Chemical Reaction in Binary Mixtures near the Critical Region: Thermal Decomposition of 2,2′-Azobis(isobutyronitrile) in CO_2/Ethanol

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Abstract: The effects of pressure and of the composition of the CO_2/ethanol mixed solvent in the critical region on the kinetics of the decomposition of 2,2′-azobis(isobutyronitrile) (AIBN) were studied at 333.15 K. The rate constants (k_d) in the mixed solvent far from the critical point and in liquid *n*-hexane and ethanol were also determined for comparison. It was found that k_d is very sensitive to pressure in the mixed solvent near the critical point. However, in the mixed solvent outside the critical region k_d is nearly independent of pressure. Interestingly, k_d in the mixed solvent in the critical region can be higher than that in ethanol at the same temperature, suggesting that no significant enhancement in the reaction rate by a small pressure change in the critical region of the mixed solvent can be achieved by changing the composition of the liquid solvent in the traditional way. Transition-state theory can predict k_d in the mixed solvent far from the critical point and in the liquid solvents well. However, it cannot predict k_d in the mixed solvent in the critical region. The special intermolecular interaction between the solvent and the reaction species may contribute to this interesting phenomenon. This work also shows that if pure CO_2 or ethanol are used as solvents, the reaction cannot be carried out in the critical region of the solvents at the desired temperature, while it can be conducted in the critical region of the mixed solvent of suitable composition, where the solvent is highly compressible.

Keywords: azo compounds · kinetics · phase diagrams · supercritical fluids

Introduction

In recent years, supercritical (SC) science and technology have received much attention.[1–3] Supercritical fluids (SCFs) can be used in many processing applications, such as extraction and fractionation,[1, 4] chemical reactions[5] including polymerizations,[6] and materials processing.[7] SCFs have also been used as the continuous phase of microemulsions for various applications.[8] In some processes, environmentally more acceptable SCFs can be used to replace organic solvents. Moreover, SC technologies have many other advantages that may solve more challenging problems after our fundamental understanding of SCFs improves.

There are unique advantages to conducting chemical reactions in SCFs, especially in the critical region.[9] For example, reaction rates, yields, and selectivity can be adjusted by varying pressure; environmentally benign SCFs (such as CO_2 and H_2O) can be used to replace toxic solvents; mass transfer is improved for heterogeneous reactions; and simultaneous separation and reaction may be accomplished for some reactions. It is not surprising that in recent years the use of SCFs, especially supercritical CO_2 and H_2O, as solvents for chemical reaction media has received much attention, and this topic has been reviewed.[10, 11]

Up to now, chemists have found or synthesized numerous compounds, but the substances which are applicable as SC solvents in practice is very limited because many factors have to be considered in industrial processes, such as critical temperature, critical pressure, toxicity, and price. Utilization of mixed fluids in the critical region may greatly enlarge the number of SC solvents in practice because the critical parameters of a mixture can be tuned by its composition.[1, 12] For example, one can obtain many SC solvents with different critical parameters by changing the composition of a binary system to meet different possible requirements. It should be mentioned that the mixed SCFs discussed in this work differ from SCF/cosolvent mixtures, which have been studied extensively. A mixed SCF may change its composition over the entire composition range, and the critical parameters are considered as a function of its composition, while the amount of the cosolvent in an SCF/cosolvent mixture is very small and its effect on the critical parameters of the SC solvent is usually neglected.

Scientists understand the properties of pure fluids in the critical region much better than those of mixed fluids, although many critical parameters of binary mixtures or more

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complicated mixtures have been determined.[13] Effective utilization of mixed SCFs is a new topic and many interesting and important questions need to be studied. For example, does a mixed fluid in the critical region have similar features to those of a pure fluid in the critical region? How do the properties of chemical reactions in a mixed fluid near the critical point change with pressure and composition?

Recently, we studied the constant volume heat capacity (C_V) of CO_2/*n*-pentane and CO_2/ethanol mixtures near their critical points at 308.15 K.[14] The results showed that the C_V of the mixtures near the critical points increase sharply as the pressure approaches the bubble point and the critical point from high pressure, and like a pure SCF, the isothermal compressibility of the mixed fluids in the critical region is also very large. Now we report the first systematic study of the effect of pressure and composition of a mixed fluid on the kinetics of a reaction near the critical region of the mixed solvent, namely the decomposition of 2,2′-azobis(isobutyronitrile) (AIBN) in CO_2/ethanol at 333.15 K. This reaction was selected mainly because its decomposition in different solvents has been well studied, including in SC CO_2 and SC CO_2 with small amounts of cosolvents.[15, 16] The results show that the rate constant k_d in the mixed solvents is very sensitive to pressure in the critical region of the mixed solvent. We believe that utilization of mixed solvents under conditions close to the critical point may become an effective way to broaden the applications of SCFs.

Results and Discussion

Phase behavior, density, and isothermal compressibility of the mixed solvents: This work focuses on how the k_d in a mixed fluid of CO_2/ethanol near the critical point changes with pressure and composition of the solvent. The experiments were carried out at 333.15 K, which is a suitable temperature at which to study the reaction kinetics of AIBN. The phase behavior and the critical point of the mixed solvent are the basis for selecting suitable reaction conditions. The critical parameters at this temperature and the bubble-point pressure and dew-point pressure of the mixed solvent with different compositions determined in this work are listed in Table 1. The phase diagram for CO_2/ethanol system at this temperature is shown in Figure 1. The data reported by Suzuki et al.[17] are also given in the figure. It can be seen from Figure 1 that the results determined in this work agree well with those reported by other authors.

At the critical point the mole fraction of ethanol x_2 is 0.112 (Table 1, Figure 1). In Figure 1 the part of the curve with $x_2 > 0.112$ is the bubble-point curve, and a homogenous mixture above the bubble point can be regarded as a subcritical fluid. The part of the curve with $x_2 < 0.112$ is the dew-point curve, and a homogeneous mixture above the dew point is a vapor or a supercritical mixture. The mixed solvent in the near-critical region at fixed temperature is defined as the solvent of which the composition and pressure are close to the critical composition and critical pressure of the mixture.

Table 1. Critical composition, critical pressure (P_C), bubble point pressure (P_B), and dew point pressure (P_D) of the CO_2 (1) + ethanol (2) system at 333.15 K.

X_2[a]	P [MPa]
0.028	$P_D = 9.00$
0.112[b]	$P_C = 10.64$
0.249	$P_B = 10.54$
0.413	$P_B = 9.72$

[a] Mole fraction of 2. [b] Critical composition.

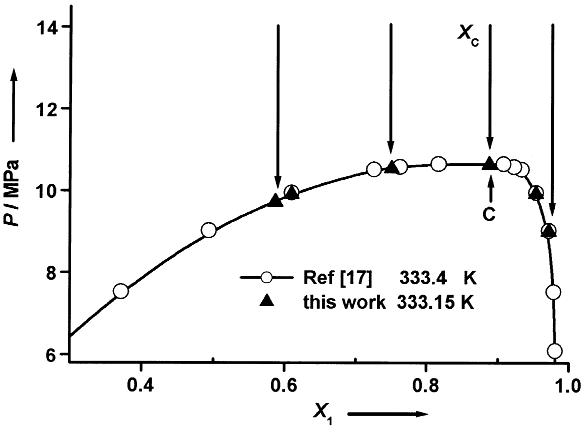

Figure 1. Phase diagram of the CO_2 (1) + ethanol (2) system at 333.15 K. P: pressure; X_1: mole fraction of CO_2 against pressure.

The isothermal compressibility K_T of a fluid is an important characteristic parameter related to the fluid structure. The K_T of fluids is calculated using the density data determined in this work (Table 2) and the following well-known equation [Eq. (1)], where ρ is the density of the fluids. The variation of K_T with pressure at different conditions is shown in Figure 2.

$$K_T = \frac{1}{\rho}\left(\frac{d\rho}{dp}\right)_T \qquad (1)$$

The decomposition rate constant of AIBN: The decomposition rate constant k_d of AIBN in CO_2/ethanol mixed solvent was studied at 333.15 K. In order to explore the features of the reaction in the critical region of the mixed solvent, we conducted the reaction in some typical subcritical and supercritical mixtures. In summary, the mole fractions of ethanol in the binary solvent were 0.0, 0.028, 0.112, 0.249, 0.413, respectively, and the experimental pressure was in the range of 9 – 14 MPa. For all the experiments, the solvents were in the single-phase region; the experimental conditions are marked in Figure 1 (the vertical lines). To study the difference of the reaction in the mixed solvent in the critical region and in conventional liquid solvents, we also measured the k_d of the reaction in *n*-hexane or ethanol at this temperature.

As examples, Figure 3 shows the UV spectra for the thermal decomposition of AIBN in the mixed fluid ($x_2 = 0.249$) at 333.15 K and 12.03 MPa. The absorption maxima at 347 and 289 nm are assigned to the absorption of AIBN and ketenimine (temporary adduct), respectively.[15] The decreasing absorption at 347 nm corresponds to the loss of AIBN. The decomposition rate can be calculated on the basis of the change of the absorption with time. In order to determine the reaction rate quantitatively from the spectra, the absorbance (A) of AIBN is required. Since the peaks of the above two

Table 2. Densities of CO_2 (1) + ethanol (2) mixtures (ρ_{mix}) at 333.15 K and various pressures.

$X_2=0.028$		$X_2=0.112$		$X_2=0.249$		$X_2=0.413$	
p [MPa]	ρ_{mix} [10^3 mol m^{-3}]	p [MPa]	ρ_{mix} [10^3 mol m^{-3}]	p [MPa]	ρ_{mix} [10^3 mol m^{-3}]	p [MPa]	ρ_{mix} [10^3 mol m^{-3}]
16.30	15.94	18.25	17.62	18.83	18.38	16.50	18.36
14.95	15.14	17.45	17.41	16.94	18.09	15.52	18.27
13.41	13.82	16.55	17.18	15.43	17.83	14.26	18.19
12.16	12.20	15.25	16.58	14.15	17.60	13.28	18.07
11.35	10.84	14.15	16.08	13.25	17.39	12.33	17.95
10.58	9.16	13.17	15.63	11.26	16.82	11.62	17.86
9.47	7.10	12.61	15.37	10.86	16.44	10.71	17.75
9.03	6.23	12.19	15.02	10.70	15.38	10.17	17.50
		11.16	14.09			9.87	17.21
		10.88	13.65			9.72	16.84
		10.75	13.14				
		10.68	12.67				

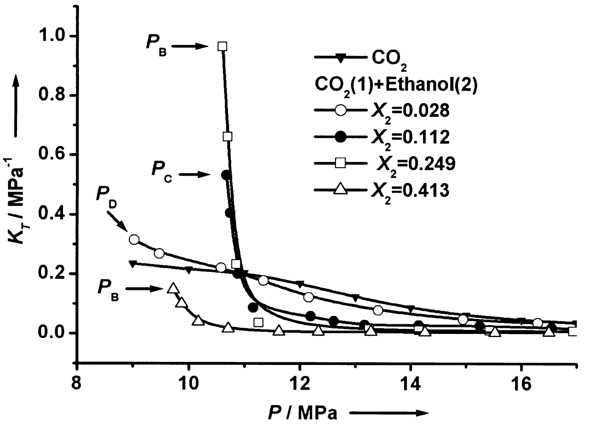

Figure 2. Isothermal compressibility K_T of pure CO_2 and CO_2 (1) + ethanol (2) mixtures at 333.15 K. P_D, P_C, and P_B denote the dew point, critical point, and bubble point, respectively.

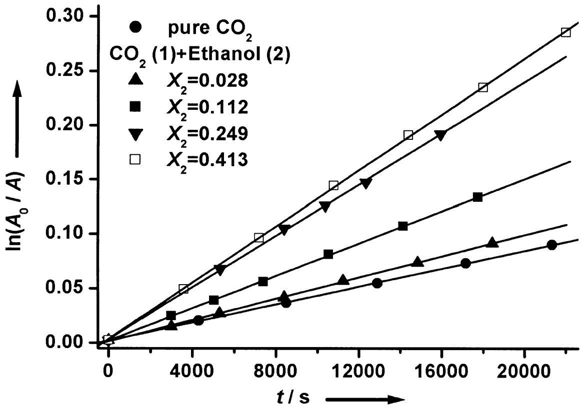

Figure 4. Dependence of $\ln(A_0/A)$ (absorbance at 347 nm) on time for AIBN thermal decomposition in pure CO_2, and CO_2 (1) + ethanol (2) mixtures at 333.15 K and 14.0 MPa.

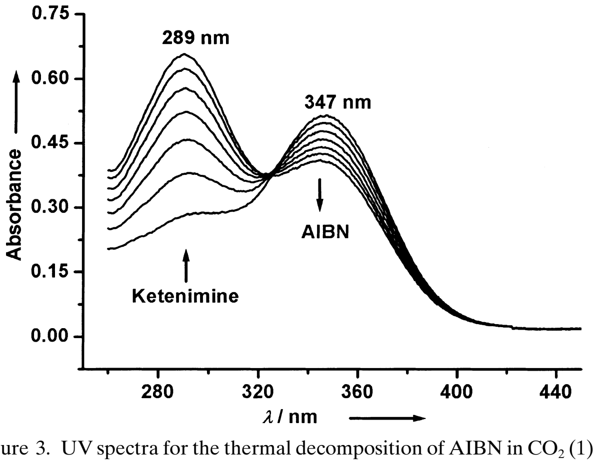

Figure 3. UV spectra for the thermal decomposition of AIBN in CO_2 (1) + ethanol (2) ($X_2=0.249$) at different times (333.15 K, 12.01 MPa).

compounds overlap to some extent, a deconvolution method was developed. The spectrum curves of the two compounds were assumed to be Gaussian. A computer routine was used to optimize the locations, heights, and variance of the two peaks, so that the sum of the deconvoluted peaks most accurately fit the experimental spectra.[16]

Figure 4 shows some typical curves of $\ln(A_0/A)$ versus time (t) for thermal decomposition of AIBN in SC CO_2 and CO_2/ethanol mixtures at 14.0 MPa, where A_0 and A stand for the absorbance of AIBN at 347 nm at $t=0$ and t, respectively. There exists a linear relationship between $\ln(A_0/A)$ and the reaction time. Under other conditions $\ln(A_0/A)$ versus time curves are also linear. This indicates that the decomposition follows first-order kinetics, and k_d can be calculated from the slope of the curves,[15, 16] as discussed briefly below.

First-order kinetics follow Equation (2), where c_{AN} is the concentration of AIBN at reaction time t. From Equation (2), we can get Equation (3). Then from this and from the Lambert–Beer Law [Eq. (4), where β_{AN} is the molar extinction coefficient of AIBN, L is the optical path length, and p_1 is a constant], we obtain Equation (5).

$$-\frac{d[c_{AN}]}{dt} = k_d\,[c_{AN}] \tag{2}$$

$$\ln c_{AN} = p_1 \times k_d \times t \tag{3}$$

$$A = \beta_{AN} \times c_{AN} \times L \tag{4}$$

$$\ln(A_0/A) = k_d \times t \tag{5}$$

The values of k_d in different solvents under various conditions are listed in Table 3. Under some conditions, the experiments were repeated three times and the repeatability was better than ±5%. The k_d values in liquid solvents n-hexane and ethanol determined in this work are also listed in Table 3.

Table 3. The values of k_d in CO_2 (1) + ethanol (2) mixture and in different liquid solvents.

CO_2 + ethanol $X_2 = 0$		CO_2 + ethanol $X_2 = 0.028$		CO_2 + ethanol $X_2 = 0.112$		CO_2 + ethanol $X_2 = 0.249$		CO_2 + ethanol $X_2 = 0.413$		n-hexane	ethanol
P [MPa]	k_d [$10^{-6}s^{-1}$]	P [MPa]	k_d [$10^{-6}s^{-1}$]	P [MPa]	k_d [$10^{-6}s^{-1}$]	P [MPa]	k_d [$10^{-6}s^{-1}$]	P [MPa]	k_d [$10^{-6}s^{-1}$]	k_d [$10^{-6}s^{-1}$]	k_d [$10^{-6}s^{-1}$]
10.00	3.87	9.04	5.25	10.70	11.48	10.61	19.86	9.72	12.62	6.08	15.27
11.06	3.96	9.50	4.57	10.80	9.25	10.75	16.05	10.06	12.04		
12.05	4.06	11.00	4.38	10.90	7.81	10.86	13.61	11.04	12.17		
13.08	4.08	12.01	4.58	11.20	7.52	11.01	12.42	12.03	12.32		
14.21	4.11	14.00	4.88	12.00	6.74	12.01	11.20	13.12	12.72		
				13.01	6.99	13.01	11.32	14.11	12.89		
				14.01	7.42	14.00	11.81				

The rate of decomposition of AIBN in a number of liquid solvents has been studied, and the polarity or dielectric constant of the solvent has been found to affect the rate constant.[15, 16, 18] However, the reaction rate is not very solvent-sensitive. The decomposition rate of AIBN in liquid solvents determined by other authors shows a solvent dependence with an overall variation in rate constant of a factor of 2–4. The rate constants measured in this work in liquid n-hexane (nonpolar) and liquid ethanol (polar) are $6.08 \times 10^{-6} s^{-1}$ and $15.27 \times 10^{-6} s^{-1}$ respectively (Table 3). The difference falls within this range.

The dependence of k_d on pressure in the solvents of different compositions is illustrated in Figure 5. It is very interesting that the k_d is very sensitive to pressure near the critical point of the mixed solvent, and the k_d increases sharply as pressure approaches the critical point and the bubble point of the mixed solvent. This indicates that the kinetic properties can be tuned by pressure in the critical region of the mixed solvent. At $x_2 = 0.112$ and 0.249, the k_d can be increased by 70–80% by a small pressure change in the critical region of the mixed solvent, as can be seen from Figure 5. This change is significant considering the fact that the reaction is not very sensitive to solvent, as described above.

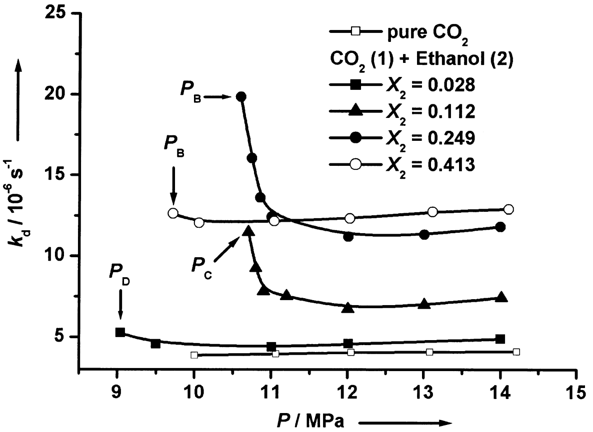

Figure 5. Dependence on pressure of the rate constant (k_d) for the decomposition of AIBN in pure CO_2 and CO_2 (1) + ethanol (2) mixtures at 333.15 K. P_D, P_C, and P_B denote the dew point, critical point, and bubble point, respectively.

The k_d increases with increasing polarity or dielectric constant of the solvent.[15, 16, 18] The results in Table 3 show another interesting phenomenon. The k_d in the mixed solvent with $x_2 = 0.249$ is higher than that in pure ethanol as the pressure approaches the bubble point, although the polarity of ethanol should be higher than that of the mixture. This indicates that the significant enhancement in the reaction rate caused by a small pressure change in the critical region cannot be achieved in a mixed liquid solvent by changing the composition of the solvent.

Figure 5 also shows that k_d is not sensitive to pressure at higher pressures for all the mixed solvents, indicating that k_d can not be adjusted effectively by pressure when the solvent is not in the critical region. The main reason is that, as shown in Figure 2, the isothermal compressibility of the solvent outside the critical region is small. Thus the properties are not greatly affected by pressure. It can be concluded that, to control k_d effectively by pressure, both pressure and composition should be close to the critical point of the mixed solvent at this temperature.

Increasing the concentration of ethanol in the solvent results in an increase in k_d at the higher pressures far from the critical point, as can be seen from Figure 5. This is easy to understand because the k_d increases with the increase in the polarity or dielectric constant of the solvent.[15, 16, 18] This hints that mixed solvents outside the critical region are similar to liquid solvents, and the polarity increases as the concentration of the polar component is increased.

The experimental pressure for the reaction in CO_2 is higher than 10 MPa because CO_2 cannot dissolve enough AIBN for the kinetic study at the lower pressures. This makes it difficult to compare the k_d in pure SC CO_2 with that in the mixed solvent over a wide pressure range. On the other hand, this indicates that more reactions can be carried out in mixed solvents in the critical region, and some properties of the reactions may be tuned significantly by pressure.

Theoretical approach to the reaction kinetics According to transition-state theory, for a simple unimolecular reaction, the quantitative effect of pressure on the rate constant can be expressed as Equation (6),[15] where $\Delta V^{\neq}$ is the activation volume and k_d is the reaction rate constant. To a first approximation, the activation volume can be regarded as the sum of an intrinsic and a solvational component [Eq. (7)].[15, 19]

$$\left(\frac{\delta \ln k_d}{\delta p}\right)_T = -\frac{\Delta V^{\neq}}{RT} \tag{6}$$

$$\Delta V^{\neq} = \Delta V^{\neq}_{\text{solvation}} + \Delta V^{\neq}_{\text{intr}} \tag{7}$$

The intrinsic activation volume ($\Delta V^{\ddagger}_{\text{intr}}$) results from the reorganization of the reacting species, that is, changes in bond lengths and angles during the formation of the transition state, and is generally considered to be independent of solvent; the solvation activation volume ($\Delta V^{\ddagger}_{\text{solvation}}$) represents all volume changes associated with solvation, which depend on polarity, electrostriction, and dipole interactions during the course of the reaction.[15] The k_d for AIBN can be expressed as a function of dielectric constant of the solvents, ε, and $\Delta V^{\ddagger}_{\text{intr}}$ by Equation (8),[15] where a and b are constants, p and T stand for pressure and temperature, respectively, and R is the gas constant. $(\varepsilon - 1)/(2\varepsilon+1)$ is the Kirkwood parameter. $\Delta V^{\ddagger}_{\text{intr}}$ is generally considered to be independent of solvent.[17] In this work we use the value reported in the *Polymer Handbook* ($\Delta V^{\ddagger}_{\text{intr}} = 13.1 \times 10^{-3}$ L mol^{-1}).[20]

$$\ln k_d = -\mathrm{a} + \mathrm{b}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \left(\frac{\Delta V^{\ddagger}_{\text{intr}}}{RT}\right)p \tag{8}$$

Rearrangement of Equation (8) gives Equation (9), where $\mathrm{c} = \Delta V^{\ddagger}_{\text{intr}}/RT$, which is a constant at a fixed temperature. To use Equation (9), dielectric constants of the solvents at different conditions are required. The dielectric constant of pure SC CO_2 can be calculated from Equation (10).[21] The density (d) of CO_2 required in Equation (10) can be calculated from Huang's equation,[22] which is very accurate for the density calculation of CO_2.

$$\ln k_d + \mathrm{c}p = -\mathrm{a} + \mathrm{b}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \tag{9}$$

$$\left(\frac{\varepsilon - 1}{d(\varepsilon + 2)}\right) = 0.007676 \tag{10}$$

Wesch et al.[23] measured the dielectric constant of CO_2 (1) + ethanol (2) mixture up to 30 MPa. They found that the dielectric constant of the mixture (ε_m) agreed well with those calculated from the model proposed by Looyenga,[24] which can be expressed as Equation (11), where ε_1 and ε_2 are the dielectric constants of components 1 and 2, respectively, and ϕ_2 denotes the volume fraction of component 2, which is calculated by Equation (12), where y_2 is mole fraction of component 2, and V_2 and V_m stand for the molar volumes of component 2 and the mixture, respectively. In this work the dielectric constant of the mixture (ε_m) calculated from Equations (11) and (12) is used, and those of liquid solvents *n*-hexane and ethanol are obtained from the *CRC Handbook*.[25]

$$\varepsilon_m = [(1 - \phi_2)\varepsilon_1^{1/3} + \phi_2\varepsilon_2^{1/3}]^3 \tag{11}$$

$$\phi_2 = y_2 V_2 / V_m \tag{12}$$

The curves for $\ln k_d + \mathrm{c}p$ versus Kirkwood parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ in different solvents are shown in Figure 6. It should be mentioned that cp is much smaller than $\ln k_d$ (cp/$\ln k_d < 6\%$) under the experimental conditions of this work. For the mixed solvent of fixed composition used in this work, the dielectric constant or the Kirkwood parameter increases with increasing pressure. The k_d in CO_2 and in the mixed solvents of different compositions at higher pressures (12, 13, 14 MPa) correlate well with Equations (9)–(12), and the results are shown by the straight line in Figure 6. The values obtained for constants a and b in Equation (9) are −12.59 and 3.58, respectively. Obviously, the k_d values in the solvents far from the critical point can be correlated well. The $\ln k_d$ + cp values of the reaction in *n*-hexane and ethanol ($p = 14$ MPa is used in the calculation) are also close to the straight line. This further suggests that the properties of mixed fluids far from the critical point of the mixture are similar to those of conventional solvents.

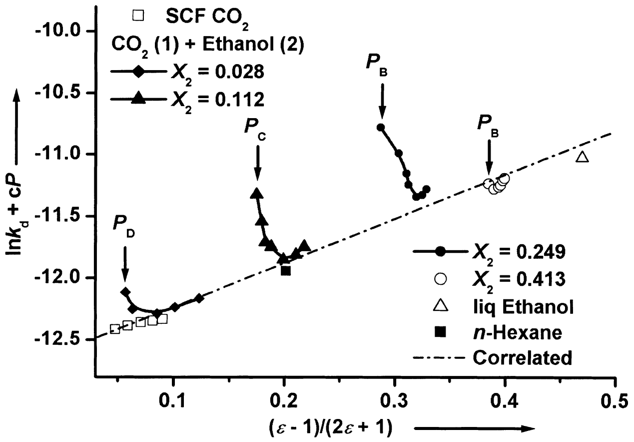

Figure 6. Dependence of $\ln k_d$ on the Kirkwood parameters in various solvents at 333.15 K. The straight line represents Equations (9)–(12) using the k_d data in pure SC CO_2 and in the mixed fluids at the higher pressures (≥12.0 MPa). The fitted parameters a and b in Equation (9) are −12.59 and 3.58, respectively. P_D, P_C, and P_B are as in Figure 5.

From Figure 6, one can observe that $\ln k_d$ + cp in the mixtures with $x_2 = 0.028$, 0.112, 0.249 increases sharply as pressure approaches the phase separation pressures from high pressure (for each curve, the smallest Kirkwood parameter corresponding to phase separation pressure). In other words, Equations (9)–(12) cannot predict the experimental k_d data in the mixed solvent near the critical point, although they fit the k_d data in the solvents outside the critical region well. This anomalous phenomenon is discussed qualitatively below.

The isothermal compressibility (K_T) of the fluids is small at higher pressures (12, 13, and 14 MPa), as shown in Figure 2. Therefore, the properties of the solvents at these pressures are not sensitive to pressure, that is, they behave like liquids. Thus the k_d values can be correlated with Equations (9)–(12). The K_T value increases sharply as pressure approaches the critical point and the bubble point, as shown in Figure 2. Theoretical[26] and experimental[27] techniques have been used to study intermolecular interaction and the microstructures of SC solvent/solute and SC solvent/cosolvent/solute solutions. The results indicate that local density of a SC solvent around a solute molecule can be higher than that in the bulk, and the solute is preferentially solvated with the cosolvents. This phenomenon is more obvious in the highly compressible region or low-density region.[2, 10, 26, 27] The inhomogeneities in SC solutions are often referred to as local density augmentation and local composition enhancement or “clustering”, although the clustering is a very dynamic process, with the frequency of exchange of cluster members with the bulk on the order of picosecond.[26]

We believe that the local density and/or local composition enhancement is also significant in the critical region of the mixed solvent. In other words, the local dielectric constant around the reaction species is larger than that in the bulk, thus accelerating the decomposition of AIBN. The local dielectric constant ε_l can be expressed as shown in Equation (13), where

$$\varepsilon_l = \varepsilon + \Delta\varepsilon_l \quad (13)$$

ε represents the dielectric constant in the bulk, and $\Delta\varepsilon_l$ is the dielectric constant increment resulting from the local density and/or local composition enhancement. At the higher pressures $\Delta\varepsilon_l$ is not significant, and the local dielectric constant is equal to that of the bulk. In the compressible region, $\Delta\varepsilon_l$ cannot be neglected. It means that the local dielectric constant around the reaction species can be much larger than that in the bulk, while this is not considered in Equations (9)–(12). This is one of the reasons for the fact that Equations (9)–(12) do not correlate with the k_d values in the solvent near the critical point.

It is very interesting that $\ln k_d + cp$ in the critical region of the mixed solvent ($x_2 = 0.249$) can be higher than that in ethanol, as shown in Figure 6. Obviously, the larger local dielectric constant cannot explain this phenomenon completely, because the local dielectric constant of the mixed solvent should be smaller than that of pure ethanol. There must be some other factors to influence the decomposition rate related to the clustering in the reaction system. This is an interesting and important topic for the reactions in SCFs or near-critical fluids. The degree of clustering between solute molecules is larger in the more compressible region of a SC solvent.[28] Therefore, the degree of solute–solute (reaction species) clustering should be larger in the critical region of the mixed solvent because the compressibility is larger, as is shown in Figure 2. The solute–solute clusters should also affect the reaction rate in ways that are different from the solute–solvent and solute–cosolvent interactions. Many researchers have discussed the effect of inhomogeneities on the reactivity,[10] including the cage effect.[10, 29] This is a very complex question that needs further investigation even for the reaction in pure SC solvents. The effect of the clustering on the reaction depends on many factors, such as the relative time scales of the reaction, the local solvation shell, the mechanism of the reaction, and the nature of the compounds involved. Unfortunately, we cannot discuss this in detail because of the lack of fundamental information about the mixed solvent in the critical region.

Conclusion

The decomposition of AIBN in CO_2 + ethanol mixed solvent was investigated in different phase regions. The k_d values in the mixed solvent were found to be very sensitive to pressure in the critical region of the mixed solvent. However, k_d in the mixed solvent outside the critical region was nearly independent of pressure. The k_d values in the mixed solvents in the critical region can be higher than that in ethanol under the same reaction conditions, suggesting that significant enhancements in the reaction rate achieved by small pressure changes in the critical region could not be achieved by changing the composition of the solvent in the traditional way. The transition-state theory can predict k_d in the mixed solvent far from the critical point and those in the liquid solvents well. However, it cannot predict k_d values in the mixed solvent in the critical region. The local density and/or local composition enhancement may contribute to this interesting phenomenon. Utilization of mixed solvents under conditions close to the critical point may become an effective way to broaden the applications of SCFs, and more processes may be carried out in the highly compressible region of the solvents, where pressure can be used to control the reaction rates and product distributions.

Experimental Section

Materials: Carbon dioxide (99.995% purity) was supplied by Beijing Analytical Instrument Factory. Ethanol (analytical grade, >99.5%) and *n*-hexane (analytical grade, >98.0%) were provided by Beijing Chemical Reagent Plant. AIBN was AR grade supplied by Beijing Chemical Reagent Plant and was recrystallized twice from methanol prior to use.

Apparatus and procedures to determine the phase behavior and density of the mixed solvent: Experimental conditions for the experiments to determine the k_d were selected on the basis of the phase behavior of the mixed solvent. The apparatus and procedures for determining critical points and phase behavior have been described previously.[30] Briefly, the apparatus consisted of a high-pressure optical cell, a constant-temperature water bath, a pressure gauge, a temperature controller, and a thermometer. The high-pressure cell was composed of a stainless steel body, a stainless steel piston and two borosilicate windows. The piston could be moved to change the volume of the optical cell from 20 to 50 cm^3. The apparatus was tested up to 40 MPa. The temperature of the water bath was controlled by a HAAKE D8 temperature controller; the temperature measurement was accurate to ±0.05 K. The pressure gauge comprised a pressure transducer (FOXBORO/ICT, Model 93) and an indicator accurate to ±0.025 MPa in the pressure range of 0–20 MPa.

In a typical experiment, the apparatus was washed thoroughly with different solvents (toluene, acetone, and ethanol) and dried under vacuum. The system was evacuated, and the desired amount of ethanol was introduced by means of a syringe of suitable volume. CO_2 was then loaded into the cell with a sample bomb of 41 mL. The mass of CO_2 used was deduced from the mass difference of the ampule before and after charging the system. The composition of the mixture in the system was calculated from the masses of the two chemicals.

The optical cell was placed into the water bath kept at 333.15 K. After thermal equilibrium had been reached, the pressure was increased by moving the piston down until a homogeneous liquidlike phase was observed. The system was allowed to equilibrate until the pressure remained constant with time, indicating that equilibrium had been reached. The volume of the system was known from the position of the piston, which was calibrated before the experiments. The density of the mixture was calculated on the basis of the masses of components and the volume of the system. The pressure was reduced by moving the piston and the density of the fluid at this new pressure was determined. This procedure was continued until phase separation was observed. The bubble point, or dew point, or critical point could be observed.[30] The critical point of a mixture could clearly be identified as marked opalescence could be observed and the mixture changed from a single phase to about 50 vol% liquid phase and 50 vol% vapor phase as the pressure was reduced slightly.[30]

Apparatus and procedures for the UV study: The experimental setup and the procedures were similar to those used in our previous work[16] to determine the decomposition rate of AIBN in SC CO_2 at 335.2 K. The main difference was that this work involved mixed solvents, which were prepared in a sample cylinder. The apparatus consisted mainly of a cylinder containing mixed solvent of the desired composition, a pressure gauge, a

UV/Vis spectrometer, a temperature-controlled high-pressure UV sample cell, and valves and fittings. The UV/Vis spectrophotometer was produced by Beijing General Instrument Company (Model TU-1201, resolution: 0.1 nm). The UV sample cell consisted mainly of a stainless steel body and two quartz windows. The exterior of the cell was wrapped with a coil of electrical heating wire and heat insulation material. The volume and the optical path length of the cell were 1.63 cm^3 and 1.1 cm, respectively. The concentration of AIBN in the sample cell was 12.4 $mol\,m^{-3}$ for all of the experiments.

In a typical experiment, the mixed fluid of CO_2 + ethanol in a desired composition was first prepared in the solvent cylinder by gravimetric method. A solution of AIBN in *n*-hexane (0.1 mL, 2.0×10^{-4} $mol\,mL^{-1}$) was introduced into the UV sample cell. CO_2 at ambient temperature and pressure was passed slowly through the cell for about 20 minutes to remove the *n*-hexane. The cell was maintained at 333.15 K, and was charged with the mixed fluid (prepared as described above) from the sample cylinder until the desired pressure was reached. To maintain the composition unchanged, the mixed solvent was always in the single-phase region when the sample cell was charged, as was known from phase behavior of the mixed fluid determined in this work. The UV spectrum of the sample was determined at different times. The UV spectrum of the mixed solvent was also determined at the same temperature and pressure, and was used as a background spectrum. The decomposition rates of AIBN in *n*-hexane and ethanol were also determined at the same temperature.

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