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Dispersion Property of CO_2 in Oil. 1. Volume Expansion of CO_2 + Alkane at near Critical and Supercritical Condition of CO_2

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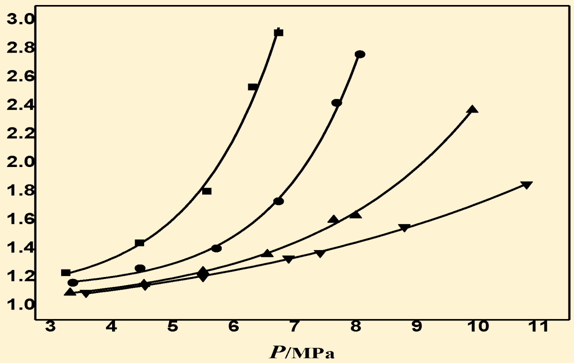
ABSTRACT: To investigate the effect of alkane molecular structure on the volume expansion of CO_2 + alkane systems, the solubility of CO_2 in hexane, octane, decane, and cyclohexane and the volume of CO_2 + alkanes at different temperature and pressure was measured with a *PVT* apparatus. The results imply that the dispersion state of CO_2 molecules in the alkane phase under near critical or supercritical condition of CO_2 plays a dominate role in increasing the volume of CO_2 + alkane systems. The solubility of CO_2 in the alkanes, the volume expansion of the CO_2 + alkane systems, and the London force operating within alkane molecules are strongly influenced by molecular structure of the alkanes and pressure.



■ INTRODUCTION

Supercritical fluid is extensively used in many industrial processes. Because of the special characteristics, CO_2 is one of the most popular materials and is widely utilized for supercritical fluid technology in different industrial processes.[1−5] Nowadays, how to utilize CO_2 to enhance oil recovery (EOR) is paid more and more attention by petroleum engineers, not only because of the particular property of CO_2 for enhancing oil recovery but also because CO_2 is one of the greenhouse gases which has already affected the global climate.[6] Researches show that for CO_2 EOR the oil recovery rate can be enhanced usually up to 8 to 16 % of the original oil in place.[7,8] Meanwhile, part of CO_2 injected into the reservoirs could be sequestrated in the reservoirs geologically.

When CO_2 is injected into oil-bearing reservoirs, as CO_2 being dissolved in crude oil, the oil volume swells, the oil viscosity is reduced, and CO_2 and oil could be miscible when the reservoir pressure is high enough, which are considered to be main contributions for EOR by CO_2 injection.[9−13] The oil swelling effect can be accurately quantified under reservoir conditions,[14,15] and the similar phenomenon of the CO_2 + oil or organic liquid system has also been reported in many papers on other chemical processes.[16−21] It is well-known that CO_2 is preferable to be dissolved in the light fractions rather than heavy fractions of oil.[12] The change of oil properties mainly results from CO_2 dissolving in oil and is affected by the dispersion property of CO_2 in the oil. Therefore, the research on the dispersion property of CO_2 in oil could provide a better understanding of CO_2 dissolving in oil, oil volume expansion, and the miscibility between CO_2 and oil for EOR and other chemical processes.

In this work, the solubility of CO_2 in hexane, octane, decane, and cyclohexane and the volume expansion of CO_2 + alkanes at different temperature and pressure were measured, and the effect of alkane molecular structure and the dispersion property of CO_2 in oil on the volume expansion of CO_2 + alkane systems were discussed. The data obtained from the experiments were correlated using the Peng−Robinson equation of state (PR EOS) with one temperature-independent binary interaction parameter, as well. The results show that the dispersion state of CO_2 molecules in the alkane phase plays a dominate role in increasing the volume of CO_2 + alkane systems under near critical or supercritical conditions of CO_2.

■ EXPERIMENTS

Materials. Carbon dioxide with a mass purity of 99.7 % was purchased from Beijing AP Beifen Gases Industry Company. Cyclohexane (mass fraction purity >0.995) was supplied by Beijing Modern Oriental Fine Chemicals Co., Ltd. Octane (mass fraction purity >0.995) and hexane (mass fraction purity >0.995) were obtained from Kemi'ou, Tianjin, and decane (mass fraction purity >0.99) was provided by Alfa Aesar.

Experimental Apparatus and Procedure. For the purpose of measuring the solubility of CO_2 in alkanes and the phase behavior of CO_2 + alkane systems, an apparatus containing a *PVT* cell was used. A schematic diagram of the pressure−volume−temperature (*PVT*) apparatus (S.T. Ltd., France) is shown in Figure 1. The pressure was generated with an automatic pump and was measured with a pressure sensor, and the temperature of the *PVT* cell was controlled by an electric heating system.

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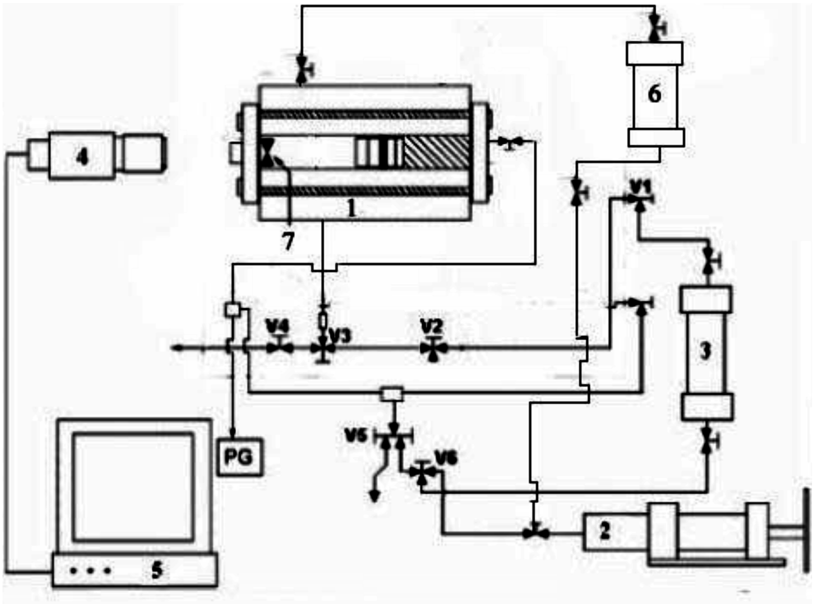

Figure 1. Schematic diagram of the *PVT* apparatus used in this work (1, visible *PVT* cell; 2, high-pressure pump; 3, sample cylinder; 4, CCD camera; 5, computer; 6, gas bottle; 7, stirrer).

Table 1. x^{exp}, x^{cal}, **RD, and AARD for the Binary Systems of** CO_2 **+ Hexane at Different Temperature and Pressure**

P/MPa	x^{exp}	x^{cal}	RD %	P/MPa	x^{exp}	x^{cal}	RD %
	308.15 K, $\delta_{ij} = 0.095$				318.15 K, $\delta_{ij} = 0.065$		
3.47	0.444	0.445	−0.23	3.62	0.451	0.449	0.51
4.51	0.588	0.584	0.68	4.57	0.546	0.560	−2.54
5.45	0.740	0.725	2.03	5.45	0.672	0.661	1.58
6.36	0.841	0.871	−3.55	6.62	0.810	0.794	1.94
6.80	0.897	0.926	−3.23	7.32	0.850	0.870	−2.35
AARD %		1.94		AARD %		1.79	
	323.15 K, $\delta_{ij} = 0.055$				333.15 K, $\delta_{ij} = 0.064$		
3.74	0.449	0.449	0.00	3.80	0.404	0.396	1.96
4.68	0.539	0.552	−2.34	4.92	0.501	0.504	−0.53
5.65	0.647	0.654	−1.15	5.55	0.561	0.563	−0.41
6.50	0.772	0.742	3.85	6.55	0.672	0.655	2.57
7.30	0.829	0.821	0.93	7.69	0.736	0.759	−3.15
8.00	0.877	0.886	−1.03	8.67	0.838	0.849	−1.31
AARD %		1.55		AARD %		1.66	

The temperature was measured with a calibrated thermocouple inside the *PVT* cell, and the pressure of the system was measured with a digital pressure indicator. A high-pressure variable view cell, with total sample volume of 240 cm^3 rated to 150 MPa and 473.15 K and equipped with a magnetic stirrer, was utilized for the experiment. The visible window was attached to the front of the cell to obtain full visibility of all the contents in the cell. The volume of the fluid phase in the *PVT* cell can be measured using a CCD camera-based measurement system with accuracy of 0.01 cm^3. The pressure and volume of the *PVT* cell can be controlled by a computer. The temperature can be controlled within ± 0.1 K and the pressure within ± 0.01 MPa. To measure the solubility of CO_2 in the alkanes which are used for this work, a 4 L gasometer (S.T., Ltd. France) with 0.01 cm^3 resolution was used for accurate measurement of gas volume at atmospheric pressure.

Before each measurement, the whole system including the *PVT* cell, the lines, and the sample cylinder was cleansed, dried, and vacuumized. A known volume (V_L) of alkane was then injected into the vacuumized cell. The value of V_L was measured by a CCD system at atmospheric pressure and experimental temperature, respectively. After the indraw of alkanes into the *PVT* cell, the temperature was set to experimental temperature. The cell was heated, while the alkane was stirred. After the temperature reached the experimental temperature and was kept for 20 min, V_L was measured by a CCD system. A sufficient amount of CO_2 was pressurized into the cell. After the termination of stirring, as indicated by the pressure of the cell being maintained for 40 min at the certain temperature and pressure, the system was considered to have reached the thermodynamic equilibrium condition. The volume of the liquid phase (V_{L1}) was measured by a camera-based measurement system, and then samples of the liquid phase were taken from the lower valves and charged into a small vacuum steel vessel, which has already been vacuumized, through a needle valve and capillary (the volumes were known). The charging process was done slowly to avoid fast decrease of pressure in the *PVT* cell. The charged liquid sample was weighted using a balance with an accuracy of 0.01 g. The vessel with the sample was cooled in ice water and

Table 2. x^{exp}, x^{cal}, RD, and AARD for the Binary Systems of CO_2 + Octane at Different Temperature and Pressure

P/MPa	x^{exp}	x^{cal}	RD %	P/MPa	x^{exp}	x^{cal}	RD %
	308.15 K, $\delta_{ij} = 0.092$				318.15 K, $\delta_{ij} = 0.087$		
3.53	0.443	0.437	1.30	3.55	0.395	0.396	−0.14
4.69	0.574	0.575	−0.17	4.46	0.492	0.508	−3.28
5.65	0.706	0.700	0.79	5.58	0.618	0.602	2.56
6.45	0.804	0.834	−3.73	6.58	0.742	0.709	4.45
6.80	0.854	0.903	−5.74	7.37	0.797	0.806	−1.13
				7.97	0.894	0.893	0.11
AARD %		2.34		AARD %		1.95	
	333.15 K, $\delta_{ij} = 0.077$				343.15 K, $\delta_{ij} = 0.082$		
3.60	0.349	0.354	−1.54	3.63	0.327	0.320	2.05
4.58	0.438	0.440	−0.46	4.39	0.379	0.380	−0.17
5.69	0.520	0.533	−2.50	5.50	0.449	0.464	−3.30
6.80	0.649	0.624	3.85	6.48	0.517	0.536	−3.61
7.68	0.697	0.696	0.14	7.60	0.604	0.615	−1.77
8.46	0.770	0.762	1.07	8.64	0.706	0.689	2.45
9.30	0.810	0.839	−3.58	9.69	0.789	0.767	2.83
AARD %		1.88		AARD %		2.31	

Table 3. x^{exp}, x^{cal}, RD, and AARD for the Binary Systems of CO_2 + Decane at Different Temperature and Pressure

P/MPa	x^{exp}	x^{cal}	RD %	P/MPa	x^{exp}	x^{cal}	RD %
	308.15 K, $\delta_{ij} = 0.092$				318.15 K, $\delta_{ij} = 0.082$		
3.25	0.404	0.393	2.68	3.37	0.368	0.376	−2.22
4.46	0.505	0.523	−3.65	4.47	0.479	0.482	−0.70
5.56	0.649	0.643	0.89	5.72	0.576	0.597	−3.70
6.31	0.757	0.734	3.01	6.74	0.722	0.692	4.17
6.74	0.779	0.802	−3.01	7.69	0.808	0.789	2.39
				8.07	0.817	0.837	−2.40
AARD %		2.65		AARD %		2.60	
	333.15 K, $\delta_{ij} = 0.083$				343.15 K, $\delta_{ij} = 0.098$		
3.32	0.314	0.316	−0.51	3.58	0.300	0.294	2.05
4.53	0.421	0.416	1.19	4.55	0.362	0.363	−0.37
5.30	0.465	0.475	−2.18	5.50	0.436	0.427	2.10
6.55	0.546	0.567	−3.94	6.90	0.516	0.516	0.00
7.64	0.659	0.644	2.33	7.42	0.547	0.547	0.00
8.00	0.667	0.669	−0.30	8.80	0.644	0.628	2.44
9.91	0.839	0.810	3.49	10.80	0.721	0.742	−2.98
AARD %		1.99		AARD %		1.42	

connected to the evacuated gasometer for measuring the volume of gaseous CO_2 at atmospheric pressure. Neglecting the vapor pressure of the alkane, the volume of the CO_2 dissolved in the alkane was measured, and because the pressure of desorbed gas was at atmospheric pressure, the quantity of CO_2 was easily calculated using the state equation for an ideal gas. The CO_2 solubility in alkane can be given by the following relation

$$x_{CO2} = \frac{n_{CO2}}{n_s} = \left(\frac{PV}{RT}\right)/n_s \tag{1}$$

where x_{CO2} is the solubility of CO_2 in alkane (mole fraction); R is the universal gas constant; V is the amount of gas released at atmospheric pressure and at the certain temperature; n_{CO2} is the mole number of CO_2 dissolved in alkane; and n_s is the total amount of sample that exists in the cell ($n_s = n_{CO2} + n_{alk}$). The measurement of CO_2 solubility in alkane is repeated three times, and the results presented are the average of the replicates.

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

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

■ MODELING

Equations of state play an important role in chemical engineering design, and they have assumed an expanding role in the study of the phase equilibrium of fluids and fluid mixtures. The PR EOS with one temperature-independent binary interaction parameter was used to correlate the VLE data obtained in this work.[22] Critical parameters were obtained from ref 23.

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

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

Table 4. x^{exp}, x^{cal}, RD, and AARD for the Binary Systems of CO_2 + Cyclohexane at Different Temperature and Pressure

P/MPa	x^{exp}	x^{cal}	RD %	P/MPa	x^{exp}	x^{cal}	RD %
	308.15 K, δ_{ij} = 0.109				318.15 K, δ_{ij} = 0.116		
3.30	0.353	0.349	1.13	3.33	0.300	0.295	1.76
3.60	0.372	0.382	−2.6	4.35	0.391	0.389	0.47
4.52	0.502	0.493	1.79	5.65	0.531	0.519	2.24
5.50	0.646	0.634	1.79	6.72	0.642	0.650	−1.32
6.50	0.810	0.851	−5.06	7.25	0.715	0.737	−3.08
7.00	0.904	0.936	−3.54				
AARD %		2.67		AARD %		1.77	
	333.15 K, δ_{ij} = 0.109				343.15 K, δ_{ij} = 0.094		
3.46	0.260	0.263	−1.03	3.38	0.246	0.247	−0.26
4.54	0.334	0.345	−3.22	4.51	0.326	0.329	−0.92
5.72	0.443	0.437	1.33	5.52	0.387	0.401	−3.60
6.78	0.514	0.522	−1.51	6.72	0.481	0.487	−1.30
7.42	0.607	0.578	4.82	7.57	0.561	0.550	1.98
8.60	0.681	0.694	−1.87	8.58	0.626	0.628	−0.29
				9.67	0.740	0.721	2.57
AARD %		2.30		AARD %		1.56	

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

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 Alkanes. Table 1 to Table 4 show the data of the mole fraction of CO_2 in the alkanes 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 were also shown in the tables.

It can be seen from Table 1 to Table 4 that for all of the binary systems of CO_2 + alkane the solubility of CO_2 in the alkanes increased as the pressure of the systems increased and decreased as the temperature of the systems increased. The value of AARD is less than 2.67 % in the study.

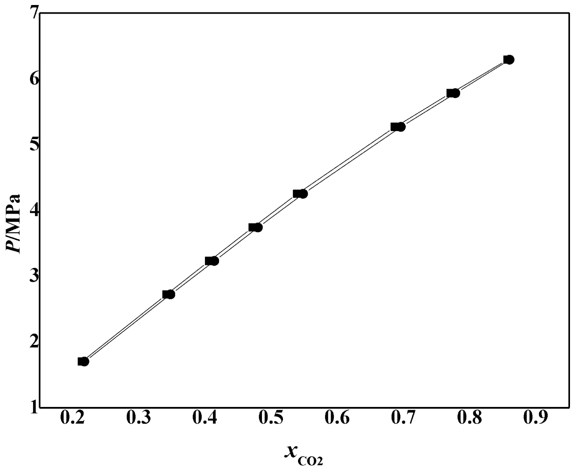

Figure 2. Pressure−x_{CO2} diagram of the CO_2 + hexane system. ■, Literature, correlated data; ●, this work, correlated data.

A careful study of Tables 1 to 4 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 + hexane was compared with those reported by Lay and Taghikhani at 308.15 K.[24] The value of AARD % of the data from the reference and our experimental data is 1.44 %. The comparison is shown in Figure 2.

Volume of the CO_2 + Alkane System. The volume expansion coefficients for each CO_2 + alkane system under different conditions were shown in Figures 3 to 6. It is clear that with increasing solubility of CO_2 in the alkanes the volume of the CO_2 + alkane is expanded with an increase of pressure. Meanwhile, with an increase of temperature, the solubility of CO_2 in the alkanes and volume expansion coefficients of the CO_2 + alkane system are decreased. Due to the fact that the alkenes are expanded with increasing temperature and shrank

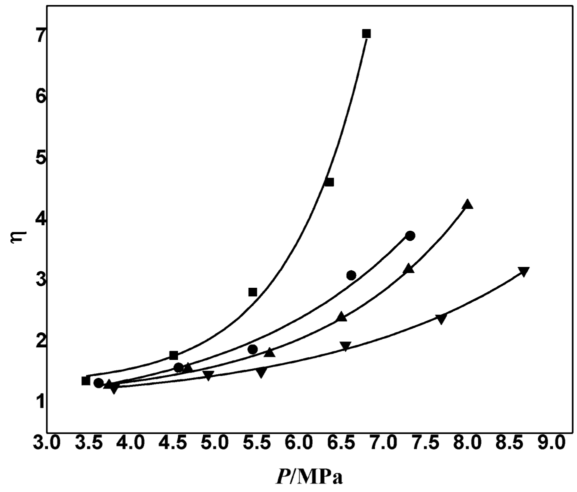

Figure 3. Volume expansion coefficient η of the CO_2 + hexane system as a function of pressure. ■, T = 308.15 K; ●, T = 318.15 K; ▲, T = 323.15 K; ▼, T = 333.15 K.

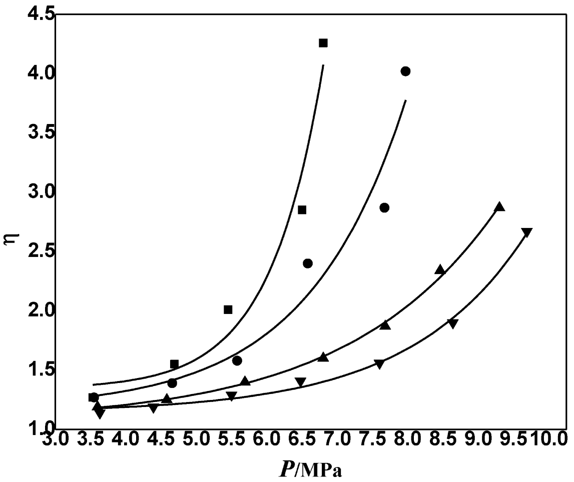

Figure 4. Volume expansion coefficient η of the CO_2 + octane system as a function of pressure. ■, T = 308.15 K; ●, T = 318.15 K; ▲, T = 333.15 K; ▼, T = 343.15 K.

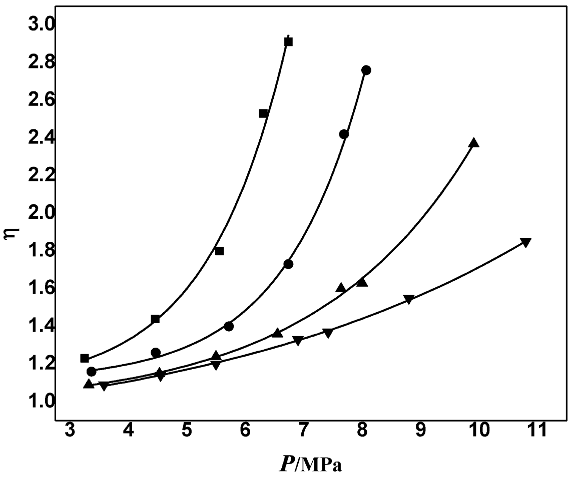

Figure 5. Volume expansion coefficient η of the CO_2 + decane system as a function of pressure. ■, T = 308.15 K; ●, T = 318.15 K; ▲, T = 333.15 K; ▼, T = 343.15 K.

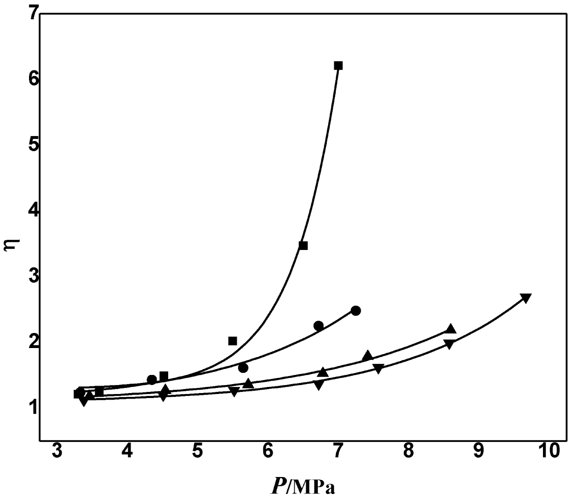

Figure 6. Volume expansion coefficient η of the CO_2 + cyclohexane system as a function of pressure. ■, T = 308.15 K; ●, T = 318.15 K; ▲, T = 333.15 K; ▼, T = 343.15 K.

with reducing of CO_2 solubility, the reduction of volume expansion coefficients indicates that a decrease of CO_2 solubility in the alkanes plays a dominate role in the volume expansion of the alkanes.

The volume expansion coefficient for different CO_2 + alkane systems under different pressure at 318.15 K is shown in Figure 7 and Figure 8. From Figure 7 it can be seen that for the three straight-chain alkanes, hexane, octane, and decane, as the chain of the alkane is increased the volume expansion coefficient is decreased under the same temperature and pressure. The order of the volume expansion coefficient for the three systems is: CO_2 + hexane > CO_2 + octane > CO_2 + decane. From Figure 8, it can be seen that for hexane and cyclohexane the volume expansion coefficient of CO_2 + hexane is larger than that of CO_2 + cyclohexane.

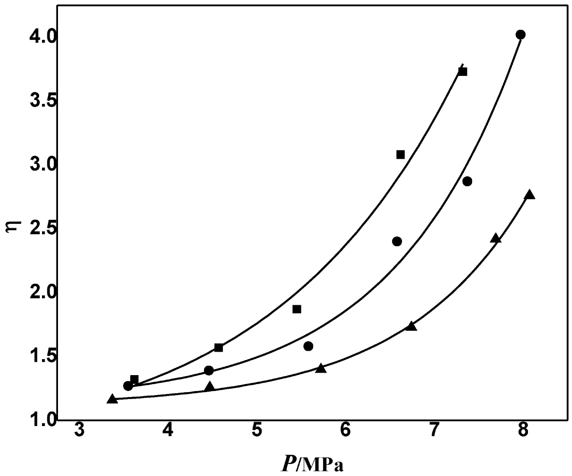

Figure 7. Volume expansion coefficient η of CO_2 + hexane, CO_2 + octane, and CO_2 + decane as a function of pressure at 318.15 K: ■, CO_2 + hexane system; ●, CO_2 + octane system; ▲, CO_2 + decane system.

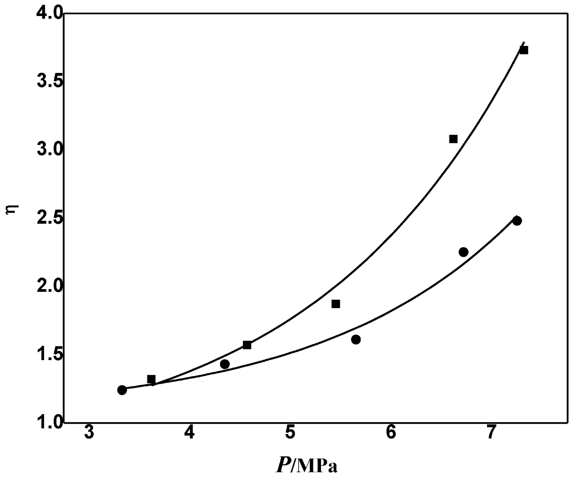

Figure 8. Volume expansion coefficient η of CO_2 + hexane and CO_2 + cyclohexane as a function of pressure at 318.15 K: ■, CO_2 + hexane system; ●, CO_2 + cyclohexane system.

Forces for the CO_2 + Alkane System at Equilibrium. For the CO_2 molecule dissolved or dispersed into the alkane phase, there are four main factors that affect the equilibrium state of CO_2 + alkane systems at different temperature and pressure: (1) Force generated by pressure, which squeezes the

CO_2 molecule into the alkane phase; (2) the intermolecular force (attractive force) between CO_2 molecules and alkane molecules which drags CO_2 molecule into the alkane phase; (3) the intermolecular force operating within alkane molecules which squeezes the CO_2 molecule out of the alkane phase and prevents CO_2 molecules from getting into the alkane phase; and (4) Brownian motion of CO_2 and alkane molecules.

It is well known that the CO_2 molecule is linear and has no overall dipole moment, and the alkanes used in the study are nonpolar molecules. Therefore, the main intermolecular force operating within the alkane molecules, the CO_2 molecules, and between the alkane and CO_2 molecules is London force (London dispersion force or dispersion force) which is an instantaneous dipole-induced dipole force.[25]The potential energy between two molecules versus separation contributed by London force is described by eq 5.[26]

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

where Φ is potential energy; h is Planck's constant; ν_i is characteristic vibrational frequency of electron i (always negative); $\alpha_{0,i}$ is polarizability of molecule i; ε_0 is 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. Size and polarizability increase as molecular weight increases. It follows that dispersion forces increase as molar mass increases. For substances of large atomic or molecular mass, dispersion forces are strong enough that the substances are solid or liquid at room temperature. Second, the larger the surface area of molecule contact, the stronger the dispersion forces are. Molecules that are roughly spherical in shape are able to contact each other only minimally. In contrast, molecules that are planar or linear in shape can maintain a large surface area of contact, with correspondingly larger dispersion forces.[25] It is also well known that whether or not two liquids are mutually soluble (miscible) depends on whether the mixed intermolecular forces can compete with the forces operating within each pure liquid alone. Substance A will dissolve in substance B if the forces operating between A and B molecules are of similar type and strength to those operating between A molecules and between B molecules.[25]

Effect of Pressure on the Volume of the CO_2 + Alkane System. As discussed above, the intermolecular forces operating within the alkane molecules, the CO_2 molecules, and between the alkane and CO_2 molecules are London forces. When the temperature is 308.15 K, due to the distance between CO_2 (gas) molecules being large at atmospheric pressure, the London force between CO_2 molecules is quite weak, and the London force between CO_2 and alkane molecules is very weak, as well. In this condition, even though the intermolecular force operating within alkane (liquid) molecules and CO_2 molecules is the same type, the strength of the London force operating within CO_2 molecules is far less than that operating within alkane molecules, so it is difficult for CO_2 to get into the alkane phase. Therefore, the solubility of CO_2 in the alkanes is very low, and the volume of the alkanes does not increase significantly.

When the temperature is kept constant and with increasing of pressure, the distance between CO_2 molecules is reduced dramatically. On the basis of eq 5, as the distance between CO_2 molecules is reduced, the potential energy and the strength of the London force operating within CO_2 molecules are increased much faster than that of operating within alkane molecules. As the strength of the London force operating within CO_2 molecules is more closed than that of operating within alkane molecules, the solubility of CO_2 in the alkanes becomes larger, and the volume of the alkanes is increased obviously, as well. During the process of increasing pressure, the pressure plays a dominate role in squeezing CO_2 molecules into the alkane phase. Due to the CO_2 molecules being squeezed into the alkane phase, the distance between alkane molecules is increased. Therefore, the London force operating within alkane molecules which tends to squeeze the CO_2 molecule out of the alkane phase and prevent CO_2 molecules from getting into the alkane phase is reduced. Meanwhile, the London force between CO_2 molecules and alkane molecules which tend to drag the CO_2 molecule into the alkane phase is increased, also. The variation of these intermolecular forces results in that the solubility of CO_2 in the alkanes is increased, and the volume of the CO_2 + alkane systems increased much faster than the solubility of CO_2 in the alkanes when the pressure is close to the critical pressure or under supercritical pressure of CO_2.

It is clear that at the experimental condition, when CO_2 is in the near critical or supercritical state, the London force operating within CO_2 molecules is still smaller than that operating within the alkane molecules, and there is an obvious interface between CO_2 and alkane phases. Because the pure alkanes are quite difficult to be condensed alone in the experimental conditions, the main reason for volume expansion of CO_2 + alkane systems is that with increasing pressure and the variation of the intermolecular forces operating within the alkane molecules, the CO_2 molecules, and between the alkane and CO_2 molecules the distance between the alkane molecules is increased as the CO_2 molecules are squeezed into the alkane phase. Figure 9 shows that the solubility of CO_2 in hexane is increased linearly with an increase of pressure. However, the volume expansion coefficient of CO_2 + hexane is increased exponentially with an increase of pressure at 308.15 K. This phenomenon, which can be observed for all the CO_2 + alkane systems in this work, indicates that the dispersion state of CO_2

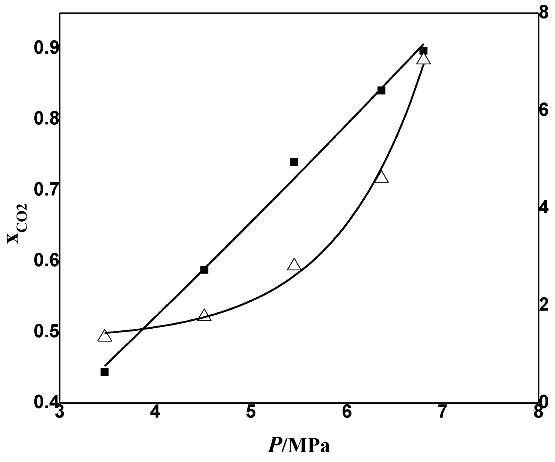

Figure 9. Solubility of CO_2 in hexane and volume expansion coefficient of CO_2 + hexane vs pressure at 308.15 K: ■, solubility of CO_2 in hexane; △, volume expansion coefficient of CO_2 + hexane.

molecules in the alkane phase under near critical or supercritical condition of CO_2 plays a dominate role in increasing the space between alkane molecules and the volume of CO_2 + alkane systems.

Effect of Temperature on the Volume of the CO_2 + Alkane System. The experimental results of the study show very clearly that for all of the CO_2 + alkane systems when the pressure is constant, with an increase of temperature, the solubility of CO_2 in the alkanes and the volume of the CO_2 + alkane systems are decreased. It is quite understandable that as temperature increases the distance between CO_2 molecules, alkane molecules, and CO_2 + alkane molecules is increased. On the basis of eq 5, as a result of increasing the distance between molecules, the intermolecular forces operating within the alkane molecules, the CO_2 molecules, and between the alkane and CO_2 molecules are decreased dramatically.

It is important to realize that the dispersion forces that operate between molecules are generally weaker, the potential wells generated by dispersion force in the range (0.1 to 5) $kJ\cdot mol^{-1}$.[25] As temperature is increased, the Brownian motion of molecules is enhanced, which makes CO_2 molecules get off the drag of alkane molecules by London force and promotes the escape of CO_2 molecules from the alkane phase. Therefore, the solubility of CO_2 in the alkanes and the volume of CO_2 + alkane systems are decreased with increasing temperature.

Effect of Alkane Molecular Structure on the Volume of the CO_2 + Alkane System. As discussed above, the solubility of CO_2 in the alkanes and the volume of the CO_2 + alkane systems are affected by the distance between CO_2 molecules, alkane molecules, and CO_2 + alkane molecules and the intermolecular forces operating within the alkane molecules, the CO_2 molecules, and between the alkane and CO_2 molecules. The effect of molecular structure of alkanes on the solubility of CO_2 in the alkanes and the volume of the CO_2 + alkane systems is strong, as well.

The length of CO_2 molecule is about 0.33 nm,[27] and for alkane, the carbon skeleton is a coplanar twisted chain; the angle of C−C−C is 109.47°; the length of the C−C bond is 0.154 nm; and the van der Waals radius of the $-CH_3$ group is 0.20 nm.[28] The length of the alkane molecule could be calculated as follows

$$L = \left[154\cdot\sin\left(\frac{109.47^\circ}{2}\right)(a - 1) + 2\cdot200\right] \tag{6}$$

where L is the length of the alkane molecule, and a is the carbon number of alkane. So the length of the hexane molecule is 1.03 nm, which is about 3 times longer than the CO_2 molecule. Because the shape of hexane, octane, and decane molecules is linear, the molecules are able to contact each other along the entirety of their length. Therefore, for the longer molecule, the molecules have a larger surface area of contact, with correspondingly larger dispersion force. Consequently, under the same pressure and temperature, the solubility of CO_2 in the alkane and the volume of the CO_2 + alkane systems are decreased as the length of the alkane molecule increases. This phenomenon indicates that the longer the alkane molecule, the stronger the London force between the alkane molecules, and the CO_2 molecules are more difficult to be squeezed into the alkane phase.

For the systems of CO_2 + hexane and CO_2 + cyclohexane, the cyclohexane molecule has the shape of chair or boat. The 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 the CO_2 + cyclohexane are less than that of hexane and the CO_2 + hexane system.

It also should be noted that London force is also affected by the polarizability of the molecule. For the alkane with a shorter alkyl chain, the molecular length is shorter, and the polarizability is weaker; therefore, the London force is smaller and the distance between the alkane molecules is bigger. Therefore, it is easier for CO_2 molecule to be squeezed into the alkane with shorter alkyl chain, and the solubility of CO_2 in alkane increases as the alkyl chain length of the alkane decreases. Because of the difference of London force and the distance between alkane molecules with different length of alkyl chain, the dispersion state of CO_2 in the alkanes should be different under the same temperature and pressure, as well.

■ CONCLUSIONS

On the basis of this study, the following conclusions can be made:

1. The dispersion state of CO_2 molecules in the alkane phase under near critical or supercritical conditions of CO_2 plays a dominate role in increasing the volume of CO_2 + alkane systems.
2. Pressure and the London force operating within alkane molecules play a dominate role in squeezing CO_2 molecules into the alkane phase, the solubility of CO_2 in the alkanes, and the volume expansion of CO_2 + alkane systems.
3. The solubility of CO_2 in the alkanes, the volume expansion of the CO_2 + alkane systems, and the London force operating within alkane molecules are strongly influenced by molecular structure of the alkanes.

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Notes

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■ REFERENCES

(1) Yu, J.; Wang, S.; Tian, Y. Experimental determination and calculation of thermodynamic properties of CO_2 + octane to high temperatures and high pressures. *Fluid Phase Equilib.* **2006**, *246*, 6−14.

(2) Chattopadhyay, P.; Gupta, R. B. Production of antibiotic nanoparticles using supercritical CO_2 as antisolvent with enhanced mass transfer. *Ind. Eng. Chem. Res.* **2001**, *40*, 3530−3539.

(3) Kalogiannis, C. G.; Eleni, P.; Panayiotou, C. G. Production of amoxicillin microparticles by supercritical antisolvent precipitation. *Ind. Eng. Chem. Res.* **2005**, *44*, 9339−9346.

(4) Kikic, I.; Lora, M.; Bertucco, A. Thermodynamic analysis of threephase equilibria in binary and ternary systems for applications in rapid expansion of a supercritical solution (RESS), particles from gassaturated solutions (PGSS) and supercritical antisolvent crystallization (SAS). *Ind. Eng. Chem. Res.* **1997**, *36*, 5507−5515.

(5) Matson, D. W.; Fulton, J. L.; Petersen, R. C.; Smith, R. D. Rapid expansion of supercritical fluid solutions: solute formation of powders, thin film and fibers. *Ind. Eng. Chem. Res.* **1987**, *26*, 2298−2306.

(6) Torp, T. A.; Gale, J. Demonstrating Storage of CO_2 in Geological Reservoirs: The Sleipner and SACS projects. *Energy*; Elsevier Science: New York, 2004; Vol *29*, pp 1361−1369.

(7) Rogers, J. D.; Grigg, R. B. A Literature Analysis of the WAG Injectivity Abnormalities in the CO_2 Process. *SPE Reservoir Eval. Eng.* **2001**, *4* (No.3), 375−386.

(8) Christensen, J. R.; Stenby, E. H.; Skauge, A. Review of WAG Field Experience. *SPE Reservoir Eval. Eng.* **2001**, *4* (No.2), 97−106.

(9) Stalkup, F. I. Status of Miscible Displacement. *J. Pet. Technol.* **1983**, *35* (No.8), SPE.

(10) Klins, M. A. *Carbon Dioxide Flooding: Basic Mechanisms and Project Design*; International Human Resources Development Corporation: Boston, MA, 1984.

(11) Chung, F. T. H.; Jones, R. A.; Burchfield, T. E. *Recovery of Viscous Oil Under High Pressure by CO_2 Displacement: A Laboratory Study*. Presented at International Meeting on Petroleum Engineering, 1−4 November 1988, Tianjin, China, SPE 17588.

(12) Welker, J. R.; Dunlop, D. D. Physical Properties of Carbonated Oils. *J. Pet. Technol.* **1963**, *15* (No.8), SPE567-PA.

(13) Moortgat, J.; Firoozabadi, A.; Farshi, M. M. A New Approach to Compositional Modeling of CO_2 Injection in Fractured Media Compared to Experimental Data. *SPE Annual Technical Conference and Exhibition*, 4−7 October 2009, New Orleans, LA, SPE 124918.

(14) Tharanivasan, A. K.; Yang, C.; Gu, Y. Comparison of Three Different Interface Mass Transfer Models Used in the Experimental Measurement of Solvent Diffusivity in Heavy Oil. *J. Pet. Sci. Eng.* **2004**, *44* (3−4), 269−282.

(15) Yang, C.; Gu, Y. *A New Method for Measuring Solvent Diffusivity in Heavy Oil by Dynamic Pendant Drop Shape Analysis (DPDSA), paper SPE 84202*. Presented at SPE Annual Technical Conference and Exhibition, Denver, CO, October 5−8, 2003.

(16) Tsutomu, A.; Takafumi, A.; Mitsuhiro, K.; Hiroshi, N. Relation between Volume Expansion and Hydrogen Bond Networks for CO_2-Alcohol Mixtures at 40 °C. *J. Phys. Chem. B* **2010**, *114*, 13628−13636.

(17) McLeod, M. C.; Kitchens, C. L.; Roberts, C. B. CO_2-expandedliquid deposition of ligand-stabilized nanoparticles as uniform, wide-area nanoparticle films. *Langmuir* **2005**, *21*, 2414−2418.

(18) Chamblee, T. S.; Weikel, R. R.; Nolen, S. A.; Liotta, C. L.; Eckert, C. A. Reversible in situ acid formation for b-pinene hydrolysis using CO_2 expanded liquid and hot water. *Green Chem.* **2004**, *6*, 382−386.

(19) Xu, Q.; Han, B.; Yan, H. Precipitation polymerization of methyl methacrylate in tetrahydrofuran with compressed CO_2 as antisolvent. *J. Appl. Polym. Sci.* **2003**, *88*, 2427−2433.

(20) Nishi, K.; Morikawa, Y.; Misumi, R.; Kaminoyama, M. Radical polymerization in supercritical carbon dioxides use of supercritical carbon dioxide as a mixing assistant. *Chem. Eng. Sci.* **2005**, *60*, 2419−2426.

(21) Bothun, G. D.; White, K. L.; Knutson, B. L. Gas antisolventfractionation of semicrystalline and amorphous poly(lactic acid) using compressed CO_2. *Polymer* **2002**, *43*, 4445−4452.

(22) Peng, D.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam* **1976**, *5*, 59−64.

(23) Chen, G. *Chemical Engineering Thermodynamic*; Petroleum Industry Press: Beijing, 2006.

(24) Nemati Lay, E.; Taghikhani, V.; Ghotbi, C. Measurement and Correlation of CO_2 Solubility in the Systems of CO_2 + Toluene, CO_2 + Benzene, and CO_2 + n-Hexane at Near-Critical and Supercritical Conditions. *J. Chem. Eng. Data* **2006**, *51*, 2197−2200.

(25) Kildahl, N. K. Concepts of Chemistry, A textbook for CH1010−1040, Chapter 6: Intramolecular and Intermolecular Forces and Molecular Energy, http://www.wpi.edu/Academics/Depts/Chemistry/Courses/General/.

(26) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*; Marcel Dekker, Inc.: New York, 1997.

(27) Xizhang, C.; Wanhui, Z. *Inorganic chemistry*; Higher Education Press: Beijing, 1986.

(28) Gongdu, Z.; Lianyun, D. *Structural Chemistry Basis*, 3rd ed.; Peking University Press: Beijing, 2002.