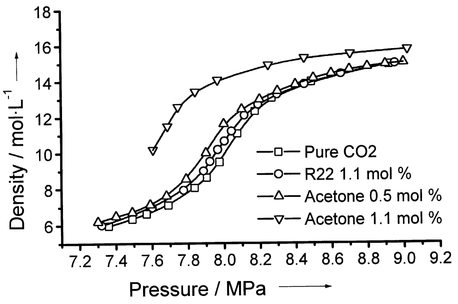


Figure 2. Densities of pure $CO_2$ and co-solvent/$CO_2$ mixtures at 308.15 K as a function of pressure.

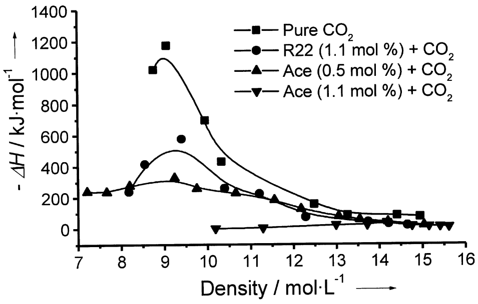


Figure 4. Enthalpy of solution of 1,4-naphthoquinone in $CO_2$, $CO_2$/$CHClF_2$ (R22) and $CO_2$/acetone at 308.15 K and different pressures.

determined by a gravimetric method[10] and the results are presented in Figure 2 and Table 2.

Figures 3 and 4 show the dependence of the solubility and enthalpy of solution on the density of the solvents modified by co-solvents. The negative enthalpy means that the dissolution process is exothermic. The corresponding pressure can be taken from the data in Table 2. Like many other systems studied, the co-solvents enhance the solubility considerably, especially in the lower density (pressure) region, at which the compressibility is high. Usually, this phenomenon is explained by the fact that the polarity of the solvent is increased and/or the interaction between the co-solvents and the solute is stronger than that between the solvent and the solute.[3i,4f,11]

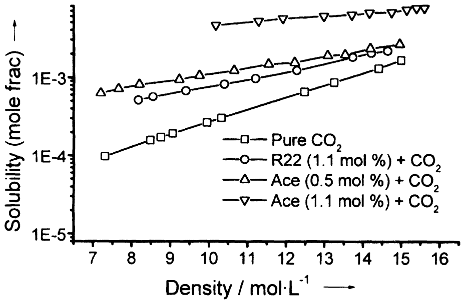


Figure 3. Solubility of 1,4-naphthoquinone in $CO_2$, $CO_2$/$CHClF_2$ (R22) and $CO_2$/acetone at 308.15 K and different pressures.

It is very interesting, and also unexpected, that the absolute value of the negative enthalpy of solution decreases significantly on addition of the co-solvents, especially in the lower density region. It means that the dissolution process becomes less exothermic as a polar co-solvent is added. In conventional solvents, strong intermolecular interaction between the solvents and solutes generally results in the dissolution process being more exothermic.[12]

It is known that solubility is related with the Gibbs free energy ($\Delta G$), and the higher the solubility is, the lower the value of $\Delta G$ is. The free energy $\Delta G$ is related with enthalpy ($\Delta H$) and entropy ($\Delta S$) of solution by the following well-known equations [Eq. (1) or (2)], in which $T$ is the absolute temperature.

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (2)$$

The solubility increases as the co-solvents are added as shown in Figure 3, indicating that $\Delta G$ decreases with the addition of the co-solvents. The absolute value of $\Delta H$ is decreased by the addition of the co-solvents; this is not

Table 2. Apparent densities of pure $CO_2$, $CO_2$-$CHClF_2$ (R22) and $CO_2$-acetone at 308.15 K and different pressures.

| Pure $CO_2$ | | $CO_2$-$CHClF_2$ (1.1 mol%) | | $CO_2$-acetone (1.1 mol%) | | $CO_2$-acetone (0.5 mol%) | |
|---|---|---|---|---|---|---|---|
| Pressure MPa | Density mol $L^{-1}$ | Pressure MPa | Density mol $L^{-1}$ | Pressure MPa | Density mol $L^{-1}$ | Pressure MPa | Density mol $L^{-1}$ |
| 7.36 | 5.97 | 7.32 | 6.00 | 7.61 | 10.18 | 7.30 | 6.20 |
| 7.49 | 6.35 | 7.60 | 6.96 | 7.69 | 11.49 | 7.40 | 6.50 |
| 7.57 | 6.63 | 7.78 | 7.93 | 7.75 | 12.56 | 7.49 | 6.72 |
| 7.69 | 7.10 | 7.89 | 8.99 | 7.84 | 13.43 | 7.59 | 7.13 |
| 7.84 | 8.05 | 7.92 | 9.52 | 7.97 | 14.05 | 7.68 | 7.61 |
| 7.91 | 8.62 | 7.97 | 10.18 | 8.25 | 14.89 | 7.79 | 8.54 |
| 7.98 | 9.50 | 8.00 | 10.65 | 8.45 | 15.27 | 7.90 | 10.00 |
| 8.08 | 11.06 | 8.04 | 11.21 | 8.71 | 15.51 | 8.00 | 11.61 |
| 8.17 | 12.32 | 8.12 | 12.10 | 9.02 | 15.75 | 8.10 | 12.44 |
| 8.27 | 13.05 | 8.19 | 12.68 | | | 8.20 | 12.97 |
| 8.49 | 13.98 | 8.30 | 13.26 | | | 8.30 | 13.43 |
| 8.92 | 14.92 | 8.45 | 13.82 | | | 8.40 | 13.80 |
| | | 8.65 | 14.39 | | | 8.50 | 14.15 |
| | | 8.95 | 14.97 | | | 8.60 | 14.40 |
| | | | | | | 8.70 | 14.62 |
| | | | | | | 8.80 | 14.79 |
| | | | | | | 8.90 | 14.91 |
| | | | | | | 9.00 | 15.01 |

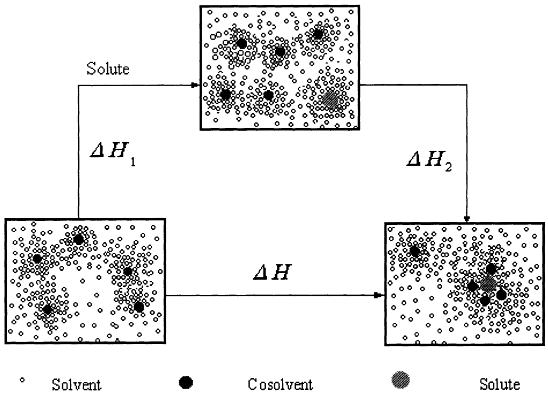
favorable to the increase of the solubility as can be seen from Equation (1). Thus, on the basis of the results in Figures 3 and 4 and Equations (1) or (2), we can obtain a new and unexpected conclusion: the significant solubility enhancement by the co-solvents results from the increase in $\Delta S$. This is qualitatively discussed below.

Many studies indicate that the local density of the SC solvent around a solute molecule can be higher than that in the bulk, especially in the highly compressible region. This is often referred to as local density and/or local composition enhancement or "clustering".[13] It should be emphasized that the term "clustering" is only used to define a situation in which the local density of the solvent about the solute exceeds, on average, that of the bulk. The term "cluster" does not imply the existence of a stable physical aggregation. Both of the co-solvents used in this work are polar compounds. It can be expected that the local density of $CO_2$ around the solute and the co-solvents is larger than that in the bulk, and that the co-solvents associate preferentially with the solute.

As discussed above, in our experiments $CO_2$ and the desired co-solvent are mixed first outside of the calorimeter, and then the enthalpy of solution in the mixed solvent is determined. Thus, the dissolution process of the solute in a $CO_2$ and co-solvent mixture can be expressed as Equation (3):

$$CO_2 + \text{co-solvent (solvated)} + \text{solute (solid)} \rightarrow \text{solute (in mixed solvent)} \quad (3)$$

It is known that thermodynamic functions are independent of the processes. The dissolution of the solute in a solvent/co-solvent mixture can be divided into two steps: 1) the solute is solvated by the solvent ($CO_2$) as in pure $CO_2$; 2) the solvated co-solvent and solvated solute interact and form the final solution. This is expressed schematically in Scheme 1.



Scheme 1.

The overall $\Delta H$ or $\Delta S$ values obtained from the sum of the two steps [Eqs. (4) and (5), respectively].

$$\Delta H = \Delta H_1 + \Delta H_2 \quad (4)$$

$$\Delta S = \Delta S_1 + \Delta S_2 \quad (5)$$

Here $\Delta H_1$, $\Delta H_2$, $\Delta S_1$, and $\Delta S_2$ are the enthalpy change and entropy change of the corresponding steps. $\Delta H_1$ or $\Delta S_1$ is equal to the enthalpy or entropy of solution of the solute in pure $CO_2$. Thus the effect of a co-solvent on $\Delta H$ and $\Delta S$ depends on the second step. The enthalpy change of the second step, $\Delta H_2$, consists of two parts. The first part is the enthalpy of the direct interaction of the solute and the co-solvent, which should be negative (exothermic), as in vacuum or in conventional liquid solutions. The second part of $\Delta H_2$ results from the fact that some of the $CO_2$ molecules around the co-solvent and the solute are removed during the process as qualitatively shown in Scheme 1; this gives a positive contribution to $\Delta H_2$. The second part is dominant, and, therefore, $\Delta H_2$ is positive. Thus, the absolute value of $\Delta H$ is less than that of $\Delta H_1$ (solution enthalpy in pure $CO_2$), that is, the dissolution process is less exothermic in the presence of the co-solvents relative to that in pure $CO_2$, which is not favorable to increase the solubility. On the other hand, a large number of $CO_2$ molecules enter into the bulk from $CO_2$/co-solvent and $CO_2$/solute clusters in the second step, and $\Delta S_2$ is increased by the addition of the co-solvents; this is favorable for the increase of the solubility. So, the enthalpy and entropy changes resulting from the addition of the co-solvents affect the solubility in opposite ways, and solubility enhancement on addition of co-solvents indicates that the entropy effect is dominant.

Figures 2–4 show that at the lower density or in the highly compressible region the reduction of $\Delta H$ is more significant. The main reason is that the local density augmentation or local composition enhancement are more pronounced, and more $CO_2$ molecules are removed during the association process of the co-solvents and the solute. Thus, the $\Delta H$ is affected more significantly by the addition of the co-solvents in the highly compressible region. At the same time, $\Delta S$ increases more significantly because larger number of $CO_2$ molecules enter the bulk from the solvated shells.

The effect of acetone on the solubility and the enthalpy of solution is more pronounced than $CHClF_2$, as can be seen from Figures 3 and 4. The main reason is that the polarity of acetone (dipole moment $m = 2.89$ D) is stronger than that of $CHClF_2$ ($m = 1.42$ D). Thus, the local density and local composition enhancement is more remarkable, and the entropy effect is more pronounced.

## Conclusion

On the basis of the experimental data and the analysis above, we can propose the new mechanism for the solubility enhancement by the co-solvents in SC $CO_2$. In the presence of the co-solvents the enthalpy change is not favorable for the solubility enhancement although the interaction between the co-solvents and the solute is stronger; however, the entropy change favors an increase in the solubility and this effect is dominant. This unusual phenomenon is related to the special solvation in SC solutions. It should be emphasized that this conclusion is only applicable in cases in which the local density of the SC solvent around the solute and the co-solvent is larger, and the co-solvent associates preferentially with the solute, that is, the local density and local composition enhancement is significant. Nevertheless, the results offer new insights into competitive enthalpy and entropy effects in dissolution processes of solutes in SC solvent near the critical condition; this is helpful for the understanding of some fundamental questions of SCF science, such as the effect of co-solvents on the thermodynamic and kinetic properties of the reactions in SCFs.

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