Enthalpy of Solution of 1,4-Naphthoquinone in CO_2 + *n*-Pentane in the Critical Region of the Binary Mixture: Mechanism of Solubility Enhancement

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Abstract: The enthalpy of solution ($\Delta_{solv}H_m$) and solubility of 1,4-naphthoquinone in CO_2 + *n*-pentane were measured at 308.15 K in the critical region of the binary fluid. In order to study the effect of phase behavior of the mixed solvent on $\Delta_{solv}H_m$, the experiments were carried out in the supercritical (SC) and subcritical region of the binary solvent. The density of the mixed solvent in different conditions was determined. The isothermal compressibility (K_T) of the mixed solvent, and the partial molar volume ($V_{n\text{-pentane}}$) of *n*-pentane in the solution were calculated. It was demonstrated that the $\Delta_{solv}H_m$ was negative in all conditions. $\Delta_{solv}H_m$ is nearly independent of pressure or density in all the solvents in a high-density region, in which compressibility of the solvent is very small; this indicates that the intermolecular interaction between the solvent and the solute is similar to that for liquid solutions. It is very interesting that $\Delta_{solv}H_m$ in the mixed SC fluid differs from the $\Delta_{solv}H_m$ in mixed subcritical fluids. The absolute value of $\Delta_{solv}H_m$ in the mixed SC fluid is close to that in pure SC CO_2 in the high-density region, and is much lower than that in pure SC CO_2 in the low-density region. In the mixed subcritical fluids, the $\Delta_{solv}H_m$ is also close to that in the pure CO_2 in the high-density region. However-

er, at the same density, the absolute value of $\Delta_{solv}H_m$ in the binary subcritical fluid is larger than that in pure CO_2 in the high-compressible region of the mixed solvent. The main reason for this is that the degree of clustering in the SC solutions is small at the density in which the degree of clustering is large in the subcritical solutions. It can be concluded that solubility enhancement by *n*-pentane in the mixed SC fluid is entropy driven. In contrast, the solubility enhancement by *n*-pentane in subcritical fluids is enthalpy driven. The intermolecular interaction in the SC solutions and subcritical solutions can be significantly different even if their densities are the same.

Keywords: co-solvent · solvent effects · supercritical fluids · thermodynamics

Introduction

Supercritical fluids (SCFs) have some unique properties.[1] They can be used in different processes, such as extraction and fractionation,[2] chemical reactions,[3] and material processing,[4] and some environmentally benign SCFs can be used as replacements for organic solvents. Moreover, supercritical (SC) technologies have many other advantages,[5] which will solve more challenging problems after our fundamental understanding of SCFs improves. It is known that small amounts of a suitable co-solvent can enhance the solubility of solutes, and can tune the reaction rates and selectiv-

ities in SCFs.[3] Co-solvent effect has played an important role and will become more and more important in SC science and technology. Also, the mechanism of co-solvent effect is an interesting topic to be studied further, and is of great importance to both pure and applied sciences.

In the recent published papers the phrases "in the critical region", or "near the critical point" were used. The fluids near their critical points have many features, which should be investigated further. The critical region of a mixture can be divided into a SC region and a subcritical region. Study of the properties of the fluids in different phase regions simultaneously is one of the effective routes to probe their features. In the previous paper, we conducted the first direct measurement of enthalpy of solution ($\Delta_{solv}H_m$) of a solute in SCF + co-solvent mixtures, and the $\Delta_{solv}H_m$ of 1,4-naphthoquinone in CO_2 + acetone and CO_2 + chlorodifluoromethane was determined in the SC regions of the mixed solvents.[6] It was demonstrated that the dissolution process became less exothermic in the presence of the co-solvents relative to that in pure CO_2, although the co-solvents en-

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hanced the solubility significantly. This indicated that an increase in the solubility by adding the polar co-solvents resulted from the increase in entropy of solution. On the basis of the unexpected results we proposed a new mechanism for solubility enhancement of a solute by the co-solvents in the SC fluids.

In this work, we study the solubility and $\Delta_{solv}H_m$ of 1,4-naphthoquinone in $CO_2 + n$-pentane mixed solvents. Experiments are carried out in both the SC and subcritical region of mixed solvents near the binary critical point. The $\Delta_{solv}H_m$ of the solute in subcritical $CO_2 +$ acetone is also determined. The intermolecular interaction in the systems is discussed.

Experimental Section

Materials: CO_2 (99.995 %) was supplied by Beijing Analytical Instrument Factory. n-Pentane (99.5 %) and acetone (99.5 %) were produced by Beijing Chemical Reagent Factory. 1,4-Naphthoquinone (99 %) was obtained from Aldrich Chemical Co., and was used as received.

Apparatus and procedures to determine the density: The densities of the mixtures were determined by the view-cell method, and the detailed measurements were showed in our previous work.[7] The accuracies of temperature and pressure measurements were ± 0.05 K and ± 0.025 MPa, respectively. In a typical experiment, the air in the view cell was removed by vacuum, and the desired amount of the liquid chemical (n-pentane) was charged. CO_2 was then added from a sample bomb. The mass of CO_2 in the view cell was known from the mass difference of the sample bomb before and after charging the system. The cell was placed in a water bath at 308.15 K. After thermal equilibrium had been reached, the piston in the optical cell was moved up and down to change the volume and the pressure of the system. The volume of the system was known from the position of the piston, which was calibrated accurately by using water as a medium. It was estimated that the accuracy of determined density data was better than ± 0.001 g·cm^{-3}.

Apparatus and procedures to determine $\Delta_{solv}H_m$: The calorimeter was a constant temperature-environment type. A detailed description of the calorimeter and the procedure was given elsewhere.[8] It consisted mainly of a gas cylinder, a calorimeter vessel, an equilibrium cell, a sample collector, a high-pressure system, thermostats, an electric calibrator, a precision thermistor thermometer, and a datum collecting 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 ± 0.001 K, and the sensitivity of the temperature measurement was ± 0.0005 K.

The $\Delta_{solv}H_m$ data reported were the average of at least three experimental runs with a reproducibility of better than ± 2.5 %. Repeatability of the measurement for an energy equivalent was better than ± 0.2 %.

region of the binary mixture. The experiments were carried out at 308.15 K. The critical composition and the critical pressure at this temperature are $x_2 = 0.021$ (mole fraction of n-pentane) and 7.47 MPa, respectively.[9] The phase diagram calculated from the Peng–Robinson equation of state[10] (PR EOS), and the experimental data are shown in Figure 1. A
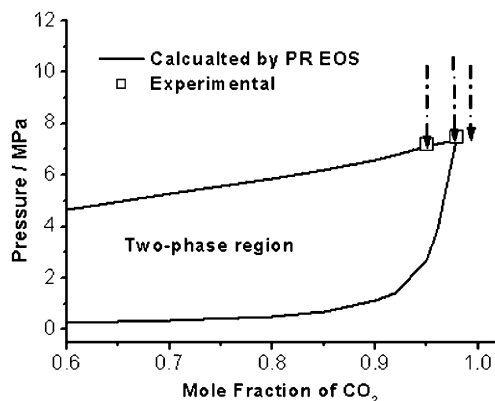

Figure 1. Phase diagram of the $CO_2 + n$-pentane system at 308.15 K.

homogenous mixture can be regarded as vapor or supercritical fluid at the right side of the binary critical composition. At the left side of the critical composition, the mixture is compressed liquid or homogenous subcritical fluid when the pressure is higher than the bubble point pressure. On the basis of the phase behavior of the mixed solvents, we selected the mixed solvents with $x_2 = 0.01$, $x_2 = 0.021$, and $x_2 = 0.05$. The experimental results are indicated in Figure 1 by the vertical lines. It should be mentioned that the experiments were carried out in a single-phase region of the mixed solvents. The mixed solvent with $x_2 = 0.01$ is in the SC region, and the mixtures with $x_2 = 0.021$ and 0.05 are above the binary critical point and the bubble point, and can be regarded as homogeneous subcritical fluids. The densities of the mixed solvents were determined in this work, and the results are given in Table 1 and Figure 2.

Solubility and enthalpy of solution ($\Delta_{solv}H_m$): The solubility and $\Delta_{solv}H_m$ of 1,4-naphthoquinone in $CO_2(1) + n$-pentane(2) mixtures are listed in Table 1. The negative enthalpy

Results

Phase behavior and the density of the mixed solvent: In this work we focus on how the solubility and enthalpy of solution ($\Delta_{solv}H_m$) of 1,4-naphthoquinone in $CO_2(1) + n$-pentane(2) mixed solvents change with pressure and composition of the mixed solvents in the critical

Table 1. The solubility (x_3, mole fraction) and enthalpy of solution ($\Delta_{solv}H_m$) [kJ mol^{-1}] of the solute, and the density (ρ) [mol L^{-1}] of the mixed solvent at 308.15 K and different pressures (p) [MPa].

| $x_2 = 0.01$				$x_2 = 0.021$				$x_2 = 0.05$			
p	ρ	$10^3 \times x_3$	$-\Delta_{solv}H_m$	p	ρ	$10^3 \times x_3$	$-\Delta_{solv}H_m$	p	ρ	$10^3 \times x_3$	$-\Delta_{solv}H_m$
7.62	8.34	0.257	274.4	7.49	12.24	1.02	285.9	7.20	14.10	2.32	363.2
7.73	9.41	0.352	244.4	7.77	13.96	1.66	209.7	7.39	14.40	2.87	288.6
7.83	10.44	0.496	223.0	7.95	14.47	1.93	169.2	7.58	14.70	3.24	233.2
7.93	11.90	0.745	163.0	8.11	14.73	2.13	128.7	7.65	14.79	3.48	196.3
8.05	13.05	1.00	88.2	8.32	15.07	2.44	101.6	7.75	14.88	3.68	176.4
8.19	13.80	1.23	77.0	8.55	15.33	2.85	72.0	7.93	15.07	4.15	150.4
8.43	14.53	1.56	63.7	8.74	15.54	3.05	56.6	8.16	15.28	4.55	117.5
8.56	14.80	1.76	55.9	8.92	15.73	3.20	48.4	8.39	15.48	5.28	87.7
8.80	15.22	2.09	41.4	9.10	15.83	3.40	43.2	8.61	15.62	5.74	64.0
8.97	15.49	2.28	37.4	9.27	15.90	3.60	38.9	8.95	15.83	6.19	52.2
				9.75	16.25	4.22	31.7				
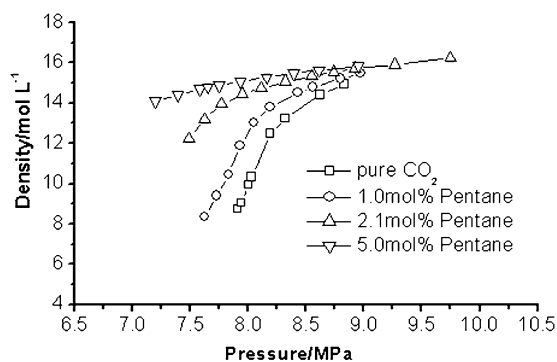
Figure 2. Density of CO_2 + n-pentane mixtures as a function of pressure at 308.15 K.

means that the dissolution process is exothermic. The results are also presented in Figures 3, 4, and 5. The data in pure SC CO_2 is also given for comparison.[6]

Isothermal compressibility of the fluids: The isothermal compressibility (K_T) of a fluid is an important characteristic parameter related to the solution structure.[11] The K_T of CO_2 + n-pentane mixtures was calculated by using the density data in Table 1, and Equation (1).
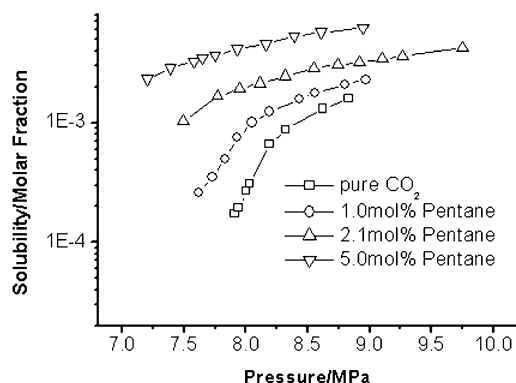
Figure 3. Solubility dependence of 1,4-naphthoquinone in CO_2 and CO_2 + n-pentane mixtures on pressure at 308.15 K.
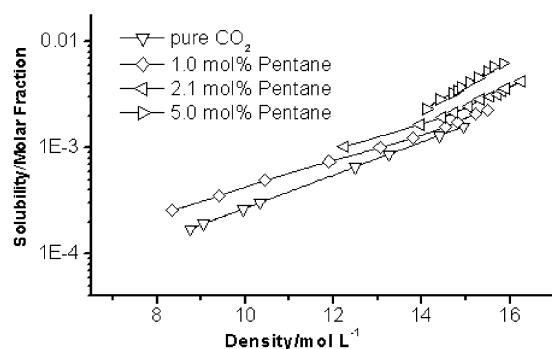

Figure 4. Solubility dependence of 1,4-naphthoquinone in CO_2 and CO_2 + n-pentane mixtures on density at 308.15 K.
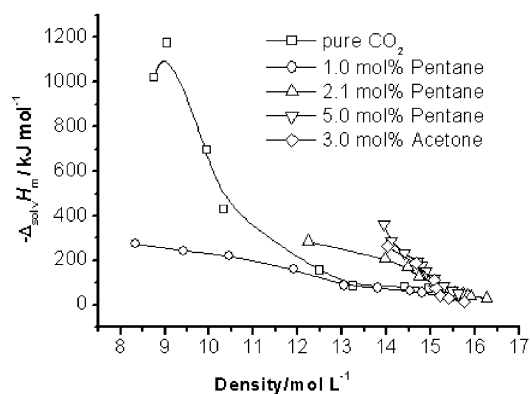

Figure 5. Enthalpy dependence of a solution of 1,4-naphthoquinone in CO_2 and CO_2 + n-pentane on density at 308.15 K.

$$K_T = \frac{1}{\rho}\left(\frac{\delta\rho}{\delta p}\right)_T \tag{1}$$

In this equation ρ is the density of the fluids. The effect of density and composition on the K_T is shown in Figure 6.
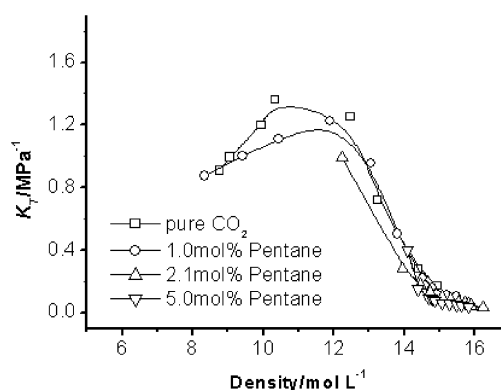

Figure 6. Dependence of isothermal compressibility of CO_2 + n-pentane mixtures on density at 308.15 K.

Partial molar volume of n-pentane in CO_2 + n-pentane mixtures: Eckert and co-workers[11,12] found that the partial molar volume (V_i) of a solute in a SCF could be a large negative value in a high-compressible region. They explained this phenomenon by "clustering" of the SC solvent around the solute. In this work, we calculated the $V_{n\text{-pentane}}$ of n-pentane in the n-pentane + CO_2 mixtures by using the density data in Table 1, and Equation (2).[13] $V_{n\text{-pentane}}$ as a function of density is shown in Figure 7.

$$V_{n\text{-pentane}} = (1/\rho - 1/\rho_0)/m - M_2/\rho \tag{2}$$

In Equation (2) ρ and ρ_0 are the densities of the mixed solvent and pure solvent, respectively; M_2 and m stand for the solute molecular mass and the molality, respectively.
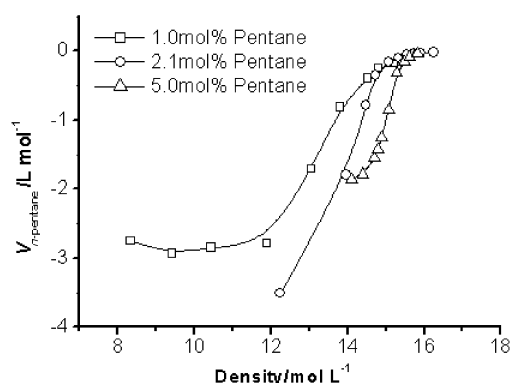
Figure 7. Dependence of partial molar volume of n-pentane in CO_2 + n-pentane mixtures on pressure at 308.15 K.

Discussion

Dependence of the solubility and density on pressure: The solvent power of a SC solvent depends mainly on its density and the intermolecular interaction between the solvent and the solute. The solubility increases with pressure and concentration of n-pentane in the solvent, as can be seen in Figure 3. At a fixed temperature and pressure, addition of a co-solvent to CO_2 results in an increase in density, especially in the low-pressure region, as is illustrated clearly in Figure 2. Meanwhile, the co-solvent also influences the intermolecular interaction between the solvent and the solute. In order to eliminate the effect of the density, Figure 4 demonstrates the solubility as a function of the density of the mixed solvent. At a fixed density, the solubility is also enhanced by the co-solvent, although it is nonpolar. The main reason for this is that n-pentane is larger than CO_2, and the dispersion force between n-pentane and the solute is stronger than that between CO_2 and the solute. Figure 4 also shows that the logarithm of the mole fraction of the solute is approximately a linear function of the density of the mixed fluid. A similar linear relationship was observed for other SC CO_2-solute systems.[14]

Enthalpy of solution in the SC region: Figure 5 shows that $\Delta_{solv}H_m$ in the mixed SC fluid ($x_2 = 0.01$) is nearly the same as that in pure CO_2, and is independent of density in the high-density region, in which the mixture is far from the binary critical point. This is because the compressibility of the solvents is very small at the higher-density region, as shown in Figure 6. Therefore, the intermolecular interaction between the solvent and solute is similar to that in ordinary liquid solutions. In the low-density region, however, the absolute value of $\Delta_{solv}H_m$ is much lower than that in pure SC CO_2. Therefore, the dissolution process becomes less exothermic as n-pentane is added, although the co-solvent enhances the solubility considerably, as shown in Figure 3 and 4. It can be concluded that the enthalpy change originated from the addition of n-pentane is not favorable for solubility enhancement, while the entropy change favors the dissolution of the solute, and the entropy effect is dominant. This is

discussed by using the following principles; the solubility is related to the Gibbs free energy ($\Delta_{solv}G_m$), and the higher the solubility is, the lower the $\Delta_{solv}G_m$ is. The $\Delta_{solv}G_m$ is related to enthalpy ($\Delta_{solv}H_m$) and entropy ($\Delta_{solv}S_m$) of solution by Equations (3) or (4), in which T is the absolute temperature.

$$\Delta_{solv}G_m = \Delta_{solv}H_m - T\Delta_{solv}S_m \tag{3}$$

$$\Delta_{solv}S_m = (\Delta_{solv}H_m - \Delta_{solv}G_m)/T \tag{4}$$

The solubility increases as n-pentane is added as shown in Figures 3 and 4, this indicates that $\Delta_{solv}G_m$ decreases with the addition of the co-solvent. Addition of n-pentane results in a decrease in the absolute value of $\Delta_{solv}H_m$, which is not favorable for solubility enhancement, as can be confirmed from Eq. (3). Therefore, an increase in solubility originates from the increase in entropy of solution.

A supercritical fluid may be considered macroscopically homogeneous, but microscopically inhomogeneous, which consists of clusters of molecules, free molecules, and free volumes. The microscopic inhomogeneity of a supercritical fluid is complex, and is relative to the molecular interactions in systems. The addition of a co-solvent makes it more complex. The data in Figure 7 indicates that the $V_{n\text{-pentane}}$ of n-pentane in the CO_2 + n-pentane mixture is close to zero in the high-density region; this suggests that the clustering between n-pentane and CO_2 is not significant. In the low-density region, in which the compressibility is high (Figure 6), $V_{n\text{-pentane}}$ is negative; this indicates significant clustering of CO_2 around n-pentane. Many authors have discussed the clustering in different SC solutions, which is often referred to as local density and/or local composition enhancement.[5, 15] The local density of CO_2 around a solute and a co-solvent is larger than that in the bulk, and the co-solvents prefer to associate with the solutes. We can discuss the phenomenon on the basis of the clustering in the solutions (Figure 5).[5,6, 15] In our experiments CO_2 and n-pentane were first mixed outside of the calorimeter, and then the enthalpy of solution of the solute in the mixed solvent was determined. Therefore, the dissolution of the solute in the CO_2 + n-pentane mixture can be expressed as Equation 5.

$$CO_2 + \text{co-solvent(solvated)} + \text{Solute(solid)} \rightarrow$$
$$\text{Solute(in mixed solvent)} \tag{5}$$
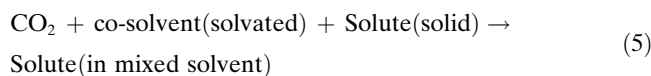
It is known that thermodynamic functions are independent of the processes. In our experiments the n-pentane was mixed with CO_2 before it had contact with the solute. Therefore, dissolution of the solute in the mixed solvent can be divided into two steps: 1) the solute is solvated by the solvent (CO_2) 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. The overall values of $\Delta_{solv}H_m$ and $\Delta_{solv}S_m$ are given by Equations (6) and (7).

$$\Delta_{solv}H_m = \Delta_{solv}H_{m1} + \Delta_{solv}H_{m2} \tag{6}$$

$$\Delta_{solv}S_m = \Delta_{solv}S_{m1} + \Delta_{solv}S_{m2} \tag{7}$$
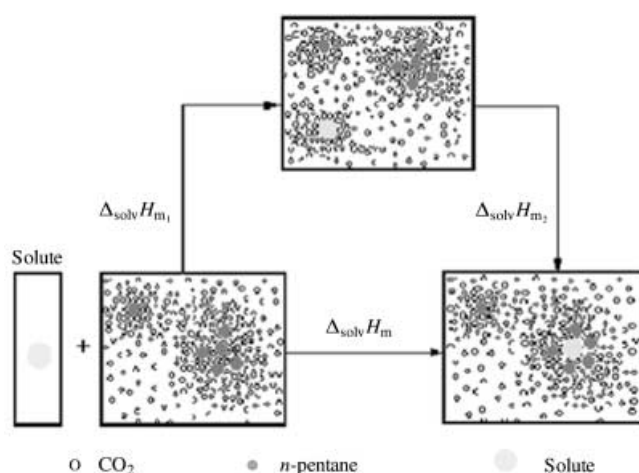
Scheme 1. $\Delta_{solv}H_m$ or $\Delta_{solv}S_m$ in Equations (3) and (4) is the sum of the two steps.

in which $\Delta_{solv}H_{m1}$, $\Delta_{solv}H_{m2}$, $\Delta_{solv}S_{m1}$, $\Delta_{solv}S_{m2}$ are the enthalpy change and entropy change of the corresponding steps.

The parameter $\Delta_{solv}H_{m1}$ or $\Delta_{solv}S_{m1}$ is equal to the enthalpy or entropy of solution of the solute in pure CO_2. The effect of the co-solvent on $\Delta_{solv}H_m$ and $\Delta_{solv}S_m$ is dependant on the second step. The enthalpy change of the second step, $\Delta_{solv}H_{m2}$, consists of two parts. The first is the enthalpy of the direct interaction of the solute and n-pentane, which should be negative (exothermic) like in a vacuum. The second part of $\Delta_{solv}H_{m2}$ 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, which is positive. In the low-density region (high-compressible region), the clustering between CO_2 and n-pentane is more significant as shown by the large negative $V_{n\text{-pentane}}$ of n-pentane (Figure 7). Therefore, the second part is dominant, and the $\Delta_{solv}H_{m2}$ is positive. Thus, the absolute value of $\Delta_{solv}H_m$ is less than that of $\Delta_{solv}H_{m1}$ (solution enthalpy in pure CO_2), that is, the dissolution process becomes less exothermic in the present of the co-solvent relative to that in pure CO_2; this is not favorable for an increase in solubility. On the other hand, a large number of CO_2 in CO_2 + n-pentane clusters enter the bulk in the second step, and $\Delta_{solv}S_{m2}$ is positive, which is favorable for an increase in solubility. Therefore, the enthalpy change and entropy change originated from the addition of the co-solvent affects the solubility in opposite ways, and an enhancement in solubility by adding the co-solvent indicates that the entropy effect is a dominant factor.

Enthalpy of solution in subcritical fluids ($x_2 = 0.021$ and 0.05): Figure 5 shows that $\Delta_{solv}H_m$ is also nearly independent of pressure in the high-density region, in which the mixed fluids are far from the phase separation point or phase boundary. This also results from the fact that intermolecular interaction in the solution is similar to that in conventional liquid solutions at higher densities.

It is very interesting that $\Delta_{solv}H_m$ in the mixed SC ($x_2 = 0.01$) and subcritical fluids exhibit are different, as shown in Figure 5. The absolute value of $\Delta_{solv}H_m$ in the mixed SC fluid is close to that in pure SC CO_2 in the high-density region, and is much lower than that in pure SC CO_2 in the low-density region. In the mixed subcritical fluids, the absolute value of $\Delta_{solv}H_m$ is also close to that in the pure CO_2 in the high-density region. However, it is higher than that in pure CO_2 in the high-compressible region. From Equations (3) and (4) it can be concluded that the solubility enhancement by n-pentane in the mixed SC fluid is entropy driven, as discussed above. On the contrary, the solubility enhancement by n-pentane in the subcritical fluids is enthalpy driven. We can discuss this further.

The compressibility of the fluids is very small as their densities are large enough, and the intermolecular interaction between the solvent and the solute is similar to that in liquid solutions. Therefore, $\Delta_{solv}H_m$ is small, and the difference in all the fluids is not significant, because CO_2 is the main component and n-pentane is also a nonpolar compound. In pure SC CO_2, CO_2-solute clusters are formed during the dissolution process in the high-compressible region, and therefore, the $\Delta_{solv}H_m$ has a large negative value.[6] The absolute value of $\Delta_{solv}H_m$ in the mixed SC fluid ($x_2 = 0.01$) is smaller than that in pure CO_2 for the reason discussed above. However, in the high-compressible region the absolute value of $\Delta_{solv}H_m$ is still larger than in the low-compressible region, that is, the clustering of the CO_2 and n-pentane with the solute results in the increase of the absolute value of $\Delta_{solv}H_m$, although it is smaller than that in pure SC CO_2. In the subcritical fluids, $V_{n\text{-pentane}}$ of n-pentane is also negative in the high-compressible region. It can be deduced that the local density and/or local composition enhancement in the solution is also significant in the high-compressible region, and therefore, the absolute value of $\Delta_{solv}H_m$ is also larger. In other words, in both SC and subcritical solutions, the absolute value of $\Delta_{solv}H_m$ increases with the degree of the clustering in the solutions. However, the degree of clustering in the SC solutions is small at the density in which the degree is large in the subcritical solutions, as is shown by $V_{n\text{-pentane}}$ in Figure 7. That is to say, at the same density the compressibility of SC CO_2 is very limited, while that of the subcritical fluids is large. Therefore, the absolute value of $\Delta_{solv}H_m$ in the mixed subcritical fluids can be larger than that in pure CO_2. From the discussion above, it can be concluded that the intermolecular interaction in the SC solutions and subcritical solutions can be significantly different if their densities are the same.

Polarity effects of the co-solvents on $\Delta_{solv}H_m$: We studied the effect of small amounts of acetone and chlorodifluoromethane on the $\Delta_{solv}H_m$ of the solute in SC CO_2 and the mixed solvents in SC regions.[6] The solubility enhancement by the polar co-solvents also results from the increase in entropy of solution. Therefore, the co-solvent effect is similar for the polar and nonpolar co-solvents in the SC region, that is, the solubility enhancement is entropy driven.

In this work, we determined the $\Delta_{solv}H_m$ of the solute in CO_2 + acetone with $x_2 = 0.03$ (mole fraction of acetone),

which is a mixed subcritical fluid based on the calculation of PR EOS.[9] The results are also illustrated in Figure 5. The $\Delta_{solv}H_m$ in the subcritical CO_2 + n-pentane and CO_2 + acetone mixtures follows a similar trend as the density of the mixed solvents is changed. Therefore, it can be concluded that the solubility enhancement by acetone also results from an enthalpy effect in the subcritical region, while that in the mixed SC solvent originates from an entropy effect.[6] On this basis, we obtain a new conclusion. For both the polar and nonpolar co-solvents, the co-solvent effect depends on the phase behavior of the mixed solvents. In the SC region of the mixed solvents, solubility enhancement is entropy driven, while the solubility enhancement is enthalpy driven in the mixed subcritical solvents.

Conclusion

Solubility and enthalpy of solution ($\Delta_{solv}H_m$) of 1,4-naphtho-quinone in SC and subcritical CO_2 + n-pentane have been determined at 308.15 K and at different pressures. The $\Delta_{solv}H_m$ is negative in all conditions. $\Delta_{solv}H_m$ is nearly independent of pressure or density of the mixed solvents in all the solvents in a high-density region, because the intermolecular interaction between the solvent and the solute is similar to that in liquid solutions. However, $\Delta_{solv}H_m$ in the mixed SC fluid shows a different behavior relative to that in the mixed subcritical fluids as the density of the solvents is varied. In the high-compressible region, the absolute value of $\Delta_{solv}H_m$ in the mixed SC fluid is much smaller than that in pure SC CO_2, while in subcritical solvents the absolute value of $\Delta_{solv}H_m$ is higher than that in pure CO_2. In other words, the solubility enhancement by n-pentane in the mixed SC fluid is entropy driven, but the solubility enhancement by the co-solvent in the subcritical fluids is enthalpy driven. The intermolecular interaction in the SC solutions and subcritical solutions can be significantly different even if their densities are the same. The $\Delta_{solv}H_m$ of the solute in CO_2 + acetone exhibits similar behavior with that in CO_2 + n-pentane, that is, in the SC region of the mixed solvents the solubility enhancement by the co-solvent is entropy driven, while that in the mixed subcritical solvent is enthalpy driven.

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