1886 *J. Chem. Eng. Data* **2008,** *53,* 1886–1891

Diffusion of Benzonitrile in CO_2-Expanded Ethanol

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The diffusion coefficients of benzonitrile in the CO_2-expanded ethanol at the temperatures of (303, 313, and 323) K and the pressures ranging from (1.49 to 9.79) MPa were measured by the chromatographic peak broadening technique. The benzonitrile diffusion coefficients in the CO_2-expanded ethanol were observed to increase with increasing CO_2 mole fraction in ethanol. For a fixed CO_2 mole fraction in ethanol, the benzonitrile diffusion coefficients were found to increase with increasing temperature at a fixed pressure and to decrease with increasing pressure at a fixed temperature. The measured diffusion coefficients could be correlated well by the modified Wilke−Chang equation with an average absolute deviation of 5.1 %.

Introduction

An environmentally benign solvent, so-called CO_2-expanded liquids (CXLs), has attracted great attention in recent years. CXL is formed by dissolving the compressed CO_2 into an organic solvent. Many advantages and applications of CXL have been reported.[1,2] When the CO_2-expanded methanol is used as the medium for hydrogenation of *p*-chloronitrobenzene (*p*-CNB), the conversion of *p*-CNB was observed to be higher than that in pure methanol.[3] Zhao et al.[4] observed that the CO_2-expanded cinnamaldehyde (CAL) was a suitable solvent for the selective hydrogenation of CAL to cinnamyl alcohol due to an increase of hydrogen solubility. Reaction rate and selectivity in CXL were also found to be enhanced for other hydrogenation reactions,[5–7] oxidation,[8–11] and hydroformylation reactions.[12,13]

The chromatographic peak broadening (CPB) technique based on the Taylor−Aris dispersion theory[14–17] has been wildly employed to measure diffusion coefficients at high pressures. To apply this technique, a sufficiently long capillary or coated capillary tube is usually needed.[18–35] The diffusion coefficients of benzene in the methanol/CO_2 mixture at 15 MPa and 313 K were measured by Sassiat et al.[29] When the mole fraction of methanol in the mixture was below 10 %, they observed that the diffusion coefficient of benzene in the CO_2-expanded mixture was about 4 times higher than that of benzene in pure methanol at 293 K. Lee and Olesik[26] measured the diffusion coefficients of benzene and anthracene in the methanol/water/CO_2 mixture at 13.8 MPa and a temperature range from (299 to 333) K. They observed that the diffusion coefficients increased with increasing temperature and CO_2 mole fraction in liquid. Souvigent and Olesik[22] observed that the diffusion coefficients of nonpolar solutes are higher than those of polar solutes in the ethanol/water/CO_2 mixture at 17.2 MPa, and the temperatures ranged from (298 to 333) K, resulting from the formation of a hydrogen bond between polar solutes and liquid solvent. Due to the fact that CXL is generally used at moderate pressures (below the CO_2 critical pressure) in most applications, the information on diffusion coefficients at high pressures may not be adequate for the CXL application.

In catalytic hydrogenation of benzonitrile in ethanol, the primary amines not the secondary amines are the desired products in most applications. When compressed CO_2 is introduced into ethanol to form the CO_2-expanded ethanol, the production rates of the primary amines are found to be faster than those of the secondary amines.[7] In this study, the diffusion of benzonitrile in the CO_2-expanded ethanol at different CO_2 mole fractions was measured to get a better understanding of the role of diffusion in hydrogenation. Because a very small amount of benzonitrile was injected into the binary solvents ethanol + CO_2, the binary solvents could be regarded as the one-component solvent, despite the presence of the possible complex interactions between a solute and the binary solvents.[27] The measurements were conducted at different temperatures, pressures, and CO_2 mole fractions in ethanol. From the regression of the measured diffusion coefficients with some existing equations, an adequate equation for estimating diffusion coefficients in CXL was proposed.

Experimental Section

Benzonitrile with a purity of 99 % was purchased from Tokyo Chemical Industry Co. Ethanol with a purity of 99.9 % was purchased from Echo Chemical in Taiwan. CO_2 with a purity of 99.5 % was purchased from Boclh Industrial Gases in Taiwan. All of the chemicals were used as received.

The experimental apparatus is illustrated in Figure 1. The diffusion of benzonitrile in the CO_2-expanded ethanol was measured in a capillary tube (Valco) with a 0.806 mm inner diameter, 15.77 m length, and 0.46 m coil diameter. The mobile phase was composed of the compressed CO_2 delivered by a syringe pump (ISCO 260D) and ethanol delivered by a HPLC pump (Consta Metric 3200). The flow rate of ethanol was maintained at $3.33 \cdot 10^{-9}\ m^3 \cdot s^{-1}$. The compressed CO_2 and ethanol were mixed in a static mixer and preheated with an 8 m coil placed in an oven in which the uncertainty of the temperature was ± 0.1 K. From the phase diagram of the CO_2 and ethanol mixture,[36,37] the mobile phase was assured to be the liquid phase at the studied temperatures

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10.1021/je800211x CCC: $40.75

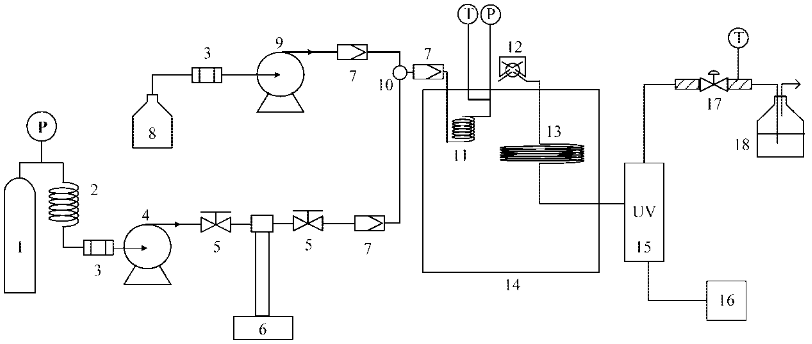

Figure 1. Experimental apparatus for the measurement of diffusion of benzonitrile in CO_2-expanded ethanol. 1, CO_2 cylinder; 2, cooler; 3, filter; 4, mini pump; 5, needle valve; 6, syringe pump; 7, check valve; 8, solvent cylinder; 9, HPLC pump; 10, static mixer; 11, coil; 12, six-way valve; 13, capillary tube; 14, oven; 15, UV detector; 16, computer; 17, back pressure regulator; 18, separator; P, pressure indicator; T, thermocouple.

Table 1. Measured Diffusion Coefficients *D* of Different Tracers in Ethanol at 313 K and 0.1 MPa

					$D/10^{-9}\ m^2 \cdot s^{-1}$	
tracer	solvent	ultraviolet/nm	$u/10^{-2}\ m \cdot s^{-1}$	$DeSc^{0.5}$	present study	lit.[31]
benzene	ethanol	254	0.73	5.07	2.24 ± 0.021	2.28 ± 0.023
toluene	ethanol	254	0.72	5.15	2.11 ± 0.012	2.12 ± 0.021
naphthalene	ethanol	254	0.73	5.78	1.72 ± 0.019	1.73 ± 0.017

and pressures. The pressure was controlled by a back pressure regulator (Tescom, model 26-1764-24-161) located after the capillary tube. A 1.0 wt % of benzonitrile concentration in ethanol was injected into the mobile phase through a six-port valve with a loop volume of 5 μL (Rheodyne 7000). The signal of benzonitrile in the effluent stream of the capillary tube was detected by a UV photometer (JASCO, UV-2075 Plus) with a constant wavelength of 254 nm.

Equations. When a pulse of tracer is injected into a laminar flow mobile phase, the dispersion of tracer occurs due to convection and diffusion in both axial and radial directions. The variance of the concentration profile of the injected tracer at the exit of the capillary tube can be written by

$$\sigma^2 = \frac{2DL}{u} + \frac{d^2uL}{96D} \tag{1}$$

where σ^2 is the peak variance; D is the diffusion coefficient of the solute; L is the capillary length; u is the linear velocity of the mobile phase; and d is the inner diameter of the capillary tube. The relationship between σ^2 and the theoretical plate height H is expressed by

$$H = \frac{\sigma^2}{L} \tag{2}$$

The diffusion coefficient can be determined by combining eqs 1 and 2 and written as

$$D = \frac{u}{4}\left[H \pm \left(H^2 - \frac{r_i^2}{3}\right)^{0.5}\right] \tag{3}$$

where r_i is the inner radius of the capillary. H is obtained from the following equation proposed by Cloete et al.[38]

$$H = \frac{LW_{0.5}^2}{5.545t_R^2} \tag{4}$$

where $W_{0.5}$ is the peak width at half-height and t_R is the retention time.

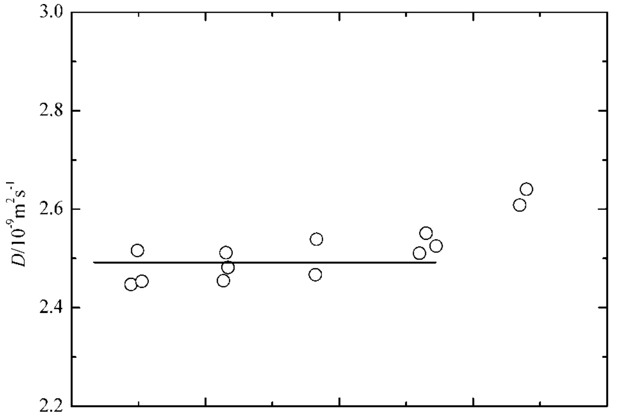

Figure 2. Effect of flow rate of the CO_2-expanded ethanol on the measured benzonitrile diffusion coefficients D at 323 K, 9.70 MPa, a CO_2 mole fraction x_{CO_2} of 0.3 in ethanol. The horizontal line represents the mean value of D for linear velocity u below 0.013 $m \cdot s^{-1}$.

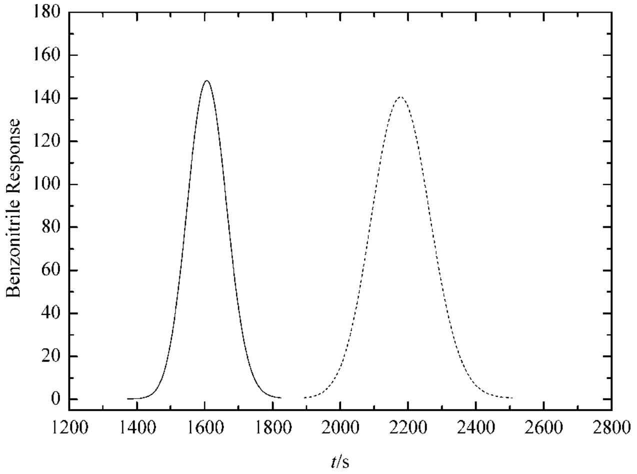

Figure 3. Two typical response curves of benzonitrile at the exit of the capillary tube at 323 K and 8.5 MPa. The solid and dashed curves represent the operations for x_{CO_2} as 0.4 and 0, respectively.

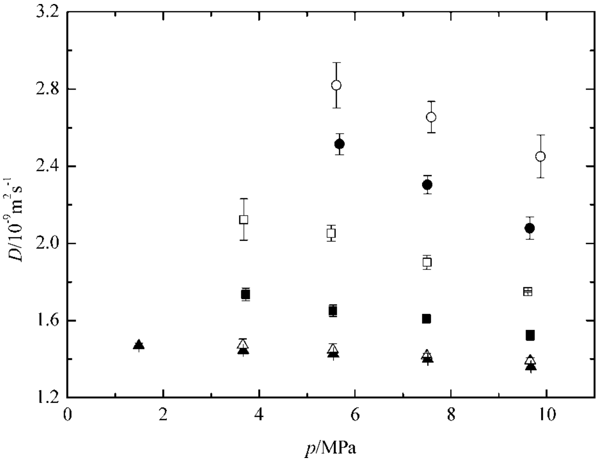

Figure 4. Measured benzonitrile diffusion coefficients D at 303 K. The symbols represent different CO_2 mole fractions x_{CO_2}: ▲, 0; △, 0.1; ■, 0.2; □, 0.3; ●, 0.4; ○, 0.5.

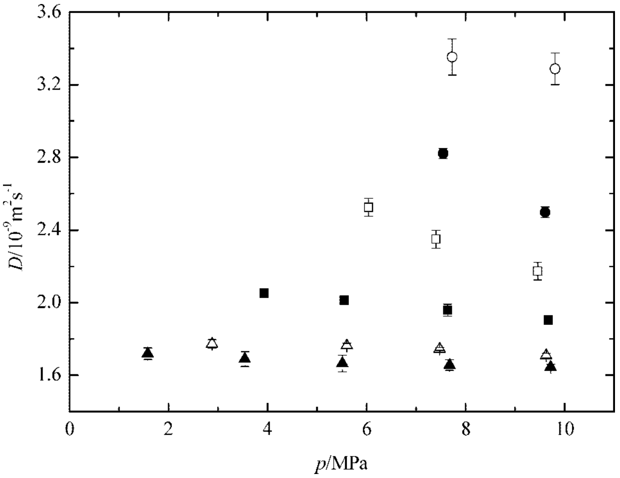

Figure 5. Measured benzonitrile diffusion coefficients D at 313 K. The symbols represent different CO_2 mole fractions x_{CO_2}: ▲, 0; △, 0.1; ■, 0.2; □, 0.3; ●, 0.4; ○, 0.5.

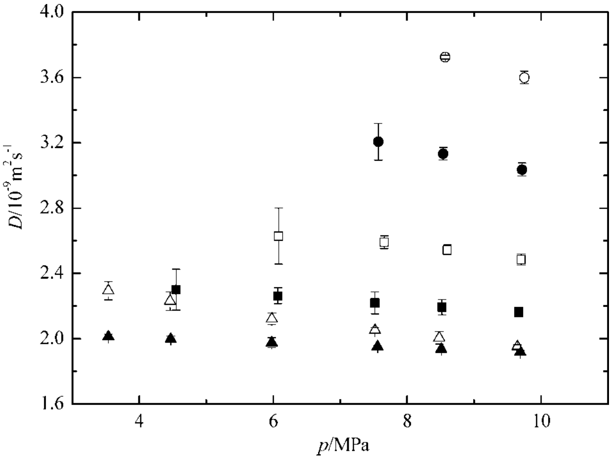

Figure 6. Measured benzonitrile diffusion coefficients D at 323 K. The symbols represent different CO_2 mole fractions x_{CO_2}: ▲, 0; △, 0.1; ■, 0.2; □, 0.3; ●, 0.4; ○, 0.5.

Table 2. Diffusion Coefficients D of Benzonitrile in the CO_2-Expanded Ethanol at 303 K

x_{CO_2}	p/MPa	$\mu/10^{-3}$ Pa·s	$D/10^{-9}$ m^2·s^{-1}	DeSc$^{0.5}$
0	1.49	0.988	1.470 ± 0.013	6.33
	3.67	0.999	1.445 ± 0.011	6.23
	5.54	1.008	1.426 ± 0.010	6.12
	7.52	1.017	1.400 ± 0.010	6.09
	9.66	1.028	1.360 ± 0.015	6.01
0.1	3.65	0.826	1.472 ± 0.032	7.03
	5.53	0.834	1.448 ± 0.033	7.03
	7.50	0.842	1.419 ± 0.011	6.89
	9.65	0.850	1.392 ± 0.015	6.72
0.2	3.71	0.667	1.736 ± 0.033	8.14
	5.54	0.673	1.651 ± 0.029	8.08
	7.48	0.680	1.609 ± 0.041	7.78
	9.65	0.687	1.524 ± 0.026	7.71
0.3	3.67	0.508	2.124 ± 0.107	8.40
	5.49	0.513	2.053 ± 0.042	8.95
	7.50	0.518	1.902 ± 0.036	8.86
	9.60	0.523	1.750 ± 0.005	8.62
0.4	5.67	0.287	2.515 ± 0.055	10.27
	7.50	0.289	2.304 ± 0.047	9.95
	9.64	0.292	2.079 ± 0.058	9.84
0.5	5.61	0.244	2.820 ± 0.117	12.07
	7.58	0.247	2.655 ± 0.081	11.71
	9.68	0.250	2.451 ± 0.110	11.49

Table 3. Diffusion Coefficients D of Benzonitrile in the CO_2-Expanded Ethanol at 313 K

x_{CO_2}	p/MPa	$\mu/10^{-3}$ Pa·s	$D/10^{-9}$ m^2·s^{-1}	DeSc$^{0.5}$
0	1.58	0.821	1.718 ± 0.032	5.96
	3.54	0.829	1.689 ± 0.041	6.10
	5.51	0.837	1.664 ± 0.046	6.08
	7.68	0.846	1.656 ± 0.029	5.91
	9.71	0.855	1.646 ± 0.014	5.99
0.1	2.88	0.692	1.782 ± 0.011	7.13
	5.60	0.699	1.763 ± 0.014	7.01
	7.48	0.707	1.745 ± 0.007	6.84
	9.62	0.714	1.709 ± 0.013	6.69
0.2	3.93	0.564	2.052 ± 0.006	7.78
	5.55	0.570	2.014 ± 0.021	7.75
	7.64	0.577	1.959 ± 0.033	7.63
	9.67	0.583	1.905 ± 0.017	7.45
0.3	6.03	0.442	2.526 ± 0.050	8.67
	7.39	0.447	2.350 ± 0.050	8.63
	9.45	0.451	2.174 ± 0.048	8.40
0.4	7.55	0.267	2.822 ± 0.028	9.89
	9.61	0.270	2.498 ± 0.030	9.73
0.5	7.73	0.227	3.354 ± 0.100	11.78
	9.79	0.230	3.288 ± 0.087	11.49

Equation 1 is applicable to a straight capillary tube. The tube generally needs to be coiled if a long capillary tube is used. To use eq 1, the effect of the secondary flow in the coiled tube on diffusion should be eliminated. To achieve this, eq 5 should be satisfied[39]

$$\mathrm{DeSc}^{0.5} < 10 \tag{5}$$

where Dean number, De, and Schmidt number, Sc, are expressed by

$$\mathrm{De} = \frac{\rho u d}{\mu}\left(\frac{d}{d_{\mathrm{coil}}}\right)^{0.5} \tag{6}$$

$$\mathrm{Sc} = \frac{\mu}{\rho D} \tag{7}$$

where ρ and μ are the density and viscosity of the mobile phase, respectively, and d_{coil} is the coiled diameter of the capillary tube.

Results and Discussion

Table 1 shows a good agreement between the measured and reported diffusion coefficients of different tracers in liquid

Table 4. Diffusion Coefficients D of Benzonitrile in the CO_2-Expanded Ethanol at 323 K

x_{CO_2}	p/MPa	$\mu/10^{-3}$ Pa·s	$D/10^{-9}$ m^2·s^{-1}	DeSc$^{0.5}$
0	3.54	0.694	2.012 ± 0.013	6.31
	4.47	0.697	1.998 ± 0.019	6.25
	5.97	0.703	1.976 ± 0.030	6.16
	7.55	0.708	1.951 ± 0.006	6.15
	8.50	0.711	1.936 ± 0.012	6.10
	9.69	0.716	1.918 ± 0.008	6.07
0.1	3.54	0.584	2.293 ± 0.055	7.00
	4.46	0.587	2.230 ± 0.056	7.11
	5.97	0.592	2.122 ± 0.036	6.98
	7.51	0.596	2.052 ± 0.016	6.87
	8.47	0.599	2.005 ± 0.038	6.76
	9.65	0.603	1.951 ± 0.012	6.60
0.2	4.54	0.484	2.300 ± 0.126	7.93
	6.06	0.488	2.263 ± 0.049	7.99
	7.51	0.492	2.220 ± 0.068	7.85
	8.52	0.494	2.194 ± 0.047	7.71
	9.67	0.497	2.162 ± 0.029	7.50
0.3	6.08	0.384	2.628 ± 0.172	9.13
	7.57	0.387	2.591 ± 0.038	8.74
	8.59	0.389	2.543 ± 0.030	8.74
	9.70	0.392	2.485 ± 0.034	8.71
0.4	7.56	0.246	3.207 ± 0.113	9.85
	8.54	0.248	3.133 ± 0.038	9.68
	9.72	0.249	3.036 ± 0.040	9.60
0.5	8.56	0.209	3.725 ± 0.013	12.10
	9.75	0.211	3.600 ± 0.039	11.96

ethanol at 313 K and 0.1 MPa, indicating the reliability of the present apparatus. In the measurement of the benzonitrile diffusion coefficients in the CO_2-expanded ethanol at 323 K and 9.70 MPa, the effect of CO_2-expanded ethanol flow rate on diffusion coefficient was investigated. It is seen from Figure 2 that the measured diffusion coefficients were more or less the same if the velocities were less than 0.013 m·s^{-1}. On the basis of this observation, the velocity of the CO_2-expanded ethanol in the subsequent measurements lay in a range of (0.007 to 0.013) m·s^{-1}.

Two typical benzonitrile response curves at the exit of the capillary tube are illustrated in Figure 3. It can be seen that both response curves exhibited a Gaussian distribution for different CO_2 mole fractions in ethanol (x_{CO_2}), indicating that the Taylor−Aris dispersion technique is applicable. The measured diffusion coefficients of benzonitrile in the CO_2-expanded ethanol in a pressure range of (1.49 to 9.79) MPa at different temperatures and CO_2 mole fractions are shown in Figures 4 to 6 and Tables 2 to 4. All the data in the figures were the average of the values of at least five measurements, and the error bars in Figures 4 to 6 represent the standard deviation of the measured diffusion coefficients. The uncertainty for all the measured diffusion coefficients is within ± 6.5 %, mainly within ± 3 %. To ensure all the measurements were carried out in the one-phase liquid, the pressure was kept as high and the temperature was kept as low. It is seen from Tables 2 to 4 that most values of DeSc$^{0.5}$ (shown in Tables 2 to 4) are less than 10 except those at high x_{CO_2}. In the measurements with high x_{CO_2}, however, the maximum velocity of the mobile phase was less than 0.013 m·s^{-1}. In this situation, the effect of the secondary flow on diffusion was assumed to neglect in the measurements.

Figures 4 to 6 and Tables 2 to 4 show that the benzonitrile diffusion coefficients decreased with increasing pressure when temperature and x_{CO_2} were maintained as constant. This behavior of diffusion was most likely due to an increase of the collisions between benzonitrile and ethanol at high pressures.[35] It is also seen from Figures 4 to 6 and Tables 2 to 4 that the benzonitrile diffusion coefficients increased with increasing x_{CO_2} under isobaric operation. The increase of diffusion with x_{CO_2} indicates that more CO_2 dissolved in ethanol, leading to reduction of collision between molecules, viscosity, and density, favors the diffusion of benzonitrile in liquid. Solvent expansion in a CXL generally becomes reduced at high temperatures.[1,40] But the benzonitrile diffusion coefficients in the CO_2-expanded ethanol were observed to increase with increasing temperature. Obviously, the mobility of benzonitrile in the CO_2-expanded ethanol plays a more important role than solvent expansion at high temperatures. Figures 4 to 6 show that the diffusion coefficients of benzonitrile in the CO_2-expanded ethanol at high x_{CO_2} and low temperature were close to those at low x_{CO_2} and high temperature, for example, at the conditions 303 K and x_{CO_2} of 0.5, 313 K and x_{CO_2} of 0.4, and 323 K and x_{CO_2} of 0.3. This observation indicates that even less dissolution of CO_2 in solvent under high temperature operations could still lead to a significant increase in diffusion, despite low solvent expansion.

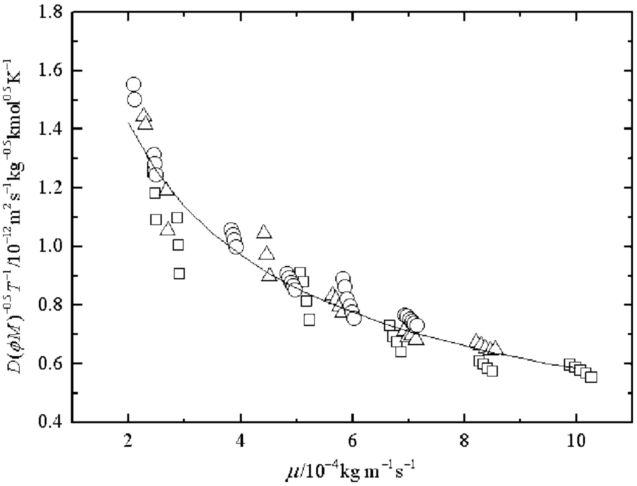

Figure 7. Plot of $D\,(\phi M)^{-0.5}/T$ vs μ. The solid curve represents the prediction by the modified Wilke−Chang equation. The symbols represent the measured diffusion coefficients at different operation temperatures T: □, 303 K; △, 313 K; ○, 323 K.

To estimate the viscosity of the CO_2-expanded ethanol, the method suggested by Sih et al.[41] which combines the equations for the estimation of viscosity for high CO_2 contents in a CXL[42] and the viscosity data of pure solvent[43] was employed. To correlate the diffusion coefficients of benzonitrile in the CO_2-expanded ethanol, some existing equations commonly used for liquids and supercritical fluids were used in this study, shown in Table 5. From the regression, the minimum average absolute deviation (AAD) was found to be 5.11 % using the modified Wilke−Chang equation. The definition of AAD is given by

$$\mathrm{AAD} = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{D_{\mathrm{exptl}} - D_{\mathrm{pred}}}{D_{\mathrm{exptl}}}\right| \tag{8}$$

where n is the number of measurements; D_{exptl} is the measured diffusion coefficient; and D_{pred} is the predicted diffusion coefficient calculated by eq 10.

Figure 7 shows the deviation of the experimental data from the predicted ones by the modified Wilke−Chang equation. When more CO_2 is dissolved in ethanol, leading to a lower viscosity, the larger deviation is observed, especially in the operation at 303 K. This suggests that a more accurate method for estimating viscosity is required to provide a more accurate equation for diffusion coefficient in CXL.

Table 5. Equations [a] Used to Correlate the Measured Benzonitrile Diffusion Coefficients *D* in the CO_2-Expanded Ethanol

		regression parameter			
reference	equation	α	β	γ	100 AAD
Wilke-Chang[29]	$D = \dfrac{1.173 \cdot 10^{-16} (\phi M)^{0.5} T}{\mu V_1^{0.6}}$ (9)	–	–	–	19.23
Modified Wilke-Chang[35]	$D = \dfrac{\alpha (\phi M)^{0.5} T}{\mu^{\beta} V_1^{\gamma}}$ (10)	$3.706 \cdot 10^{-15}$	0.552	0.595	5.11
Sun and Chen[30]	$\dfrac{D (M)^{1/3} (M_1)^{1/6} (V_{c1})^{1/3}}{(V_c)^{2/3} T^{0.5}} = \alpha \left(\dfrac{V}{V_c} - \beta \right)$ (11)	$1.702 \cdot 10^{-9}$	0.268	–	8.30
Modified Stokes−Einstein[31]	$\dfrac{D}{T} = \alpha \mu^{\beta} V_{c1}^{\gamma}$ (12)	$1.137 \cdot 10^{-14}$	−0.744	−0.619	13.30
Funazukuri and Nishimoto[24]	$\dfrac{D}{T} = \alpha \mu^{\beta}$ (13)	$1.613 \cdot 10^{-13}$	−0.49	–	5.57

[a] ϕ is association factor; M/kg·kmol^{-1} and M_1/kg·kmol^{-1} are molecular weights of the mobile phase and solute, respectively; V_1/m^3·kmol^{-1} is the molar volume of solute at normal boiling point; V/m^3·kmol^{-1} is the molar volume of the mobile phase; V_c/m^3·kmol^{-1} and V_{c1}/m^3·kmol^{-1} are critical molar volumes of the mobile phase and solute, respectively; T/K is temperature; and μ/Pa·s is viscosity of the mobile phase.

Conclusions

The diffusion coefficients of benzonitrile in the CO_2-expanded ethanol in a temperature range from (303 to 323) K, a pressure range of (1.49 to 9.79) MPa, and a mole fraction of CO_2 in liquid range of (0 to 0.5) were measured by the chromatographic peak broadening technique. The benzonitrile diffusion coefficients in the CO_2-expanded ethanol were found to be higher than those in pure ethanol and increased with increasing CO_2 mole fraction in ethanol for fixed temperatures and pressures, indicating the benefit of the dissolution of CO_2 in ethanol for diffusion. The benzonitrile diffusion coefficients were also found to decrease with increasing pressure, resulting from an increase in the collisions between solute and solvent. For a fixed pressure, the benzonitrile diffusion coefficients were observed to increase with temperature in the studied ranges of CO_2 mole fraction in liquid. Among the existing equations used to correlate the measured benzonitrile diffusion coefficients, the modified Wilke−Chang equation is proposed.

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Received for review March 27, 2008. Accepted May 16, 2008. Financial support from the National Science Council of ROC, the grant number NSC 96-2628-E-007-125-MY3, is gratefully acknowledged.

JE800211X