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Solubilities and diffusion coefficients of high boiling compounds in supercritical carbon dioxide – A review

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Text p.1-44, Figures 1-12, Tables 1-5

A brief introduction of the data sources and the applications of correlation methods for the solubilities and diffusion coefficients of high-boiling compounds (mainly in solid state) in supercritical carbon dioxide are reviewed. Empirical equations, equations of state, solution models, and the Monte Carlo simulation for the calculation of solubilities in supercritical carbon dioxide are discussed. The application of empirical equation based on the Stokes-Einstein model, rough hard sphere theory, Schmidt number correlation, and molecular dynamics simulation for the calculation of diffusion coefficients in supercritical carbon dioxide at infinite dilution condition are reviewed. Further, the application of the Darken equation and the Leffler and Cullinan equation for the calculation of concentration dependence of diffusion coefficients in supercritical carbon dioxide are presented.

1. Introduction

Recently, a large number of applications of supercritical fluid technology have been proposed for many processings of foods, pharamaceuticals, flavors, and chemicals. Among the proposed supercritical fluids, carbon dioxide is highly promising due to its near ambient critical temperature (t_C=31.0 ^{o}C), and its nontoxic and inflammable characteristics. A quantitative understanding of equilibrium and transport properties such as solubility and diffusion coefficient is very important for many of the proposed process designs. Fundamentals and applications of supercritical fluid technology have been described in several monographs, such as Paulaitis et al. (1983), Bruno and Ely (1991), King and List (1996), Smith and Hawthorne (1997), Clifford (1999), and ACS symposium series (Squires and Paulaitis, 1987; Charpentier and Sevenants, 1988; Johnston and Penninger, 1989; Hutchenson and Foster, 1995).

There are many ways to measure the solubilities and diffusion coefficients in supercritical fluids. Several reviews articles have been reported for experimental data and techniques for phase equilibrium measurement, e.g., Deiters and Schneider (1986), Fornari et al. (1990), Bartle et al. (1991b), Dohrn and Brunner (1995), Lucien and Foster (2000), and for diffusivity measurement, e.g., Liong et al. (1991a) and Suarez et al. (1998). Saito (1995) reviewed the research activities on supercritical fluid science and technology in Japan.

One of the main objectives of this paper is to review the data sources, such as previous reviews and the correlation methods for the solubilities and diffusion coefficients of high-boiling compounds in supercritical carbon dioxide including the recent studies of the authors and the Japanese workers.

2. Available Data

2.1 Solubility

Experimental techniques used to investigate multiphase equilibria can be classified by the method employed to determine compositions: analytical or direct sampling methods and synthetic or indirect methods, also called stoichiometric determinations. Direct sampling methods require composition analysis following the attainment of equilibrium and indirect methods involve an indirect determination of equilibrium composition without sampling. Most techniques used for measuring solubilities of solid components in supercritical fluids belong to the direct sampling methods and may be classified into four different categories (Bruno and Ely, 1991), namely (a) flow or dynamic methods and (b) static methods, (c) chromatographic methods, and (d) spectroscopic methods. The flow method is usually the simplest and most straightforward approach. Experimental methods for investigation of high pressure phase equilibria and available data have been detailed reviewed by Fornari et al. (1990) and Dohrn and Brunner (1995). Bartle et al. (1991b) reviewed the solubilities of solids and liquids of low volatility in supercritical carbon dioxide. Lucien and Foster (2000) reviewed the solubilities of solid mixtures in supercritical carbon dioxide and Erkey (2000) reviewed the extraction of metals from aqueous solutions by using supercritical carbon dioxide. Guclu-Ustundag and Temelli (2000) reviewed the solubilities of lipids in supercritical carbon dioxide. In recent works, the solubilities of antibiotics (Gordillo et al., 1999) and dyes (Sung and Shim, 1999; Lee et al., 1999; Wanger et al., 1999; Muthukumaran et al., 1999) in supercritical carbon dioxide have been reported and metal complex solubilities and metal extraction using chelating agents have been investigated using supercritical fluids (Özel et al., 2000). Mochizuki et al. (1999) reported perfluorocarboxylic acid counter ion enhanced the extraction of aqueous alkali metal ions with supercritical carbon dioxide. Kawakami et al. (2000) discussed the effect of counter cation on solubility of fluorocarbon surfactant in supercritical carbon dioxide.

Typical behavior of the solubility of a solid in supercritical carbon dioxide is shown in Figure 1. As shown in the figure, the solubilities are changed markedly by pressure at a given temperature. Further, the temperature dependence of solubilities differs in the low pressure (< 12 MPa) and high pressure (> 12 MPa) regions. On the other hand, solubility in ideal gas is decreased with pressure increase. It is noted that the solubility, in general, is smaller than that in liquid solvents, but that the solubility of a solid in a supercritical fluid is extremely sensitive to pressure. These features allow separations to be relatively simple for supercritical fluid solvents compared with liquid solvents. To increase the solid solubility in a supercritical fluid, sometimes entrainers (cosolvents) are added. In recent works, the solubilities of polychlorinated biphenyl (PCB) and behenic acid in supercritical carbon dioxide with cosolvents have been reported (Anitescu and Tavlarides, 1999; Guan et al., 1999).

2.2 Diffusion Coefficient

Experimental techniques, available data, and modeling of diffusivities in supercritical fluids were reviewed by Liong et al. (1991a) and Suarez et al. (1998). Suarez et al. (1998) listed the data of diffusion coefficients in supercritical fluids and illustrated correlation results. The experimental techniques used to determine diffusion coefficients in supercritical fluids may be classified into five different categories (Liong et al., 1991a), namely (a) solid dissolution method (pseudo-steady state and non-steady state), (b) capillary peak broadening method, (c) photon correlation spectroscopy, (d) nuclear magnetic resonance, (e) radioactive tracer response. The Taylor dispersion method (Taylor, 1953, 1954; Aris, 1956) is the most widely used technique to measure diffusion coefficients in supercritical fluids. According to that method, a narrow pulse of solute will broaden into a peak with the combined action of convection along the axis of the tube and molecular diffusion in the radial direction. Diffusion coefficients can be calculated by analytical description for the dispersion of solute pulse in pipelines. Many available diffusivity data are measured under the infinite dilution condition. Thus, several correlation equations for diffusion coefficients in supercritical fluids are generally based on condition at infinite dilution. Near the spinodal curve, there appears to be a decrease in the diffusion coefficient as shown by theoretical derivations and experimental measurements (Tsekhanskaya, 1971; Dysthe and Hafskjold, 1995; Nishiumi et al., 1996; Ago and Nishiumi, 1998). There may be consideration of concentration in the Taylor method as shown by Funazukuri et al. (2000a). The experimental diffusion coefficients for methane + *n*-decane system measured by Dysthe and Hafskjold (1995) are shown in Figure 2. As shown in this figure, the diffusion coefficients show large concentration dependence and an anomalous decrease near the critical concentration. In the recent works by Tuan et al. (1999a), a new technique for the measurement of diffusion coefficients is proposed. Concentration dependences of diffusion coefficients in supercritical carbon dioxide can be observed by the new technique and correlation methods for concentration dependence of diffusion coefficients in supercritical carbon dioxide have been discussed (Tuan et al., 1999c).

3. Correlations

3.1 Solubility

3.1.1 Thermodynamic Basis

For solid-gas equilibria, the equations of equilibrium which must be satisfied are of the form:

$$f_i^{\mathrm{G}} = f_i^{\mathrm{S}} \tag{1}$$

where f_i^{G} is the fugacity of component i in the gas (supercritical fluid) phase and f_i^{S} is that in the solid phase.

The fugacity of solute in the supercritical phase is represented by the following expression.

$$f_2^{\mathrm{G}} = p\phi_2^{\mathrm{G}} y_2 \tag{2}$$

where p is the pressure, ϕ_2^{G} the fugacity coefficient, and y_2 the solubility (mole fraction) in a supercritical fluid. For phase equilibrium between a high-boiling compound and a supercritical fluid whose critical temperature is low, the following three assumptions commonly invoked: (1) the solid solute remains pure; (2) the molar volume of solid solute can be treated as a constant with respect to pressure; and (3) the saturated vapor of solid solute-vapor (pure) system behaves as an ideal gas. Using assumption (1), the fugacity of solute in the solid state, f_2^{S}, is equal to the pure solid fugacity, $f_2^{0\mathrm{S}}$, and it can be derived as:

$$f_2^{\mathrm{S}} = f_2^{0\mathrm{S}} = p_2^{\mathrm{sat}}\phi_2^{0\mathrm{G}} \exp\left(\int_{p_2^{\mathrm{sat}}}^{p} \frac{v_2^{\mathrm{S}}}{RT} dp\right) \tag{3}$$

where R is the gas constant, T the temperature, p_2^{sat} the saturated vapor pressure, and v_2^{S} the solid-state molar volume of the solute. Based on assumptions (2) and (3), and the thermodynamic equilibrium condition, Eq.(1), the solubility can be calculated by the following equation.

$$y_2 = \frac{p_2^{\mathrm{sat}}}{p}\frac{\phi_2^{0\mathrm{G}}}{\phi_2^{\mathrm{G}}} \exp\left(\int_{p_2^{\mathrm{sat}}}^{p} \frac{v_2^{\mathrm{S}}}{RT} dp\right) = \frac{p_2^{\mathrm{sat}}}{p}\frac{1}{\phi_2^{\mathrm{G}}} \exp\left[\frac{v_2^{\mathrm{S}}\left(p - p_2^{\mathrm{sat}}\right)}{RT}\right] \tag{4}$$

where the gas-phase fugacity coefficient of the pure solid, ϕ_2^{0G}, has been set equal to unity. The saturated vapor pressure and solid molar volume are physical properties of the pure solid solute and can be obtained from literature data or by using an appropriate correlation equation. Therefore, the solute solubility is primarily a function of solid solute pure compound physical properties, the system temperature and pressure, and the fugacity coefficient of the solid solute in the supercritical fluid.

3.1.2 Empirical Equation

By adopting the Leiden-type virial equation of state with second and third virial coefficients to evaluate the fugacity coefficient, ϕ_2^{G}, in Eq.(4), the solubility can be derived as follows:

$$\ln y_2 = \ln\left(\frac{p_2^{\mathrm{sat}}}{RT}\right) + \frac{v_2^{\mathrm{S}}\left(p - p_2^{\mathrm{sat}}\right)}{RT} - \ln\rho_1 - 2B_{12}\rho_1 - \left(3/2\right)C_{112}\rho_1^{2} \qquad (5)$$

where ρ_1 is the density of a supercritical fluid, and B_{12} and C_{112} are the cross second and third virial coefficients, respectively. As shown in Eq.(5), the solubility depends on the density of the supercritical fluid and the interaction between solute and supercritical fluid indicated by the cross second and third virial coefficients. Quiram et al. (1994) applied the density series virial equation of state truncated at the third virial coefficient to evaluated for describing the fluid nonideality of systems of pure solids in equilibrium with near-critical carbon dioxide including systems with cosolvents.

Several empirical equations for the solubility in a supercritical fluid have been proposed as a function of density for a supercritical fluid. Schmitt and Reid (1985) proposed the following equation.

$$\ln E = a\rho_1{}^{*} + b + c\left(T - d\right) \qquad (6)$$

where $E(=Py_2/p_2^{\mathrm{sat}})$ is the enhancement factor, $\rho_1^{*}(=\rho_1/\rho_{1\mathrm{C}})$ the reduced density of the supercritical fluid, and *a*, *b*, *c* and *d* are the empirical parameters. Figure 3 shows the relationship between the enhancement factor of naphthalene and the density of supercritical carbon dioxide. As shown in Figure 3, the enhancement factor increases linearly with the reduced density. The deviations at 308.2 K would belong to the reliability of equation of state which is used to calculate the density of supercritical fluids, because the temperature is very close to the critical temperature of carbon dioxide. However, the enhancement factor may increase more linearly when the density of mixture is adopted. This relationship between the enhancement factor and the reduced density can be converted to those between the solubility and the density of a supercritical fluid. Some other empirical equations are proposed as Eqs.(7)-(9).

$$\ln y_2 = a \ln \rho_1 + b \qquad \text{Stahl et al. (1978)} \qquad (7)$$

$$\ln y_2 = a\delta_1^{\ 2} + b\delta_1 + c\,,\quad \delta_1 = \left(\delta_1^{\mathrm{L}} / \rho_1^{\mathrm{L}}\right)\rho_1 \qquad \text{Czubryt et al. (1970)} \qquad (8)$$

$$y_2 = \rho_1^{\ c} \exp\left(a/T + b \right) \qquad \text{Chrastil (1982)} \qquad (9)$$

where δ_1 is the solubility parameter of a supercritical fluid.

The Krischevskii parameter, $\left(\partial p / \partial x\right)_{T,v}^{\infty,C}$, can also be used to check the consistency of data obtained in different sets of experiments. The Krischevskii parameter is defined as the change in pressure that occurs when a solute is added to a solvent at its critical point, temperature and volume being kept constant. Furuya and Teja (2000) were calculated the Krischevskii parameters from measurements of the solubility of heavy *n*-alkanes in supercritical carbon dioxide. Mendez-Santiago and Teja (1999, 2000) have been investigated the consistency of solubility data for the design of extraction and separation equipments.

3.1.3 Equation of State

The thermodynamic definition of the fugacity coefficient is given by the following equation:

$$\ln \phi_2{}^{\mathrm{G}} = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T,V,ni\neq j} - \frac{RT}{V} \right] dV - \ln z \tag{10}$$

where z is the compressibility factor. Cubic equations of state such as Soave-Redlick-Kwong (SRK) equation (Soave, 1972) and Peng-Robinson (PR) equation (Peng and Robinson, 1976) are widely used to evaluate the fugacity coefficient. The cubic equation of state proposed by Yu et al. (1987a, b) is introduced here:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+c)+b(3v+c)} \tag{11}$$

where, a, b, and c are parameters which can be determined from the critical properties and the acentric factors of the pure components. The equation of state is given by Eq.(11) and has been developed to represent the pVT relationship with a good correlation in a wide range substances from low-boiling compounds (e.g., carbon dioxide) to high-boiling compounds (e.g., naphthalene). To apply the equation of state to a mixture, the following mixing and combining rules can be used:

$$a = \sum\sum y_i y_j a_{ij} \ , \ \ a_{ij} = \left(1-k_{ij}\right)\left(a_i a_j\right)^{0.5} \tag{12}$$

$$b = \sum\sum y_i y_j b_{ij} \ , \ \ b_{ij} = \left(1-l_{ij}\right)\left(b_i + b_j\right)/2 \tag{13}$$

$$c = \sum\sum y_i y_j c_{ij} \ , \ \ c_{ij} = \left(1-l_{ij}\right)\left(c_i + c_j\right)/2 \tag{14}$$

where k_{ij} and l_{ij} denote the characteristic parameters between unlike molecules i and j. Figure 4 shows correlation results for the solubilities of naphthalene and dimethylnaphthalene isomers in supercritical carbon dioxide. The physical properties and the values of the parameters used for the correlation are listed in Tables 1 and 2.

The calculated results show good agreement with the experimental results by adjusting the characteristic parameters. As the solubility is usually small, it is noted that the introduction of l_{12} as well as k_{12} is effective to give good correlations (Iwai et al., 1989). Eqs.(11)-(14) can also be adopted to correlate entrainer effects as shown in Figure 5. This figure shows the correlation results of entrainer effect on the solubilities for aciridine in supercritical carbon dioxide. The properties and the parameters are listed in Tables 1 and 2. The calculated results of entrainer effect on the solubilities show good agreement with the experimental data. Interaction parameters k_{12} and l_{12} are considered to be large values for complex and polar molecules. . Trabelsi et al. (1999) used the PR equation of state and equation for perturbed hard-sphere to estimate the solubilities of solids in dense carbon dioxide. Yamamoto et al. (2000) correlated solubilities and entrainer effects for fatty acids and higher alcohols in supercritical carbon dioxide using SRK equation of state with association model.

Equations of state such as the predictive Soave-Redlich-Kwong (PSRK) method (Holderbaum and Gmehling, 1991) or Peng-Robinson equation of state with the analytical solutions of group (PRASOG) method (Tochigi, 1995) can be used to calculate the solubility of solute in supercritical fluids by a molecular group contribution. Solubilities in supercritical fluids can be estimate by predicting the excess Gibbs free energy using group contribution methods. Tochigi et al. (1998) applied PRASOG to estimate the solubilities in supercritical carbon dioxide and indicated the applicability of PRASOG.

3.1.4 Solution Model

In the supercritical state, a fluid has a high density when compared with a gas. In fact, the density of a supercritical fluid is closer to that of a liquid than that of a gas. In theoretical treatments, the supercritical fluid phase can be treated approximately as an expanded liquid. This allows the phase equilibria between the solute and the supercritical fluid to be represented thermodynamically by solid-liquid equilibrium relations and conventional activity coefficients.

$$f_i^{\mathrm{L}} = f_i^{\mathrm{S}} \tag{15}$$

The fugacity of solute in the supercritical fluid phase and the solid phase can be represented by the following expressions, respectively.

$$f_2^{\mathrm{L}} = \gamma_2^{\mathrm{L}} y_2 f_2^{\mathrm{0L}} \tag{16}$$

$$f_2^{\mathrm{S}} = \gamma_2^{\mathrm{S}} x_2 f_2^{\mathrm{0S}} \tag{17}$$

where f_2^{0L} and f_2^{0S} are the fugacities of pure solute, and γ_2^{L} and γ_2^{S} denote the activity coefficients of solute in the expanded liquid phase (supercritical fluid phase) and the solid phase, respectively. When the solubility of supercritical fluid in solid phase is negligible (x_2=1 and γ_2^{S}=1) and the solubility in supercritical carbon dioxide can be assumed to be at infinite dilution condition, the solubility can be determined by the following equation as proposed by Kramer and Thodos (1988).

$$y_2 = \frac{1}{\gamma_2^{\infty}} \frac{f_2^{\mathrm{0S}}}{f_2^{\mathrm{0L}}} \tag{18}$$

where γ_2^{∞} is the activity coefficient of solute at infinite dilution in the expanded liquid (supercritical fluid phase). The ratio of the fugacities can be approximated by the next equation.

$$\ln \frac{f_2^{\mathrm{0S}}}{f_2^{\mathrm{0L}}} = \frac{\Delta h_2^{m}}{RT} \left(\frac{T}{T_2^{m}} - 1 \right) \tag{19}$$

where T_2^{m} is the melting point of the solid and Δh_2^{m} is the heat of fusion. The infinite dilution activity coefficients can be evaluated by using solution theory.

The regular solution model (Hildebrand et al., 1970) coupled with the Flory-Huggins theory (Flory, 1942) can be used to correlate solubilities in supercritical fluids. Further, the solution model can also be applied to correlate entrainer effects. The solubility in supercritical carbon dioxide at infinite dilution condition can be calculated by the following equation (Koga et al., 1996):

$$\ln y_2 = \frac{\Delta h_2^{\mathrm{m}}}{RT}\left(\frac{T}{T_2^{\mathrm{m}}}-1\right) - \frac{v_2}{RT}\left\{(\delta_1-\delta_2)^2\phi_1 + (\delta_2-\delta_3)^2\phi_3 - (\delta_1-\delta_3)^2\phi_1\phi_3\right\} - \ln\frac{\phi_2}{y_2} - 1 + \frac{\phi_2}{y_2} \tag{20}$$

where 1, 2, 3 refer to the supercritical fluid, solute, and entrainer, respectively. The v_i and δ_i are the molar volume and the solubility parameter of component i in the supercritical fluid phase. For assumption of infinite dilution of solute, the volume fractions of component i, ϕ_i , are denoted by Eqs.(21) and (22). By letting ϕ_3=0, Eq.(20) can be applied to a binary system.

$$\phi_i = \frac{y_i v_i}{y_1 v_1 + y_3 v_3} \quad (i\text{=1 or 3}) \tag{21}$$

$$\frac{\phi_2}{y_2} = \frac{v_2}{y_1 v_1 + y_3 v_3} \tag{22}$$

The solubility parameter of supercritical carbon dioxide can be calculated by the method proposed by Giddings et al. (1968).

$$\delta_1 = 1.25\sqrt{p_{1\mathrm{C}}}\,\frac{\rho_1{*}}{\rho_1^{\mathrm{L}}{*}} \tag{23}$$

where $p_{1\mathrm{C}}$ is the critical pressure of carbon dioxide. The ρ_1* and ρ_1^{L}* are the reduced densities of carbon dioxide at experimental conditions and at liquid state. The value of

$\rho_1^{L}*$ is fixed at 2.66.

On the other hand, the solubility parameters of solute and entrainer can be estimated by the following equations.

$$\delta_i = \sqrt{\frac{\Delta u_i}{v_i}} \quad (i\text{=2 or 3}) \tag{24}$$

where the values of the internal energy change of vaporization for component i, Δu_i can be calculated by the following equation.

$$\Delta u_i = \Delta u_i * \{1 + 1.13\alpha_{V,i}(T * - T)\}^2 \{1 - \alpha_{V,i}(T * - T)\} \tag{25}$$

where T^* is the standard temperature (=298.15 K), Δu_i^* is the internal energy change of vaporization at T^*, and $\alpha_{V,i}$ is the isobaric thermal expansivity. The value of Δu_i^* can be calculated by the group contribution method proposed by Fedors (1974). The value of $\alpha_{V,i}$ is fixed at 1.0×10^{-3} K^{-1} for all solid components as a simplifying.

The molar volume of solute in supercritical fluid phase can be empirically expressed as a function of the density of the supercritical fluids ρ_1 (Iwai et al., 1992). This leads to:

$$\ln v_2 (\mathrm{m}^3 \cdot \mathrm{mol}^{-1}) = \alpha_2 \ln \rho_1 (\mathrm{kg} \cdot \mathrm{m}^{-3}) + \beta_2 \tag{26}$$

where the density of supercritical carbon dioxide was calculated with the equation of state of Adachi and Sugie (1986). Other equations of state for carbon dioxide have been proposed by Huang et al. (1985) and Span and Wagner (1996). The coefficients α_2 and β_2 can be determined by data regression. It is found that α_2 can be considered to be a constant for homologous solute group such as fatty acids or higher alcohols, and β_2 can be related with the critical volume of the solute. The parameters used in the correlations are listed in Table 3. Figure 6 shows the calculated results for solubilities of fatty acids and higher alcohols in supercritical carbon dioxide. The calculated results are in good agreement with the experimental data.

By considering the solvation structure, the entrainer effect on the solubility can be correlated. Eq.(26) can be used to estimate the molar volume of an entrainer in the supercritical carbon dioxide. Through various spectroscopic studies it is known that solute molecules in a supercritical fluid may be apt to cluster with entrainer molecules. The volume occupied by a solute thus can be considered to depend on the local composition of entrainer bound to the solute. A possible approximation for the volume of solute was given by Koga et al. (1996):

$$v_2 = v_2^{(1)} + \theta \Delta v_2 \tag{27}$$

$$\Delta v_2 = v_2^{(3)} - v_2^{(1)} \tag{28}$$

where θ is the local composition of entrainer around solute, and $v_2^{(1)}$ and $v_2^{(3)}$ are the volume of solute in the pure supercritical fluid and in the pure entrainer, respectively. Based on the spectroscopic information (Yonker and Smith, 1988), the local composition can be calculated from the following equation.

$$\theta = \frac{y_3}{\left(p / p^{\text{bulk}} \right) + \left[1 - \left(p / p^{\text{bulk}} \right) \right] y_3} \tag{29}$$

where p^{bulk} means the pressure at the point where the local composition of the entrainer is equal to bulk composition, y_3. The Δv_2 and p^{bulk} can be used as adjustable parameters for the calculation of entrainer effects. Figure 7 shows the calculated results of entrainer effect on the solubilities of stearic acid in supercritical carbon dioxide. The parameters are listed in Table 3. The calculated results of entrainer effect on the solubilities are in good agreement with the experimental data. Solution model was applied to correlate the solubilities of flavone, 3-hydroxyflavone, and polymers in supercritical carbon dioxide (Uchiyama et al., 1997; Mishima et al., 1998, 1999). Guigard and Stiver (1998) and Stiver et al. (2000) also calculated solubilities by using a solubility parameter.

3.1.5 Molecular Simulation

The Henry constant can be written as follows for conditions of infinite dilution (Iwai et al. (1995a)).

$$H_2 = \rho_1 k_\mathrm{B} T \exp\left(\frac{\mu_2{}^\mathrm{r}}{k_\mathrm{B} T}\right) \tag{30}$$

where ρ_1 is the number density of the supercritical fluid, k_B is the Boltzmann constant, and $\mu_2{}^\mathrm{r}$ is the residual chemical potential of the solute. As the solubility in supercritical fluids is usually very small, it can be assumed by the following equation.

$$y_2 = f_2{}^\mathrm{G} / H_2 \tag{31}$$

Since the fugacity of solute in the supercritical phase is equal to that of the pure solid phase, the following equation can be derived:

$$f_2{}^\mathrm{G} = f_2{}^\mathrm{S} = p_2{}^\mathrm{sat} \exp\left[\frac{v_2{}^\mathrm{S}\left(p - p_2{}^\mathrm{sat}\right)}{RT}\right] \tag{32}$$

From Eqs.(31) and (32), the solubility in supercritical fluid can be given as follows:

$$y_2 = \frac{p_2{}^\mathrm{sat}}{H_2} \exp\left[\frac{v_2{}^\mathrm{S}\left(p - p_2{}^\mathrm{sat}\right)}{RT}\right] \tag{33}$$

For a binary mixture consisting of supercritical fluid and high-boiling compound, the residual chemical potential is given as:

$$\mu_2{}^\mathrm{r} = -k_\mathrm{B} T \ln\left\langle \exp\left(-\frac{\psi_2}{k_\mathrm{B} T}\right)\right\rangle_N \tag{34}$$

where ψ_2 is the potential energy experienced by a solute placed at a random location in a fluid of N particles of supercritical fluid and $\langle\rangle_N$ is the canonical ensemble average of the system of N particles. The test particle method proposed by Widom (1963) can be applied to calculate the residual chemical potential of supercritical fluid mixtures.

The Lennard-Jones (12-6) potential function and combining rules are shown as follows:

$$\phi_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{35}$$

$$\varepsilon_{12} = (1-k_{12})(\varepsilon_{11}\varepsilon_{22})^{1/2} \tag{36}$$

$$\sigma_{12} = (1-l_{12})(\sigma_{11}+\sigma_{22})/2 \tag{37}$$

In these equations, ϕ is the intermolecular potential, ε and σ are the energy and size parameters, r is the molecular distance, k_{12} and l_{12} are the intermolecular interaction parameters between unlike molecules. These relations allow calculation of the solubilities of high-boiling compounds in supercritical carbon dioxide.

The corresponding state principle assures that all Lennard-Jones fluids for pure components obey the same reduced equation of state by using the reduced variables:

$$\rho^* = N\sigma^3/V\ ,\quad T^* = k_\mathrm{B}T/\varepsilon \ \text{ and } \ p^* = \sigma^3 p/\varepsilon \tag{38}$$

where N is the number of particles, V the volume of the system, k_B the Boltzmann constant, and superscript * means the reduced property. Equations of state for Lennard-Jones fluid have been reported by Nicolas et al. (1979) and Johnson et al. (1993). Reduced properties proposed by Nicolas et al. (1979) of ρ_C^*, T_C^*, and p_C^* at the critical point as 0.35, 1.35, and 0.1418, respectively. The potential parameters of carbon dioxide and high-boiling compounds can be calculated by using T_C and p_C. The k_{12} and

l_{12} can be adjusted to give good representation of the solubilities in supercritical carbon dioxide. The parameters and properties are listed in Table 4. Figure 8 shows the simulated results of solubilities for naphthalene in supercritical carbon dioxide. As shown in Figure 8, the simulated results of solubilities are in good agreement with the experimental data. The site model potential function can be used for complex solute molecules (Koga et al., 1994; Iwai et al., 1995b, 1996, 2000) and entrainer effects can also be calculated by molecular simulation (Iwai et al., 1994; Koga et al., 1997).

3.2 Diffusion Coefficient

3.2.1 Classifications of Diffusion Coefficient

According to classification by Reid et al. (1987), diffusion coefficients are classified to the self-diffusion coefficients (D_{11} and D_{22}), tracer diffusion coefficients (D_{12}* and D_{21}*), mutual diffusion coefficients ($D_{21}(=D_{12})$), and infinite dilution diffusion coefficients (D_{12}^0 and D_{21}^0) as shown in Figure 9. Figure 9 shows the diffusion coefficients for *n*-octane + *n*-dodecane system (Van Geet and Adamson, 1964). Tracer diffusion coefficients which are sometimes referred to as intradiffusion coefficients relate the diffusion of a labeled component within a homogeneous mixture. As well as the mutual diffusion coefficients, tracer diffusion coefficients depend on the composition. As the mole fraction of component 1 approaches unity, D_{21}* and D_{12}* approach D_{21}^0 and D_{11}, respectively. Therefore, for the case of infinite dilution, tracer diffusion coefficients of the solute and supercritical fluid coincide with the mutual and self-diffusion coefficients, respectively.

3.2.2 At Infinite Dilution Condition

Most equations for predicting diffusion coefficients in supercritical fluids are applied at infinite dilution conditions in comparison with the actual experimental data that can only approach this state. Funazukuri et al. (1991) and Funazukuri (1996) tested various correlations for diffusion coefficients in supercritical carbon dioxide. Liu and Macedo (1995) used a density expansion equation and modified free-volume model. Liu and Ruckenstein (1997a) applied the Stokes-Einstein type equation and Eaton and Akgerman (1997) proposed a predictive equation based on rough hard sphere theory. Thus, many correlation methods for diffusion coefficients in supercritical fluids at infinite dilution were based on a Stokes-Einstein based empirical equation or rough hard sphere theory. In recent works, new predictive expressions have been also proposed (Liu and Ruckenstein, 1997b; Liu et al., 1997; He and Yu, 1997, 1998).

(a) Stokes-Einstein Based Equation

As the order of diffusion coefficients in supercritical fluid is similar to those in liquids, several authors have attempted to correlate diffusion coefficients in supercritical fluids using empirical relations developed for liquid systems. Typical empirical correlation models, such as proposed by Wilke and Chang (1955), Scheibel (1954), Reddy and Doraiswamy (1967), and Lusis and Ratcliff (1968), can be derived from the following Stokes-Einstein expression.

$$D_{21}{}^{0} = \frac{k_{\mathrm{B}}T}{6\pi\mu_1 R_0} \tag{39}$$

where k_{B} is the Boltzmann constant, μ_1 is the viscosity of supercritical fluid, and R_0 is the radius of the solute. The applicability of these empirical equations is discussed in the review of Liong et al. (1991a). For example, the calculated results of diffusion coefficients for naphthalene in supercritical carbon dioxide by Wilke-Chang equation are shown in Figure 10. The Wilke-Chang equation is given as follows:

$$D_{21}{}^{0} = 7.4\times10^{-11}\frac{T\sqrt{\phi M_1}}{\mu_1 v_{\mathrm{b}2}{}^{0.6}} \tag{40}$$

where ϕ is the association factor (ϕ=1 for carbon dioxide), M_1 is the molecular weight of supercritical carbon dioxide, and $v_{\mathrm{b}2}$ is the molar volume of solute at boiling point. The values of M_1 and $v_{\mathrm{b}2}$ are listed in Table 5. The calculated results show good agreement with the experimental data for diffusion coefficient of naphthalene in supercritical carbon dioxide. However, some modifications are needed for other systems (Sassiat et al., 1987).

(b) Rough Hard Sphere Theory

The rough hard sphere (RHS) theory for transport coefficients of dense fluids can be derived from the model of self-diffusion (Chandler, 1975) and that of mutual diffusion (Bertucci and Flygare, 1975). The validity of RHS theory to the high pressure region was studied by Dymond (1985) and Erkey et al. (1990).

One expression that has been established for self-diffusion is shown as follows (Funazukuri and Wakao, 1995):

$$D_{11} \approx D_{11}{}^{\mathrm{RHS}} = A_{11}D_{11}{}^{\mathrm{SHS}} \tag{41}$$

where

$$D_{11}{}^{\mathrm{SHS}} = C_{\mathrm{S}}D_{11}{}^{\mathrm{E}} \tag{42}$$

$$C_{\mathrm{S}} = \frac{D_{11}{}^{\mathrm{SHS}}}{D_{11}{}^{\mathrm{E}}} \tag{43}$$

$$D_{11}{}^{\mathrm{E}} = \frac{3}{8g_{11}(\sigma_{\mathrm{HS},1})}\left[\frac{RT}{\pi M_1}\right]^{1/2}\frac{1}{n\sigma_{\mathrm{HS},1}{}^{2}} \tag{44}$$

$$g_{11}(\sigma_{\mathrm{HS},1}) = \frac{1-0.5\varepsilon}{(1-\varepsilon)^3} \tag{45}$$

$$\varepsilon = \frac{\pi n \sigma_{\mathrm{HS,1}}{}^{3}}{6} \tag{46}$$

For mutual diffusion coefficients at infinite dilution conditions, the expressions were developed:

$$D_{21}{}^{0} \approx D_{21}{}^{\mathrm{RHS}} = A_{21} D_{21}{}^{\mathrm{SHS}} \tag{47}$$

where

$$D_{21}{}^{\mathrm{SHS}} = C_{\mathrm{B}} D_{21}{}^{\mathrm{E}} \tag{48}$$

$$C_{\mathrm{B}} = \frac{D_{21}{}^{\mathrm{SHS}}}{D_{21}{}^{\mathrm{E}}} \tag{49}$$

$$D_{21}{}^{\mathrm{E}} = \frac{3}{8 g_{21}\left(\sigma_{\mathrm{HS,21}}\right)} \left[\frac{RT}{\pi M_{21}}\right]^{1/2} \frac{1}{n \sigma_{\mathrm{HS,21}}{}^{2}} \tag{50}$$

$$g_{21}\left(\sigma_{\mathrm{HS,21}}\right) = \frac{1}{1-\varepsilon} + \frac{3\varepsilon\gamma}{(1-\varepsilon)^{2}(1+\gamma)} + \frac{\varepsilon^{2}\gamma}{2(1-\varepsilon)^{3}} \tag{51}$$

$$\varepsilon = \frac{\pi n \sigma_{\mathrm{HS,1}}{}^{3}}{6} \tag{52}$$

$$n = n_1 + n_2 \approx n_1 \tag{53}$$

$$\sigma_{\mathrm{HS,12}} = \frac{1}{2}\left(\sigma_{\mathrm{HS,1}} + \sigma_{\mathrm{HS,2}}\right) = \frac{\sigma_{\mathrm{HS,2}}}{2}(\gamma + 1) \tag{54}$$

$$\gamma = \frac{\sigma_{\mathrm{HS,2}}}{\sigma_{\mathrm{HS,1}}} \tag{55}$$

$$M_{12} = \frac{2}{\frac{1}{M_1} + \frac{1}{M_2}} \tag{56}$$

In Eqs.(41)-(56), RHS, SHS, HS and E refer to rough hard sphere, smoothed hard sphere, hard sphere and Enskog theory. In these equations, *n* is the number density, and

σ_{HS} and M are the effective hard sphere diameter and the molecular weight, respectively

Funazukuri and Wakao (1995) modified the expressions for self- and mutual diffusion coefficients as follows:

$$D_{11} = (AC)_{\mathrm{S}} D_{11}{}^{\mathrm{E}} \tag{57}$$

$$D_{21}{}^{0} = (AC)_{\mathrm{B}} D_{21}{}^{\mathrm{E}} \tag{58}$$

where

$$(AC)_{\mathrm{S}} = A_{11}\left(D_{11}{}^{\mathrm{SHS}} \big/ D_{11}{}^{\mathrm{E}} \right) \tag{59}$$

$$(AC)_{\mathrm{B}} = A_{21}\left(D_{21}{}^{\mathrm{SHS}} \big/ D_{21}{}^{\mathrm{E}} \right) \tag{60}$$

A_{11} and A_{21} are the translational-rotational coupling parameters which show the deviation from a sphere particle (A_{11}=1 for sphere particle, A_{11}<1 for non-sphere particle). Funazukuri and Wakao (1995) proposed the following empirical equation for diffusivity in supercritical carbon dioxide.

$$(AC)_{\mathrm{B}} = 1.86\gamma_{\mathrm{vw}}{}^{0.38}(AC)_{\mathrm{S}}\left(v \big/ v_0 \right)^{-0.447} \tag{61}$$

where v and v_0 are the molar volume and hard sphere close-packed molar volume of supercritical carbon dioxide, respectively. The hard sphere close-packed molar volume can be estimated by the following polynomial equation (Funazukuri et al., 1992).

$$v_0 = \frac{1}{1.384}\sum_{i=0}^{4} a_i T^i \tag{62}$$

where a_0=4.452×10^{-5}, a_1=-1.152×10^{-7}, a_2=2.749×10^{-10}, a_3=-3.073×10^{-13}, a_4=1.290×10^{-16}. The γ_{vw} is the ratio of the van der Waals diameters calculated by Bondi method (1964). $(AC)_{\mathrm{S}}$ is given by the following polynomial equations.

$$(AC)_{\mathrm{S}} = \sum_{i=0}^{4} b_i \left[\ln\left({}^{v}\!/_{v_0} \right) \right]^i \tag{63}$$

where b_0=0.284093, b_1=2.55177, b_2=-2.26978, b_3=0.756249, b_4=-0.08903.

The effective hard-sphere diameter of supercritical carbon dioxide was calculated by

$$v_0 = N_{\mathrm{AV}} \sigma_{\mathrm{HS},1}{}^3 / \sqrt{2} \tag{64}$$

where N_{AV} is the Avogadro number and v_0 can be calculated by Eq.(62). The effective hard-sphere diameter of the solute can be calculated by Eq.(64). The ratio of the hard sphere diameters, γ, can be replaced by the ratio of van der Waals diameters, γ_{vw}. The van der Waals diameters are listed in Table 5.

Calculated results for diffusion coefficients of naphthalene in supercritical carbon dioxide by this method are shown in Figure 10. Calculated results for this system and other systems are in good agreement with experimental data (Funazukuri and Wakao, 1995).

(c) Schmidt Number Correlation

The Schmidt number correlation proposed by Funazukuri (2000b) is shown as follows.

$$\ln\left(Sc^{+} - 1\right) = \sum_{i=0}^{5} c_i \left(\frac{v_0}{v} \right)^i \tag{65}$$

where v and v_0 are the molar volume and the hard sphere closed-packed volume of supercritical carbon dioxide, respectively. The a_i are coefficients determined as follows: c_0=-4.92519817, c_1=54.5529385, c_2=-245.231443, c_3=607.893924, c_4=-708.884016, c_5=329.611433. The Sc^{+} is defined by

$$Sc^{+} = Sc / Sc* \tag{66}$$

where Sc*=5/6 for self-diffusion. For mutual diffusion coefficients at infinite dilution, the following equation was proposed:

$$Sc^* = \frac{5}{6}\left(\frac{\sigma_{\mathrm{HS},1}+\sigma_{\mathrm{HS},2}}{2\sigma_{\mathrm{HS},1}}\right)^2\left(\frac{2M_2}{M_1+M_2}\right)^{1/2} \tag{67}$$

The effective hard sphere diameters and the closed-pack molar volume can be obtained by the same method as those used in RHS theory. The density and viscosity of supercritical carbon dioxide, which are necessary to convert the Schmidt number to diffusion coefficient, were calculated by the equations of Angus et al. (1976) and Chung et al. (1988), respectively. New equations for transport properties of carbon dioxide have been proposed by Vesovic et al. (1990) and these equations show the high reliability even at the critical region. The calculated results for diffusion coefficients of naphthalene in supercritical carbon dioxide are shown in Figure 10. The calculated results by the Schmidt number correlation show good agreement with the experimental data.

(d) Molecular Simulation

Molecular dynamics simulation has been used to calculate the self- and tracer diffusion coefficients in supercritical fluid. Katagiri et al. (1993) calculated the diffusion coefficients of naphthalene in supercritical carbon dioxide by MD simulation with the Lennard-Jones potential. They also used the Lorentz-Berthelot mixing rules in spite of the unsymmetrical nature of the system. They pointed out the restriction of the diffusive motion of naphthalene due to the formation of the solvation structure. Inomata et al. (1996) performed the molecular dynamics simulation of infinite dilute solutions of benzene in supercritical carbon dioxide. They reported the solvation structures and translational and rotational diffusion coefficients of benzene in supercritical carbon dioxide. Iwai et al. (1997) and Higashi et al. (1998a) reported the calculated results of diffusion coefficients of aromatic compounds in supercritical carbon dioxide by using single-site model molecular dynamics simulations. Kataoka (1998) performed the 2-dimensional molecular dynamics simulation to calculate the mutual diffusion coefficient in the supercritical region and reported anomalous behavior of the diffusion coefficients. De Oliveira et al. (2000) reported the comparison between experimental results and molecular dynamics simulation results of diffusion coefficients. Others of non-equilibrium molecular dynamics simulations have been applied to calculate diffusion coefficients (Wang and Cummings, 1989; Van de ven-Lucassen et al., 1998) in the critical region. It is interesting to apply the non-equilibrium molecular dynamics simulation for direct calculation of mutual diffusion coefficients in the supercritical conditions.

The self-diffusion coefficients of supercritical carbon dioxide and tracer diffusion coefficients of a solute molecule in supercritical carbon dioxide can be calculated by the following two methods. In the first method, the mean square displacement (MSD) of aromatic compound is used and the self-diffusion coefficients of carbon dioxide and tracer diffusion coefficients of a high-boiling compound are calculated by the Einstein relationship:

$$D_{11} = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left[\mathbf{r}_1(t) - \mathbf{r}_1(0) \right]^2 \right\rangle \tag{68}$$

$$D_{21}{*} = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left[\mathbf{r}_2(t) - \mathbf{r}_2(0) \right]^2 \right\rangle \tag{69}$$

where **r** is the position vector of molecules and *t* is the time.

In the second method, the velocity auto-correlation function (VAF) of a high-boiling compound is used and the self- and tracer diffusion coefficients are calculated by the following equations.

$$D_{11} = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_1(t)\cdot \mathbf{v}_1(0)\rangle \mathrm{d}t \tag{70}$$

$$D_{21}{*} = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_2(t)\cdot \mathbf{v}_2(0)\rangle \mathrm{d}t \tag{71}$$

where **v** is the velocity vector of molecules.

The same potential function and combining rules shown in Eqs.(35)-(37) can be used for molecular dynamics simulations of the diffusion coefficients. The intermolecular interaction parameters adjusted to the solubility data can be applied to simulate diffusion coefficients (Higashi et al., 2000). Figure 11 shows simulation results for the diffusion coefficients of carbon dioxide and naphthalene in supercritical carbon dioxide. For this case, the interaction parameters were adjusted to give good correlation of the experimental the solubility data. Calculated results using the RHS theory and the Schmidt number correlation are also illustrated in Figure 11. Simulation results of diffusion coefficients show good agreement with experimental diffusivity data. However, the anomalous decrease in diffusion coefficients near the critical point cannot be represented by this method as well as other methods that use the infinite dilution state.

3.2.3 Concentration Dependence

Correlation equations for the diffusivity in liquids have been adopted to investigate their applicability to represent the concentration dependence of diffusion coefficients in supercritical fluids. The anomalies of diffusion coefficients near the critical point are represented by their equations (Clifford and Coleby, 1991; Bartle et al., 1991a; Dysthe and Hafskjold, 1995; Nishiumi et al., 1996; Ago and Nishiumi, 1998).

The correlation equation developed by Darken (1948) to represent the concentration dependence for mutual diffusion coefficient at finite concentration is given as:

$$D_{21} = \left(y_2 D_{11}{*} + y_1 D_{21}{*}\right)\alpha \tag{72}$$

where y and $D*$ are the mole fraction and tracer diffusion coefficient, respectively. In Eq.(72), α is the thermodynamic factor that is calculated according to the following expression:

$$\alpha = \left(\frac{\partial \ln f_2}{\partial \ln y_2}\right) \tag{73}$$

where f_2 is the fugacity of the solute.

As the solubility of naphthalene in supercritical carbon dioxide is the order of 10^{-3} and the concentration dependence of tracer diffusion coefficient is very small, the concentration dependent diffusion coefficients can be represented by

$$D_{21} = \left(y_2 D_{11} + y_1 D_{21}{}^{0}\right)\left(\frac{\partial \ln f_2}{\partial \ln y_2}\right) \tag{74}$$

where D_{11} and $D_{21}{}^{0}$ are the self-diffusion coefficient of supercritical carbon dioxide and the infinite dilution diffusion coefficient of solute, respectively.

Higashi et al. (1999) applied the Darken equation for the correlation of the mass-fixed diffusion coefficients, D_2, of naphthalene in supercritical carbon dioxide. The relationship between the mutual diffusion coefficient and the mass-fixed diffusion coefficient are presented by the following expression (Hartlay and Crank, 1949; Fitts, 1962):

$$D_2 = \frac{D_{21}}{C\bar{v}_1} \tag{75}$$

where C is the molar density of carbon dioxide containing solute and $\bar{v}_1$ denoted the partial molar volume of carbon dioxide.

In their correlation, the molar density, the partial molar volume, and the fugacity was calculated by the Iwai-Margerum-Lu (IML) equation of state (Iwai et al., 1988) and the mole fraction of solute, y_2, was approximated by the saturated solubility devided by two, $y_2^{\mathrm{sat}}/2$. Mixing and combining rules are given by Eqs.(12)-(14). The k_{ij} and l_{ij} were adjusted to fit the solubility data, and this allowed the anomalous decrease and concentration dependence of the diffusion coefficients to be decreased by the Darken equation and the IML equation of state as shown in Figure 10.

Tuan et al. (1999c) applied the Leffler and Cullinan equation (1970) for the calculation of the concentration dependence of diffusion coefficient of lipid in supercritical carbon dioxide. Their equation is shown as follows.

$$D_{21} = \left\{\left(\mu_1 D_{21}{}^{0}\right)^{y_1} + \left(\mu_2 D_{12}{}^{0}\right)^{y_2}\right\}\frac{1}{\mu}\alpha \tag{76}$$

where μi is the velocity of each component and μ denoted that of mixture.

They applied the Peng-Robinson (PR) equation of state (Peng and Robinson, 1976) to calculate the thermodynamic factor α, and only a single binary interaction parameter, k_{ij}, was used in the mixing and combining rules. The values of diffusion coefficients of methyl oleate and carbon dioxide at infinite dilution were estimated by the method of Liong et al. (1991b) and that of Wilke and Chang (1955), respectively. Viscosities of carbon dioxide were interpolated from the tabulated values available in the literature (Stephan and Lucas, 1979). The viscosity of methyl oleate was estimated by the methods of Kashulines et al. (1991). The viscosity of the mixture was estimated by the Ely and Hanley corresponding state method (Tuan et al., 1999b). The calculated diffusion coefficients were corrected by the following equation:

$$D_{21,\mathrm{corr.}} = D_{21} + \frac{y_2}{y_2^{\mathrm{sat}}} D_{21}{}^{\mathrm{sat}} \tag{77}$$

The correlation results by Tuan et al. for the concentration dependence of diffusion coefficients of methyl oleate in supercritical carbon dioxide at 313.2 K are shown in Figure 12. The correlation results show good agreement with the experimental results.

4. Conclusion

The application of empirical equations, equation of state, solution models, and Monte Carlo simulation for the calculation of solubilities of high-boiling compounds in supercritical carbon dioxide were reviewed. For simple convenience of the usage, empirical equations can be used to investigate consistency of solubility data for design of a supercritical extraction process. Correlation methods using equation of state and solution model can be used to estimate solubilities and entrainer effects in supercritical fluids. When the critical properties, the vapor pressure, and the solid molar volume of the solute are unknown, solution model may be more useful because it needs only the melting point and the heat of fusion.

The applications of empirical equation based on the Stokes-Einstein model, the rough hard sphere theory, the Schmidt number correlation, and molecular dynamics simulation for the calculation of diffusion coefficients in supercritical carbon dioxide at infinite dilution condition are reviewed. Further, the application of the Darken equation and the Leffler and Cullinan equation are reviewed to calculate the concentration dependence of diffusion coefficients. Modification of empirical equations will be needed to correlate diffusion coefficients in supercritical fluids. The rough hard sphere theory and the Schmidt number correlation can be used to estimate diffusion coefficients in supercritical carbon dioxide. Concentration dependence of diffusion coefficients in supercritical carbon dioxide can be evaluated by the equation for diffusivity in liquids.

Molecular simulation can be used to calculate the solubility and diffusion coefficient in supercritical fluids. Not only properties such as solubility and diffusion coefficient, but also solvation structure and molecular interaction can be obtained by molecular simulation. Molecular simulation has become an available technique to investigate the characteristics of supercritical fluids.

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