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Dispersion Property of CO_2 in Oil. 2: Volume Expansion of CO_2 + Organic Liquid at Near-Critical and Supercritical Conditions of CO_2

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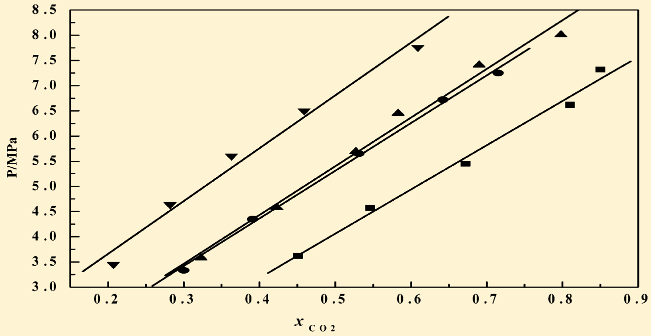
ABSTRACT: To investigate the effect of polarity of organic liquids and the dispersion state of CO_2 in organic liquids on the volume expansion of CO_2 + organic liquid systems, the solubility of CO_2 in methylbenzene and ethanol and the volume of CO_2 + methylbenzene and ethanol at different temperatures and pressures were measured with a *PVT* apparatus. The results imply that the microscopic dispersion state of CO_2 molecules in organic liquids under near-critical or supercritical conditions play a dominant role for increasing the volume of the CO_2 + organic liquid systems. The microscopic dispersion state and the solubility of CO_2 in the organic liquids and the volume expansion of the CO_2 + organic liquid systems are affected by the polarity and the structure of the organic liquid molecule obviously. When pressure and temperature are fixed, the intermolecular force between CO_2 molecule and the organic liquids and the intermolecular force operating within the organic liquids play a dominate role in the volume expansion of the CO_2 + organic liquid systems.



INTRODUCTION

Because of special characteristics of CO_2, which is one of the most popular supercritical fluids, CO_2 has been utilized in industrial processes widely,[1] such as generating microparticles, nanoparticles, and pharmaceuticals, polymers, biological-active protein, pigments, catalysts, and superconductor production.[2−4] The systems of supercritical CO_2 and alcohols or alkanes with lower molar mass are paid more attention because of their importance as a supercritical fluid or cosolvent pairs for the separation of biomaterials.[5−8] The use of CO_2 for miscible flooding of petroleum is paid more and more attention by petroleum engineers as well, not only because of the particular property of CO_2 for enhance oil recovery (EOR), but also because CO_2 is one of the greenhouse gases which have already affected the global climate.[9] The CO_2 flooding technique for producing petroleum has already been under intensive laboratory and field study.[10−15]

The organic liquids used with supercritical fluid of CO_2 in chemical processes contain polar substances with small molecules. It is clear that the phase behavior of such systems can be significant and of technological interest.[16] Many researchers have studied the binary systems of CO_2 + methylbenzene, to calculate the equilibrium ratios for carbon dioxide and methylbenzene in the binary system, Ng and Robinson[17] determined vapor and liquid equilibrium phase composition of the CO_2 + methylbenzene mixtures at temperatures of (311.15, 352.59, 393.71, and 477.15) K and at different pressures up to 15 MPa. Sebastian et al.[18] reported vapor−liquid equilibrium data for the CO_2 + methylbenzene system from 393.15 K up to 543.15 K and with pressure in the range of (1 to 5) MPa. Tochigi et al.[19] reported the vapor−liquid equilibrium data for CO_2 + methylbenzene systems at (323.15 and 333.15) K and at higher pressures up to 10 MPa. The vapor-phase solubility of methylbenzene in compressed CO_2 was reported by Prausnitz and Benson[20] at temperatures of (323.15 and 348.15) K and in the pressure range of (2 to 9) MPa. Choon-Ho Kim and Vimalchand[21] studied the vapor−liquid equilibrium data for CO_2 + methylbenzene at temperatures of (353, 373, and 393) K. For the process development of supercritical or near-critical fluid extraction, alcohols are utilized as cosolvents; the study on the vapor−liquid equilibrium of CO_2 + alcohol is quite significant. A number of previous investigations studied the equilibrium phase behavior for the system of CO_2 + ethanol. Tian et al. studied the vapor−liquid equilibrium of CO_2 + ethanol at temperatures of (333.15, 353.15, 413.15, and 453.15) K with pressures up to 14.5 MPa.[22] Vapor−liquid equilibrium (VLE) data were measured for CO_2 + ethanol system by Joung et al.[23] with temperatures ranging from (313.15 to 343.15) K and with pressure up to 6.92 MPa. Chang et al.[24] reported $P-x-y$ diagrams and Henry's constants for the CO_2 + ethanol system from (291.15 to 313.15) K with pressures up to 8 MPa.

When CO_2 being dissolved in organic liquids or oil, the volume of organic liquids or oil is swollen, and the viscosity of the organic liquids or oil is reduced.[25−29] The research on the

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dispersion property of CO_2 in the organic liquids or oil could provide a better understanding of CO_2 dissolving in the organic liquids or oil, the volume expansion of the organic liquids or oil, and the miscibility between CO_2 and the organic liquids or oil for relevant chemical processes and enhance oil recovery. Due to oils (crude oils) containing both polar and nonpolar substances, we plan to study the dispersion properties of CO_2 in nonpolar substances, such as alkanes, and polar substances, such as aliphatic alcohols, resin, and asphaltene, respectively. In our previous work,[30] the effect of alkane molecular structure on the volume expansion of CO_2 + alkane systems at different temperatures and pressures were studied. The results show that the dispersion state of CO_2 molecules in the alkane phase under near-critical or supercritical conditions of CO_2 play a dominate role in increasing the volume of CO_2 + alkane systems.

In this work, our interest is focused on the effect of polarity of aliphatic alcohols, resin, and asphaltene on the dispersion state of CO_2 molecules in oils and the volume expansion of CO_2 + organic liquid systems under near-critical or supercritical conditions of CO_2. Because the molecular structure of resin and asphaltene are complicate multi-ring structures with a high uncertainty, we selected methylbenzene to present ring structure molecules. Because Tsutomu et al.[1] have published results for CO_2−methanol, -ethanol, -propanol, -butanol, isopropyl alcohol, and *tert*-butyl alcohol which showed that there were few differences in mole fraction of CO_2 in the alcohols at 313.15 K due to pressure and the expansion coefficient of CO_2−alcohol system decreased with increasing alkyl chain length, we only selected ethanol to present aliphatic alcohols. The solubility of CO_2 in methylbenzene or ethanol and the volume of CO_2 + methylbenzene or ethanol at different temperatures and pressures were measured. Based on a comparison of the data of CO_2 + methylbenzene or ethanol systems with the data of CO_2 + cyclohexane or hexane systems which we measured in our previous work,[30] the study shows that the polarity of organic liquids and the microscopic dispersion state of CO_2 molecules in the organic liquids play a dominate role in increasing the volume of CO_2 + organic liquid systems under near-critical or supercritical conditions of CO_2.

EXPERIMENTS

Materials. Carbon dioxide with a mass purity of 0.997 was purchased from Beijing AP Beifen Gases Industry Company. Methylbenzene (mass fraction purity > 0.995) and ethanol (mass fraction purity > 0.995) are supplied by Beijing Modern Oriental Fine Chemicals Co., Ltd.

Experimental Apparatus and Procedure. The apparatus used and the procedures of the data measurement in this work are described in detail on our previous work.[30]

The quantity of CO_2 was calculated using the state equation for an ideal gas. The CO_2 solubility in organic liquids can be given by the following relation:

$$x_{CO_2} = \frac{n_{CO_2}}{n_s} = \left(\frac{PV}{RT}\right)/n_s \tag{1}$$

where x_{CO_2} is the solubility of CO_2 in organic liquids (mole fraction), R is the universal gas constant, P is the atmospheric pressure, V is the amount of gas released at atmospheric pressure and at the certain temperature, n_{CO_2} is the mole number of CO_2 dissolved in organic liquids, and n_s is the total amount of sample that exists in the cell ($n_s = n_{CO_2} + n_{org}$). The measurement of CO_2 solubility in organic liquids is repeated three times, and the results presented are the average of the replicates.

In this work, the volume expansion is described by expansion coefficient η, which is defined as the following:

$$\eta = \frac{V_{L1}}{V_L} \tag{2}$$

V_{L1} is the volume of the liquid phase and V_L is the volume of organic liquids which was measured by a charge-coupled device (CCD) system at atmospheric pressure and experimental temperatures of (308.15, 318.15, 333.15, and 343.15) K, respectively.

MODELING

The Peng−Robinson equation of state (PR EOS) with one temperature-independent binary interaction parameter was used to correlate the VLE data obtained in this work.[31]

The relative deviation (RD %) and the average absolute relative deviation percent (AARD %) is defined as the following equations, and the AARD % was minimized to obtain the values of the binary interactions.

$$\text{RD } \% = \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \cdot 100\ \% \tag{3}$$

$$\text{AARD } \% = \frac{\sum_i^n \left| \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \right|}{N} \cdot 100\ \% \tag{4}$$

where N is the number of experimental points. The superscripts “exp” and “cal” stand for the experimental and calculated values, respectively.

RESULTS AND DISCUSSION

Solubility of CO_2 in Organic Liquids. Tables 1 and 2 show the data of the mole fraction of CO_2 in the organic liquids which was measured in the experiment and calculated with PR EOS, respectively. The data of relative deviation (RD %) and the average absolute relative deviation percent (AARD %) of the PR EOS from the experimental data are also shown in the tables.

It can be seen from Tables 1 and 2 that, for the binary systems of CO_2 + methylbenzene and CO_2 + ethanol, the solubility of CO_2 in the organic liquids increased with the pressure of the systems increased and decreased as the temperature of the systems increased. The value of ARRD is less than 2.51 % in the study.

A careful study of Tables 1 and 2 indicated that the results obtained from the PR EOS can accurately correlate the experimental solubility data at different pressures and temperatures (based on the value of AARD %). The values for the binary interaction parameters δ_{ij} at different temperatures were reported for each specified binary system.

The correlated liquid-phase mole fraction of CO_2 for the systems of CO_2 + methylbenzene was compared with those reported by Nemati Lay et al.[16] at 308.15 K. The comparison is shown in Figure 1.

The solubility of CO_2 for each CO_2 + organic liquid system under different pressures at 318.15 K is shown in Figure 2. It can be seen that the solubility of CO_2 in the organic liquids increases as pressure increased. It should be noted that the curves of CO_2 + methylbenzene and CO_2 + cyclohexane almost coincided when pressure is lower than about 5.5 MPa. When pressure is higher than 5.5 MPa, the solubility of CO_2 in cyclohexane is slightly higher than that in methylbenzene. The order of the solubility of CO_2 in the organic liquids is: hexane >

Table 1. x^{exp}, x^{cal}, RD, and ARRD for Binary Systems of CO_2 + Methylbenzene at Different Temperatures and Pressures

P/MPa	x^{exp}	x^{cal}	RD %	P/MPa	x^{exp}	x^{cal}	RD %
	308.15 K, δ_{ij} = 0.093				318.15 K, δ_{ij} = 0.095		
3.21	0.335	0.335	0.00	3.58	0.323	0.320	1.06
4.60	0.506	0.488	3.53	4.58	0.423	0.409	3.29
5.45	0.584	0.595	−1.96	5.69	0.527	0.513	2.64
6.50	0.770	0.789	−2.47	6.45	0.583	0.590	−1.20
6.90	0.883	0.899	−1.81	7.41	0.690	0.710	−2.94
				8.01	0.798	0.825	−3.38
ARRD %		1.95		ARRD %		2.42	
	333.15 K, δ_{ij} = 0.085				343.15 K, δ_{ij} = 0.081		
3.61	0.277	0.281	−1.29	3.30	0.233	0.236	−1.12
4.50	0.345	0.347	−0.58	4.50	0.301	0.317	−5.32
5.58	0.430	0.427	0.67	5.46	0.389	0.380	2.31
6.65	0.509	0.507	0.41	6.64	0.470	0.457	2.77
7.68	0.575	0.586	−1.91	7.48	0.510	0.512	−0.39
8.74	0.672	0.674	−0.30	8.65	0.592	0.589	0.51
9.37	0.746	0.734	1.61	9.46	0.631	0.645	−2.22
ARRD %		0.97		ARRD %		2.09	

Table 2. x^{exp}, x^{cal}, RD, and ARRD for Binary Systems of CO_2 + Ethanol at Different Temperatures and Pressures

P/MPa	x^{exp}	x^{cal}	RD %	P/MPa	x^{exp}	x^{cal}	RD %
	308.15 K, δ_{ij} = 0.091				318.15 K, δ_{ij} = 0.083		
3.60	0.239	0.240	0.28	3.45	0.207	0.213	3.03
4.35	0.302	0.299	0.97	4.64	0.282	0.294	4.20
5.45	0.427	0.400	6.24	5.60	0.363	0.367	1.10
6.48	0.536	0.539	0.59	6.50	0.459	0.445	3.09
6.76	0.591	0.616	4.23	7.76	0.609	0.602	1.15
ARRD %		2.46		ARRD %		2.51	
	333.15 K, δ_{ij} = 0.096				343.15 K, δ_{ij} = 0.091		
3.62	0.171	0.173	1.17%	3.80	0.169	0.171	1.18%
4.60	0.224	0.223	0.58%	4.50	0.199	0.204	2.57%
5.60	0.277	0.275	0.72%	5.64	0.258	0.259	0.39%
6.70	0.338	0.336	0.59%	6.45	0.303	0.299	1.28%
7.92	0.402	0.408	1.49%	7.42	0.342	0.349	2.16%
9.09	0.479	0.486	1.50%	8.45	0.410	0.403	1.67%
9.46	0.492	0.514	4.57%	9.42	0.452	0.459	1.55%
				10.28	0.521	0.512	1.67%
ARRD %		1.52		ARRD %		1.56	

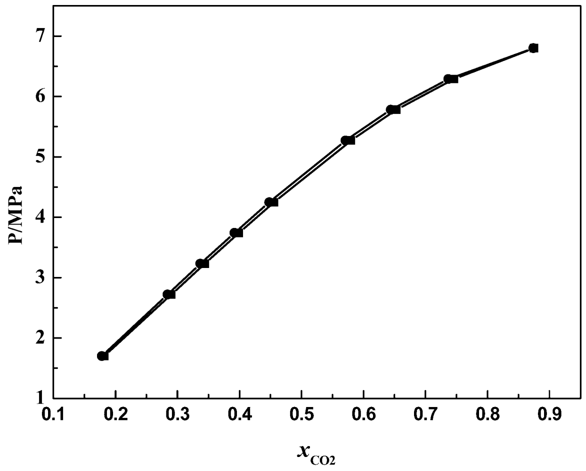

Figure 1. Pressure−x_{CO_2} diagram of the CO_2 + methylbenzene system. ■, Literature, correlated data; ●, this work, correlated data.

cyclohexane > methylbenzene > ethanol when pressure is higher than 5.5 MPa at 318.15 K.

Volume of CO_2 + Organic Liquid System. The volume expansion coefficients for CO_2 + methylbenzene and CO_2 + ethanol systems under different conditions were shown in Figures 3 and 4. It is clear that, as the solubility of CO_2 in the organic liquids increases, the volume of the CO_2 + organic liquids is expanded with increasing pressure. Meanwhile, with increasing temperature, the volume expansion coefficients are decreased.

The volume expansion coefficient for different CO_2 + organic liquid systems under different pressures at (308.15, 318.15, and 333.15) K are shown in Figures 5, 6, and 7, respectively. It can be seen from Figure 5 that, for the CO_2 + organic liquid systems, when pressure is below 5.5 MPa the curves of CO_2 + methylbenzene and CO_2 + cyclohexane are almost coincident like the curves of solubility of CO_2 in the organic liquids at 318.15 K in Figure 2. The order of the volume expansion coefficient of the CO_2 + organic liquid systems is CO_2 + hexane > CO_2 + methylbenzene = CO_2 + cyclohexane > CO_2 + ethanol which is as same as the order of the solubility of CO_2 in the organic liquids when pressure is 5.5 MPa at 308.15 K.[30] When pressure is about 6.7 MPa, the order of the volume expansion coefficient of the CO_2 + organic

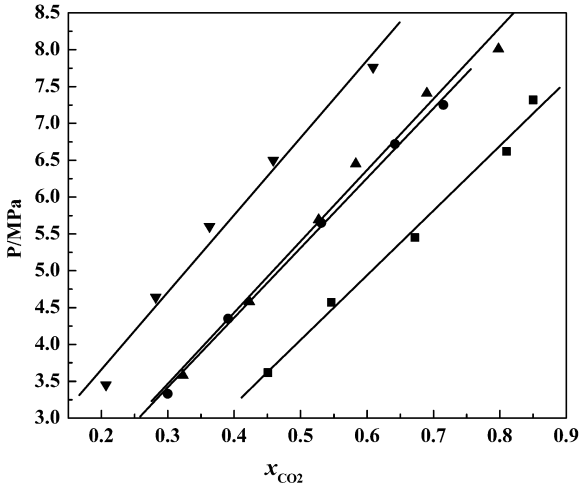

Figure 2. Pressure−x_{CO_2} diagram of CO_2 + organic liquid systems at 318.15 K. ■, hexane; ●, cyclohexane; ▲, methylbenzene; ▼, ethanol.

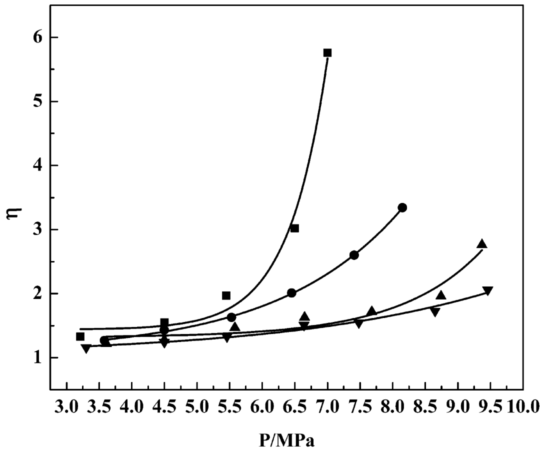

Figure 3. Volume expansion coefficient η of the CO_2 + methylbenzene system as a function of pressure. ■, T = 308.15 K; ●, T = 318.15 K; ▲, T = 333.15 K; ▼, T = 343.15 K.

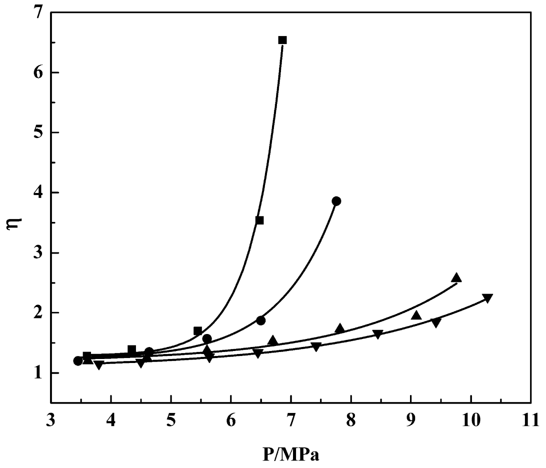

Figure 4. Volume expansion coefficient η of the CO_2 + ethanol system as a function of pressure. ■, T = 308.15 K; ●, T = 318.15 K; ▲, T = 333.15 K; ▼, T = 343.15 K.

liquid systems is CO_2 + hexane > CO_2 + ethanol > CO_2 + cyclohexane > CO_2 + methylbenzene at 308.15 K.[30]

Figure 6 shows that when pressure is below 7.4 MPa the curves of CO_2 + methylbenzene and CO_2 + cyclohexane almost coincided, as well. The order of the volume expansion coefficient of the CO_2 + organic liquid systems is CO_2 + hexane > CO_2 + methylbenzene = CO_2 + cyclohexane > CO_2 + ethanol

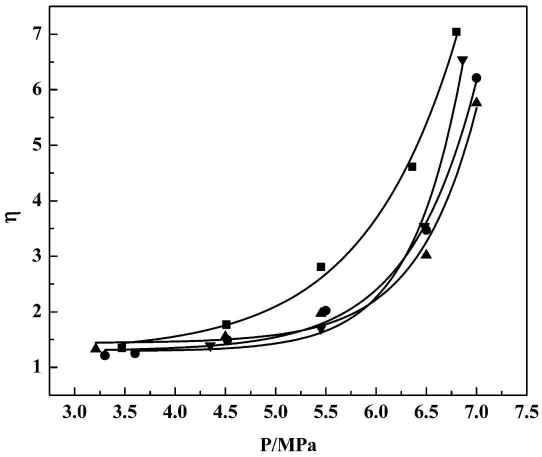

Figure 5. Volume expansion coefficient η of CO_2 + organic liquid systems as function of pressure at 308.15 K. ■, hexane; ●, cyclohexane; ▲, methylbenzene; ▼, ethanol.

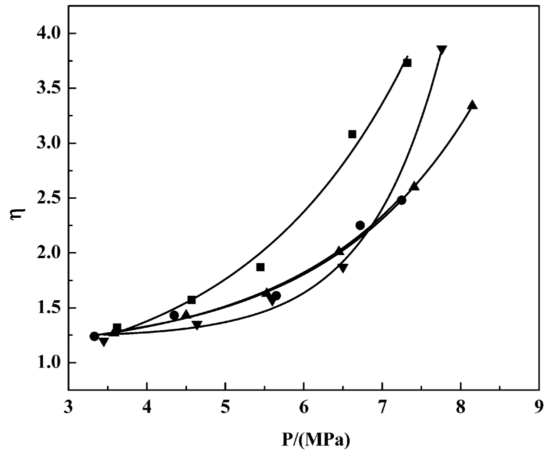

Figure 6. Volume expansion coefficient η of CO_2 + organic liquid systems as function of pressure at 318.15 K. ■, hexane; ●, cyclohexane; ▲, methylbenzene; ▼, ethanol.

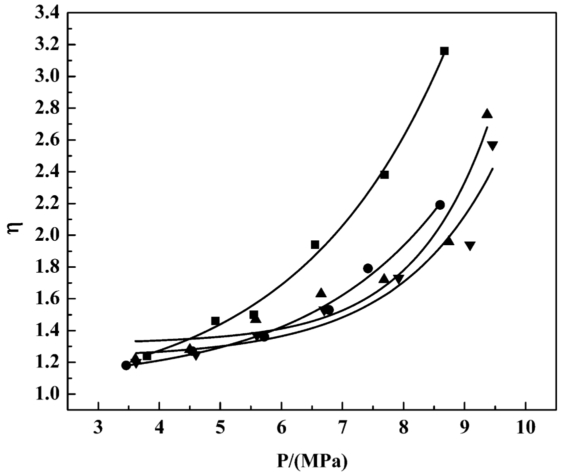

Figure 7. Volume expansion coefficient η of CO_2 + organic liquid systems as function of pressure at 333.15 K. ■, hexane; ●, cyclohexane; ▲, methylbenzene; ▼, ethanol.

when pressure is below 6.5 MPa at 318.15 K. When pressure is about 7.5 MPa, the order of the volume expansion coefficient of the CO_2 + organic liquid systems is CO_2 + hexane > CO_2 + ethanol > CO_2 + cyclohexane = CO_2 + methylbenzene at 318.15 K.

Figure 7 shows that when pressure is below about 6.8 MPa the order of the volume expansion coefficient of the CO_2 + organic liquid systems is CO_2 + hexane > CO_2 + methylbenzene > CO_2 + ethanol = CO_2 + cyclohexane at 333.15 K. When pressure is about 8.7 MPa, the order of the volume expansion coefficient of the CO_2 + organic liquid systems is CO_2 + hexane > CO_2 + cyclohexane > CO_2 + methylbenzene > CO_2 + ethanol at 333.15 K which is as same as the order of the solubility of CO_2 in the organic liquids when pressure is about 8.7 MPa at 333.15 K.[30]

Forces for the CO_2 + Organic Liquid System. There are two forces affect the solubility of CO_2 + organic liquid systems: (1) the intermolecular force (attractive force) between CO_2 molecules and organic liquid molecules which drags the CO_2 molecule into the organic liquid phase; (2) the intermolecular force operating within organic liquid molecules which squeezes the CO_2 molecule out of the organic liquid phase and prevents CO_2 molecules to get into the organic liquid phase.

The intermolecular forces are affected by pressure and temperature. With increasing pressure, the distance between CO_2 molecules and organic liquid molecules is decreased, and the intermolecular force between CO_2 molecules and organic liquid molecules is increased; there are more CO_2 molecules which get into the organic liquid phase, which causes the distance between organic liquid molecules to increase. Therefore, the intermolecular force operating within organic liquid molecules which tends to squeeze CO_2 molecule out of the organic liquid phase and prevent CO_2 molecules to get into the organic liquid phase is reduced.[30] The variation of these intermolecular forces results in that the solubility of CO_2 in the organic liquids is increased, and the volume of the CO_2 + organic liquid systems increased much faster than the solubility of CO_2 in the organic liquids when the pressure is closed to the critical pressure or under supercritical pressure of CO_2.

Temperature affects the distance between molecules and intermolecular force, as well. As temperature is increased the distance between molecules is increased, and the intermolecular force between CO_2 molecules and organic liquid molecules is decreased, which promotes CO_2 molecules escaping from the organic liquid phase. Therefore, the solubility of CO_2 in the organic liquids and the volume of CO_2 + organic liquid systems are decreased with increasing temperature.

Under the same conditions of temperature and pressure, the solubility of CO_2 in the organic liquids and the volume expansion of the CO_2 + organic liquid systems is affected by the intermolecular force which operates within organic liquid molecules, squeezes CO_2 molecule out of the liquid phase, and prevents CO_2 molecules from getting into the organic liquid phase, and the intermolecular force between CO_2 molecules and the organic liquid molecules which drags the CO_2 molecule into the organic liquids phase.

For the binary systems of CO_2 + hexane, CO_2 + cyclohexane, and CO_2 + methylbenzene, the main intermolecular force operating within the organic liquid molecules, the CO_2 molecules, and between the organic liquids and CO_2 molecules is the London force (London dispersion force or dispersion force) which is an instantaneous dipole−induced dipole force.[32] The potential energy between two molecules versus separation contributed by London force is described by eq 5.[33]

$$\Phi = -\frac{3h}{2}\frac{\nu_1\nu_2}{\nu_1 + \nu_2}\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\varepsilon_0)^2}\frac{1}{l^6} \tag{5}$$

where Φ is potential energy, h is Planck's constant, ν_i is the characteristic vibrational frequency of electron i (always negative), $\alpha_{0,i}$ is the polarizability of molecule i, ε_0 is the permittivity of vacuum, and l is the separation between two molecules.

Dispersion forces depend on two features of molecular structure. First, they increase in magnitude with the size and distortability (usually called the polarizability) of the electron clouds of the interacting particles. The size and polarizability increase as molar mass increases. It follows that dispersion forces increase as molar mass increases. Second, the larger the surface area of molecule contact is, the stronger the dispersion forces is.

For the CO_2 + ethanol system, the intermolecular force operating within ethanol molecules is a Coulomb permanent dipole (dipole−dipole) force and hydrogen bonding (H-bonding).[32] The potential energy between two ethanol molecules versus separation contributed by the Coulomb force is described by eq 6. The intermolecular force operating within ethanol and CO_2 molecules is the Debye force which is a permanent dipole−induced dipole force and the potential energy between ethanol and CO_2 molecules versus separation contributed by Debye force is described by eq 7.[33]

$$\Phi = \frac{(\text{constant})\mu_1\mu_2}{4\pi\varepsilon_0 l^3} \tag{6}$$

$$\Phi = -\frac{(\alpha_{0,1}\mu_2^2 + \alpha_{0,2}\mu_1^2)}{(4\pi\varepsilon_0)^2 l^6} \tag{7}$$

where Φ is potential energy, μ_i is a dipole moment, $\alpha_{0,i}$ is the polarizability of molecule i, ε_0 is the permittivity of vacuum, and l is the separation between two molecules. The numerical constant (including sign) depends on the orientation: constant = $2^{1/2}$ for average overall orientation; const = +2 for parallel and −2 for antiparallel alignment.

Hydrogen bonding is a special kind of dipole−dipole force that occurs when a hydrogen atom is bonded to one of the very electronegative atoms, F, O, or N. The H−F, H−O, and H−N bonds are very polar, because the electronegative atom draws the bonding electron pair strongly to itself.[32]

Effect of Organic Liquid Molecule Polarity on the Solubility of CO_2 in the Organic Liquids and the Volume of CO_2 + Organic Liquid Systems. As discussed in our previous study, the solubility of CO_2 in the organic liquids and the volume of the CO_2 + organic liquid systems are affected by the distance between CO_2 molecules, organic liquid molecules, CO_2 and organic liquid molecules, and the intermolecular forces operating within the CO_2 molecules, the organic liquid molecules, between the organic liquids and CO_2 molecules. The effect of molecular structure of organic liquids on the solubility of CO_2 in the organic liquids and the volume of the CO_2 + organic liquid systems is strong as well.

Figure 2 shows that the curves of CO_2 + methylbenzene and CO_2 + cyclohexane almost coincided when pressure is lower than 5.5 MPa at 318.15 K. When pressure is higher than 5.5 MPa, the solubility of CO_2 in cyclohexane is slightly higher than that in methylbenzene, and the order of the solubility of

CO_2 in the organic liquids is hexane > cyclohexane > methylbenzene > ethanol.

Due to hexane molecules being linear and short, the surface area of contact among hexane molecules is small. Therefore, the dispersion force between hexane molecules is weak. Under the effect of pressure at a fixed temperature the CO_2 molecules are more easily dragged into the hexane phase, so that the solubility of CO_2 in hexane and the volume expansion coefficient of CO_2 + hexane system are larger.

The cyclohexane molecule has a shape of chair or boat, and the cyclohexane molecule has a higher polarity than hexane molecule, so cyclohexane molecules have a large surface area of contact and larger dispersion force than hexane molecules. Therefore, under the same pressure and temperature, the solubility of CO_2 in cyclohexane and the volume of CO_2 + cyclohexane are less than that of hexane and the CO_2 + hexane system.

The shape of the methylbenzene molecule is a ring structure which is similar to a cyclohexane molecule; the intermolecular force operation within methylbenzene or cyclohexane molecules is quite close, and the surface area of contact is larger than a hexane molecule, as well. From Figure 2, it is known that the solubility of CO_2 in both methylbenzene and cyclohexane is almost the same when the pressure is lower than 5.5 MPa. When the pressure is higher than 5.5 MPa the solubility of CO_2 in cyclohexane is slightly higher than that in methylbenzene. Figures 5, 6, and 7 show that, in the most cases, the volume expansion coefficient of the CO_2 + cyclohexane system is slightly larger than the CO_2 + methylbenzene system under higher pressure. Because the methyl group on the methylbenzene ring makes the molecule a little more polar than cyclohexane molecules, the dispersion force operation within methylbenzene molecules is larger than that within cyclohexane molecules.

For the CO_2 + ethanol system, although an ethanol molecule is shorter than that of hexane, the existence of a hydroxyl group causes an ethanol molecule with a higher polarity, and the intermolecular force operating within ethanol molecules is a permanent dipole force and hydrogen-bond force. It is clear that the forces operating within ethanol molecules are much larger than that (dispersion force) operating within methylbenzene, cyclohexane, or hexane molecules. The potential wells between two molecules caused by the hydrogen bond force are in the range (5 to 50) $kJ \cdot mol^{-1}$, and the potential wells between two molecules generated by dispersion force are in the range (0.1 to 5) $kJ \cdot mol^{-1}$.[32] It is difficult for CO_2 molecules to be dragged into ethanol and maintained in the ethanol phase; consequently the solubility of CO_2 in ethanol is the smallest among the four binary systems under the same pressure and temperature.

It is most interesting that Figure 2 shows that the solubility of CO_2 in ethanol is smaller than that in cyclohexane and methylbenzene obviously. However, Figures 5 and 6 show that the volume expansion coefficient of CO_2 + ethanol system is larger than that of the CO_2 + cyclohexane system and the CO_2 + methylbenzene system when pressure is higher than about 6.6 MPa. This phenomenon indicates that at experiment conditions the distance between the CO_2 molecule and ethanol molecule is larger than that between the CO_2 molecule and cyclohexane or the methylbenzene molecule. The other possibility is the distance between CO_2 molecules themselves in ethanol is increased dramatically. Anyway, the phenomenon implies that the microscopic dispersion state of CO_2 in ethanol is different from the microscopic dispersion state of CO_2 in cyclohexane or methylbenzene under near-critical or supercritical conditions of CO_2. The variation of the volume expansion coefficient of the four CO_2 + organic liquid systems under near-critical or supercritical conditions of CO_2 shows that the microscopic dispersion state of CO_2 in the organic liquids and the volume expansion of the CO_2 + organic liquid systems are affected by the polarity of the organic liquid molecule and the molecular structure obviously, as well.

■ CONCLUSIONS

Based on this study, the following conclusions can be made:

1. The microscopic dispersion state of CO_2 molecules in organic liquids under near-critical or supercritical conditions plays a dominant role in increasing the volume of CO_2 + organic liquid systems.
2. The microscopic dispersion state and the solubility of CO_2 in the organic liquids and the volume expansion of the CO_2 + organic liquid systems are affected by the polarity and the structure of the organic liquid molecule obviously.
3. When pressure and temperature are fixed, the intermolecular force between CO_2 molecule and the organic liquids and the intermolecular force operating within organic liquid play a dominate role in the solubility of CO_2 in the organic liquids and the volume expansion of the CO_2 + organic liquid systems.

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Notes

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