Solubility Parameter of Carbon Dioxide—An Enigma

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ABSTRACT: The solubility of gaseous carbon dioxide in a variety of solvents has been extensively studied, the solute interacting with most solvents via dispersion forces. Hence, its Hildebrand solubility parameter, \( \delta_H \), may be used to predict its dissolution in liquids. The usual definition of \( \delta_H \) involves \( \Delta_H \), the molar enthalpy of vaporization, strictly applicable to liquids. This expression is inapplicable for carbon dioxide, being a gas at the temperatures of technical interest (298 \( \leq T/K \leq 333 \)), and various indirect methods have been employed for the determination of \( \delta_H(CO_2, T) \). The appreciable polarizability of CO\(_2\) and its ability to accept hydrogen bonds from suitable donor solvents prompted the determination of its Hansen solubility parameters. Finally, supercritical carbon dioxide has been extensively used as a solvent so that its \( \delta_H(scCO_2, T, P) \) is a useful quantity to know. The large discrepancies between the reported quantities for \( \delta_H(CO_2, T) \) are analyzed and discussed.

INTRODUCTION

Carbon dioxide is a major greenhouse gas, and its concentration in the atmosphere has increased manifold in the last century. It is produced naturally by volcanic eruptions, but its major source is human-made, by the burning of fossil fuels. It may eventually disappear from the atmosphere by dissolution in the oceans and by precipitating there as calcite because of the calcium ion content of the ocean water. However, this is a very slow process and will not reach equilibrium values in millennia to come. Therefore, efforts are made to capture carbon dioxide from flue gases and concentrate it for appropriate storage in a manner that will not permit its return to the atmosphere.

One method that is currently in use for achieving this goal is the capture of carbon dioxide in aqueous solutions of ethanolamine, but its economics are unsatisfactory. Hence, other solvents are sought for the purpose of capturing and storing carbon dioxide economically, with the emphasis being placed on the so-called “green” solvents, for example, room-temperature ionic liquids and deep eutectic solvents. These solvents should be environmentally friendly, biodegradable, and nonhazardous. Therefore, the solubility of gaseous carbon dioxide in a variety of solvents has been extensively studied as a function of temperature and, in some cases, also pressure.

Carbon dioxide is a nonpolar but polarizable gas, and its interactions with most solvents are via dispersion forces. The Hildebrand solubility theory has therefore been applied to its dissolution in liquids. The application of this theory requires the knowledge of the Hildebrand solubility parameter, \( \delta_H \), of the solute (CO\(_2\)) and that of the prospective liquid solvent. Whereas the \( \delta_H \) values of the solvents are generally well-known or readily ascertained, the \( \delta_H \) value of CO\(_2\) appears to have considerable uncertainty, as discussed in the present paper. This quantity is generally defined as

\[
\delta_H = \left( \frac{\Delta_H - RT}{V} \right)^{1/2} \tag{1}
\]

where \( \Delta_H \) is the molar enthalpy of vaporization and \( V \) is the molar volume at the temperature \( T \), strictly applicable to liquids (i.e., the solvents in which carbon dioxide is to dissolve). However, this expression is inapplicable for the determination of the solubility parameter of carbon dioxide, being a gas at the temperatures of interest (298 \( \leq T/K \leq 333 \)). Various indirect methods have had to be employed for the determination of \( \delta_H(CO_2, T) \), and these are discussed in this paper.

The critical point of carbon dioxide is at the temperature \( T_c = 304.1 \text{ K} \) and pressure \( P_c = 7.19 \text{ MPa} \), which is convenient for the use of supercritical carbon dioxide (scCO\(_2\)) as a solvent for the extraction of desired solutes from liquid or solid substrates or in liquid chromatography. The ability of scCO\(_2\) to do this has, again, been described in terms of its solubility parameter, \( \delta_H(scCO_2, T > T_c, P > P_c) \). Its determination is also discussed in this paper.

Finally, although carbon dioxide is nonpolar, its appreciable polarizability and ability to accept hydrogen bonds from suitable donor solvents prompted the determination of its Hansen solubility parameters that deal with its interactions beyond those due to the dispersion forces. Their relationship to the total (Hildebrand) solubility parameter is

\[
\delta_H^2 = \delta_{H^2}^2 + \delta_{P^2}^2 + \delta_{HB^2}^2 \tag{2}
\]

where \( \delta_H \) is the parameter due to the dispersion forces alone, \( \delta_P \) is due to the dipole-induced dipole interactions, and \( \delta_HB \) is due to the hydrogen bonding. The estimation of these parameters is also dealt with in this paper.

It turns out that there are large discrepancies between the values of \( \delta_H \) reported for a given temperature and pressure by diverse authors. These discrepancies lead to an uncertainty as to

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which value to use in new situations, where the solubility of carbon dioxide in liquid solvents or of solutes in scCO$_2$ is to be estimated. This paper should provide definite answers to this problem.

**SOLUBILITY PARAMETERS OF GASEOUS CARBON DIOXIDE**

Gjaldbæck$^5$ appears to be the first to calculate the solubility parameter for carbon dioxide gas for the estimation of its solubility in a variety of solvents. He modified eq 1 by using $p\Delta V$ instead of $R$, where $p$ is the saturated vapor pressure and $\Delta V$ is the difference in the molar volumes of the gas and liquid states of carbon dioxide. These values as well as $\Delta H$ were taken from the Quinn and Jones compilation.$^6$ He reported the value $\delta_{fl}/$MPa$^{1/2}$ = 12.27 for 298.15 K (converted as above), based in part on the data of Gjaldbæck$^5$ and also on those of Williams.$^8$ This value, 12.3, was subsequently quoted and employed by LaPack et al.$^9$ for the calculation of the membrane permeascivity of carbon dioxide. King et al.$^{10}$ calculated the Hildebrand solubility parameter from the internal energies reported by Din,$^{11}$ the quantity $U_m^a - U_m$, replacing $\Delta H - RT$ of eq 1, to yield $\delta_{fl}/$MPa$^{1/2}$ = 11.67 (converted as above) at $T = 298.15$ K. Lawson$^{12}$ reported the value $\delta_{fl}/$MPa$^{1/2}$ = 6.77 (converted as above) at 298.15 K in a table along with values for other gases, without reference to its source. Sebastian et al.$^{13}$ arbitrarily chose the value (converted as above) of $\delta_{fl}/$MPa$^{1/2}$ = 6.14 for carbon dioxide at $T \geq 340$ K to fit with its solubility in hydrocarbons.

Camper et al.$^{14}$ reported the following expression for the solubility parameter of gaseous carbon dioxide:

$$\delta_{fl}/$MPa$^{1/2} = 28.26 - 0.0535(T/K)$$  (3)

traced to Prausnitz et al.$^{15}$ and eventually to Barton.$^{16}$ from which the values $\delta_{fl}/$MPa$^{1/2}$ = 12.31 at $T = 298.15$ K and $\delta_{fl}/$MPa$^{1/2}$ = 11.5 at $T = 313.15$ K result. The latter value, 11.51 at $T = 313.15$ K, was confirmed in a subsequent paper by Camper et al.$^{17}$ This particular temperature was relevant to the capture of carbon dioxide from the atmosphere. Kilaru et al.$^{18}$ reported a slightly different value of $\delta_{fl}/$MPa$^{1/2}$ = 12.1 for this temperature, $T = 313.15$ K, as resulted from eq 3 that they quoted, with no reason for the discrepancy. Moganty and Balta$^{19}$ also used eq 3 and calculated from it, correctly, $\delta_{fl}/$MPa$^{1/2}$ = 12.3 at $T = 298.15$ K and $\delta_{fl}/$MPa$^{1/2}$ = 11.5 at $T = 313.15$ K.

A value of the solubility parameter of carbon dioxide at 298.15 K and 0.1 MPa that is much larger than that obtainable from eq 3, namely, $\delta_{fl}/$MPa$^{1/2}$ = 17.4, resulted from the evaluation of the Hansen solubility parameters (cf. eq 2),$^{20}$ of which due to the dispersion forces alone was $\delta_{fl}/$MPa$^{1/2}$ = 15.6, according to Williams et al.$^{21}$ A slightly different value, $\delta_{fl}/$MPa$^{1/2}$ = 17.85, was reported by Sistla et al.$^{22}$ on the same basis, with $\delta_{fl}/$MPa$^{1/2}$ = 15.7.

Indirect values for the solubility parameter of carbon dioxide have been obtained by the application of the nonrandom two-liquid model to its solutions in a variety of solvents, both polar and nonpolar, by Vetere.$^{23}$ He reported the absolute differences between the solubility parameters of carbon dioxide and those of benzene, toluene, methyl acetate, and methanol at $T = 313.15$ K (311.3 for toluene) calculated from this model as $\Delta \delta_{fl}/$MPa$^{1/2}$ = 3.97, 3.87, 3.49, and 9.11, respectively. The values of $\delta_{fl}/$MPa$^{1/2}$ for these liquid solvents are 18.5, 17.9, 18.8, and 28.6 (from $\Delta H(T)$ and $d(T)$ data by Riddick et al.$^{24}$). The mean value resulted for carbon dioxide is $\delta_{fl}/$MPa$^{1/2}$ ± $\Delta \delta_{fl}$ that is, the upper value 21.5 ± 1.2 or the lower value 14.3, which is incompatible with the data for methanol. This, indeed, is an unreasonably large value for this temperature, even if the data for methanol are excluded.

The results of the solubility parameters of carbon dioxide as a solute from these studies are summarized for ambient pressure and two temperatures 298.15 and 313.13 K in Table 1, which shows clearly the diversity of the reported values.

### Table 1. Reported Solubility Parameters of Gaseous Carbon Dioxide

| Author      | Ref | $\delta_{fl}/$MPa$^{1/2}$ | $T$ = 298.15 K | Author      | Ref | $\delta_{fl}/$MPa$^{1/2}$ | $T$ = 313.15 K |
|-------------|-----|---------------------------|---------------|-------------|-----|---------------------------|---------------|
| Gjaldbæck   | 5   | 8.45 (10.43)              |               | Camper      | 14  | 11.51                     |               |
| Prausnitz   | 7   | 12.27                     |               | Kilaru      | 18  | 12.1                      |               |
| LaPack      | 9   | 12.3                      |               | Vetere      | 23  | 14.3 (21.5)               |               |
| King        | 10  | 11.67                     |               | Lawson      | 12  | 6.77                      |               |
| Sebastian   | 13  | 6.14                      |               | Williams    | 21  | 17.4                      |               |
| Camper      | 14  | 12.31                     |               | Sistla      | 22  | 17.85                     |               |
| Marcus      | _a_ | 9.35                      |               |             |     |                           |               |

*This study.*

**SOLUBILITY PARAMETERS OF SCCO$_2$**

The solubility parameters of scCO$_2$ as a solvent have been estimated by several authors, the earliest report being that of Allada.$^{25}$ The internal energy differences $U_m^a - U_m$ are employed instead of $\Delta H - RT$ of eq 1 because $\Delta H$ is meaningless for a supercritical fluid. The critical constants for carbon dioxide are the temperature $T_c = 304.1$ K, the pressure $P_c = 7.19$ MPa, and the compressibility factor $Z_c = P_cV_c/RT_c$ = 0.274.$^{25}$ The required $U_m^a - U_m$ and $Z$ (yielding $V$ values) data for scCO$_2$ were taken from Hougen et al.$^{26}$ yielding curves of $\delta_{fl}(T)$ for temperatures varying from 290 to 490 K and discrete values of pressure, $P_s \leq P \leq 220$ MPa. Being obtained from a small-scale figure and converted to the appropriate units, the values for two temperatures relevant to the use of scCO$_2$ as a solvent, 313 and 333 K, are $\delta_{fl}/$MPa$^{1/2}$ = 6.1 and 3.7 at $P = 8.1$ MPa, $\delta_{fl}/$MPa$^{1/2}$ = 12.9 and 8.8 at $P = 14.7$ MPa, and $\delta_{fl}/$MPa$^{1/2}$ = 14.3 and 12.9 at $P = 29.5$ MPa, respectively.

Mishra et al.$^{27}$ used the expression suggested by Giddings et al.$^{28}$ according to which, after conversion to the appropriate units,

$$\delta_{fl}/$MPa$^{1/2} = 3.02(P/\text{MPa})^{1/2} \rho_s = 8.10\delta_{fl}(\text{CO}_2)$$  (4)

where $\rho_s$ is the reduced density of the fluid, $\rho/\rho_s$. The first equality here pertains to any supercritical fluid, and the second pertains to scCO$_2$ with the appropriate value of $\rho_s$. On taking the density data for pure carbon dioxide from Pensado et al.$^{29}$

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Table 2. Reported Solubility Parameters of scCO₂ at Two Temperatures and Specified Pressures P/MPa

| P/MPa | Author, ref | δ_p/MPa₁/₂ | Author, ref | δ_p/MPa₁/₂ | Author, ref | δ_p/MPa₁/₂ |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|
|       | T/K = 313.15 |             | T/K = 318.15 |             | T/K = 333.15 |             |
| 7     | a           | 4.7         | a           | 5.5         | a           | 6.3         |
| 8.1   | Allada 25,  | 6.1         | Allada 25,  | 6.1         | Allada 25,  | 6.4         |
|       | Mishra 27,  | 9.5         | Mishra 27,  | 9.5         | Mishra 27,  | 9.5         |
| 8.5   | a           | 14.7        | Ougiyanagi  | 4.9         | Zhang       | 4.8         |
|       | Ougiyanagi  | 14.7        | Zhang       | 7.6         | Mishra 27,  | 12.6        |
| 10    | a           | 14.6        | Ougiyanagi  | 14.3        | Zhang       | 12.6        |
|       | Mishra 27,  | 13.4        | Mishra 27,  | 13.4        | Mishra 27,  | 13.4        |
| 14.7  | Allada 25,  | 12.9        | Allada 25,  | 12.9        | Mishra 27,  | 15.0        |
|       | Mishra 27,  | 13.4        | Mishra 27,  | 15.0        |            |             |
| 20    | a           | 14.6        | Ougiyanagi  | 14.3        | Mishra 27,  | 15.0        |
|       | Ougiyanagi  | 14.3        | Mishra 27,  | 15.0        |            |             |
| 22.7  | a           | 14.6        | Zhang       | 13.3        |            |             |
|       | Mishra 27,  | 15.7        | Mishra 27,  | 15.7        |            |             |
| 29.5  | Allada 25,  | 14.3        | Allada 25,  | 14.3        |            |             |
|       | Mishra 27,  | 15.7        | Mishra 27,  | 15.7        |            |             |
| 30    | Mishra 27,  | 15.7        | Mishra 27,  | 15.7        |            |             |
| 40    | a           | 14.6        | Mishra 27,  | 15.7        |            |             |

**HANSEN SOLUBILITY PARAMETERS OF CARBON DIOXIDE**

The Hansen solubility parameters of carbon dioxide have been dealt with extensively by Williams, both at 298.15 K (his _T_ = 298.15 K and 1 atm (0.101325 MPa) and at other temperatures and pressures, for which the reference volume, _V_ = 39.13 cm³/mol⁻¹, is required. The values at 298.15 K and 1 atm (the reference values, see below) are _δ_ = 15.6 for the dispersion contribution, _δ_ = 5.2 for the polar contribution, and _δ_ = 5.8 for the hydrogen-bonding contribution. The resulting total (Hildebrand) solubility parameter is _δ_ = 17.44 according to eq 2. For no clear reason, Sistla et al. referred to the same source but reported slightly different values: _δ_ = 15.7, _δ_ = 6.3, and _δ_ = 14.85 (the main difference being in the polar term).

Williams also showed that values of the Hansen solubility parameters at other temperatures and pressures can be calculated from the following expressions:

\[
\delta_d = \delta_d(V_r/\sqrt{V})^{1.25}
\]

\[
\delta_p = \delta_p(V_r/\sqrt{V})^{0.5}
\]

\[
\delta_h = \delta_h[V_0(0.00132(298.15 - T/\text{K}) + \ln(V_r/\sqrt{V})^{0.5})]
\]

Hence, the key value for obtaining the Hansen solubility parameters at other than the reference conditions is the molar volume of the substance at the desired thermodynamic states, and these should be available via the appropriate equation of state. Thus, at _T_ = 298.15 K and _P_ = 20 MPa, _δ_d/MPa₁/₂ = 12.2, _δ_p/MPa₁/₂ = 4.7, and _δ_h/MPa₁/₂ = 5.2 and _δ_h/MPa₁/₂ = 14.0, considerably lower than those at ambient pressure (the
reference values). For supercritical conditions, Williams et al.\cite{9} showed small-scale three-dimensional plots of the total (Hildebrand) and the three Hansen solubility parameters of carbon dioxide at temperatures up to 423 K and pressures up to 60 MPa using the semiempirical Huang 27-coefficient equation of state\cite{5} to obtain the molar volumes $V$ of eqs 5–7.

\section*{DISCUSSION}

The purpose of obtaining the solubility parameter of carbon dioxide is for the prediction of solubilities of this substance as a gaseous solute or as a solvent in its supercritical fluid state. The solubility parameters of the solvents for gaseous CO$_2$ and of the solutes for scCO$_2$ are taken as known.\cite{16} The regular solution theory is then applied in the following form, the so-called “extended Hildebrand solubility expression”, where subscript $u$ is used for the solute and subscript $v$ is used for the solvent:

$$
\log x_u = \log x_u^\text{id} + (V_v/RT)(\delta_Hu - \delta_Hv)^2 + \log(V_v/V_u)
+ [1/\ln(10)](1 - V_u/V_v)
$$

(8)

In this expression, $x_u$ is the mole fraction of the solute in the saturated solution and $x_u^\text{id}$ is the “ideal” solubility, defined below, and the terms behind the solubility parameter term have to be used if there are large discrepancies between the molar volumes of the solute and the solvent. For solid solutes,

$$
\log x_u^\text{id} = \Delta H/RT \log(10)\brackets{T_i - T}/T_i T
$$

(9)

where $\Delta H$ is the molar enthalpy of fusion at the temperature of fusion $T_i$. For carbon dioxide, the value of $\log x_u^\text{id}$ at $T = 298.15$ K is $-1.4209$.\cite{16} Equation 8 has been used for the indirect estimation of $\delta_Hu$ for gaseous carbon dioxide from its solubility in a variety of solvents; for example,\cite{25} a more sophisticated approach, pertaining to polar solutes or solvents, for which the regular solution theory is not supposed to be applicable, is to use the Hansen solubility parameters and the so-called “solubility sphere”:

$$(Ra)^2 = 4(\delta_Hu - \delta_Hv)^2 + (\delta_{pu} - \delta_{pv})^2 + (\delta_{shu} - \delta_{shv})^2
$$

(10)

“Good solvents” are those for which the solubility is larger than the ideal, “bad solvents” are those where the opposite occurs, and the criterion is $Ra < 4.0$. This approach was used by Williams\cite{36} for the estimation of the Hansen and total solubility parameters of carbon dioxide from its solubility in 101 solvents at 298.15 K and 0.101325 MPa, only 10 of which were deemed to be good solvents.

Although the temperature dependence of the solubility parameter of carbon dioxide eq 3 was referenced to Prausnitz,\cite{7} and eventually to Barton,\cite{16} this appears to be incorrect. Although Barton reported the expression $\delta_Hu/\text{MPa}^{1/2} = m(T/K) + b$, no values for $m$ and $b$ were reported for carbon dioxide, but only those for hydrocarbons were reported.

The most recent and definite equation of state of Span and Wagner\cite{35} for carbon dioxide yielded numerical data reported by them of the specific enthalpies and densities of the condensed and gaseous states at saturation in the temperature range 218 $\leq T/K \leq 304$, where 216.59 K is the triple point and 304 K is just below the critical point. These can be described by the quadratic expression for the Hildebrand solubility parameter according to eq 1:\cite{38}

$$
\delta_Hu/\text{MPa}^{1/2} = -36.72 + 0.5447(T/K) - 0.001309(T/K)^2
$$

(11)

and yielded an accurate value of $\delta_Hu/\text{MPa}^{1/2} = 9.35$ at 298.15 K, shown in Table 1. This value is in between those reported by Gjaldbeck,\cite{5} being smaller than those near 12 reported by Prausnitz,\cite{7} King,\cite{10} and Camper,\cite{14} considerably larger than those reported by Lawson\cite{12} and Sebastian\cite{13} near 6, and much smaller than the values reported by Williams\cite{21} and Sistla\cite{22} near 17. The difficulty arises from the fact that carbon dioxide at ambient conditions is a gas, and it sublimes from the solid to the gaseous state at ambient pressures without passing through a liquid state. Therefore, the quantity $\Delta H$ in eq 1 cannot be readily evaluated nor can the solubility parameter unless a reliable equation of state is available, as provided by the reference data and the numerical data of Span and Wagner.\cite{35} Estimates of $\delta_Hu/\text{MPa}^{1/2}$ at 298.15 K near 6 and 12 arise from the inadequate data in older equations of state for carbon dioxide. Estimates of $\delta_Hu/\text{MPa}^{1/2}$ at 298.15 K near 17 arise from a trial and error evaluation of the Hansen solubility parameters\cite{4, 22} from the measured solubility, application of eq 2, and an arbitrary criterion for distinction between good and bad solvents.

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\section*{Notes}

The author declares no competing financial interest.

\section*{REFERENCES}

(1) IPCC Special Report on Carbon Dioxide Capture and Storage; Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., Eds.; Cambridge University Press: Cambridge, U.K., 2005.

(2) Abu-Zahra, M. R. M.; Niedere, J. P. M.; Feron, P. H. M.; Veersteeg, G. F.; CO$_2$ capture from power plants. Int. J. Greenhouse Gas Control 2007, 1, 135–142.

(3) Sarmad, S.; Mikkola, J.-P.; Ji, X. Carbon dioxide capture with ionic liquids and deep eutectic solvents: a new generation of sorbents. ChemSusChem 2017, 10, 324–352.

(4) Marcus, Y.. Gas solubility in deep eutectic solvents. Monatsh. Chem. ahead of print, DOI:10.1007/s00706-017-2031-8.

(5) Gjaldbæk, J. C. The solubility of carbon dioxide in perfluoro-n-heptane, normal heptane, cyclo-hexane, carbon tetrachloride, benzene, carbon disulphide and aqueous solution of aerosol. Acta Chem. Scand. 1953, 7, 537–544.

(6) Quinn, E. L.; Jones, C. L. Carbon Dioxide; ACS Monograph Series: New York, 1936.

(7) Prausnitz, J. M.; Shair, F. H. A thermodynamic correlation of gas solubilities. AIChE J. 1961, 7, 682–687.

(8) Williams, D. L. US AEC Comm. 1952, LA-1484, pp 3–14.

(9) LaPack, M. A.; Tou, J. C.; McGuiffin, V. L.; Enke, C. G. The correlation of membrane permeability with Hildebrand solubility parameters. J. Membr. Sci. 1994, 86, 263–280.

(10) King, M. B.; Kassim, K.; Al-Najjar, H. The solubilities of carbon dioxide, hydrogen sulphide and propane in some normal alkanes solvents—II. Chem. Eng. Sci. 1977, 32, 1247–1252.

(11) Dinh, F. Thermodynamic Functions of Gases; Butterworth: London, 1956.

(12) Lawson, D. Methods of calculating engineering parameters for gas separations. Appl. Energy 1980, 6, 241–255.

(13) Sebastian, H. M.; Lin, H.-M.; Chao, K.-C. Correlation of the solubility of carbon dioxide in hydrocarbon solvents. Ind. Eng. Chem. Process Des. Dev. 1981, 20, 508–511.
(14) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. Gas solubilities in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* 2004, 43, 3049−3054.
(15) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice-Hall: Upper Saddle River, NJ, 1999.
(16) Barton, A. F. M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters; CRC Press: Boca Raton, FL, 1983.
(17) Camper, D.; Becker, C.; Koval, C.; Noble, R. Low pressure hydrocarbon solubility in room temperature ionic liquids containing imidazolium rings interpreted using regular solution theory. *Ind. Eng. Chem. Res.* 2005, 44, 1928−1933.
(18) Kilrau, P. K.; Condemarin, R. A.; Scovazzo, P. Correlations of low-pressure carbon dioxide and hydrocarbon solubilities in imidazolium-, phosphonium-, and ammonium-based room-temperature ionic liquids. Part I. Using surface tension. *Ind. Eng. Chem. Res.* 2008, 47, 900−909.
(19) Moganty, S. S.; Baltus, R. E. Regular solution theory for low pressure carbon dioxide solubility in room temperature ionic liquids: ionic liquid solubility parameter from activation energy of viscosity. *Ind. Eng. Chem. Res.* 2010, 49, 5846−5853.
(20) Hansen, C. M. *Hansen Solubility Parameters*, 2nd ed.; CRC, Taylor & Francis, 2007.
(21) Williams, L. L.; Rubin, J. B.; Edwards, H. W. Calculation of Hansen solubility parameter values for a range of pressure and temperature conditions, including the supercritical fluid region. *Ind. Eng. Chem. Res.* 2004, 43, 4967−4972.
(22) Sistla, Y. S.; Jain, L.; Khanna, A. Validation and prediction of solubility parameters of ionic liquids for CO₂ capture. *Sep. Purif. Technol.* 2012, 97, 51−64.
(23) Vetere, A. An empirical method to evaluate the solubility of several gases in polar and non-polar solvents. *Fluid Phase Equilib.* 1997, 132, 77−91.
(24) Riddick, J. A.; Burger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley: New York, 1986.
(25) Allada, S. R. Solubility parameters of supercritical fluids. *Ind. Eng. Chem. Process Des. Dev.* 1984, 23, 344−348.
(26) Hougen, O. A.; Watson, K. M.; Ragatz, R. A. *Chemical Process Principles*, 2nd ed.; Asia Publishing House: Bombay, India, 1960; Chapter 14, Part II.
(27) Mishra, V. K.; Temelli, F.; Ooraikul, B. Modeling binary phase behavior of supercritical carbon dioxide and fatty acid esters. *J. Supercrit. Fluids* 1993, 6, 51−57.
(28) Giddings, J. C.; Myers, M. N.; McLaren, L.; Keller, R. A. High pressure gas chromatography of nonvolatile species. *Science* 1968, 162, 67−73.
(29) Pensado, A. S.; Pádua, A. A. H.; Comuñas, M. J. P.; Fernández, J. Viscosity and density measurements for carbon dioxide + pentaerythritol ester lubricant mixtures at low lubricant concentration. *J. Supercrit. Fluids* 2008, 44, 172−185.
(30) Ougiyanagi, J.; Meguro, Y.; Yoshida, Z.; Imura, H.; Ohashi, K. Solvent effect on distribution ratio of Pd(II) in supercritical carbon dioxide extraction and solvent extraction using 2-methyl-8-quinolinol. *Talanta* 2003, 59, 1189−1198.
(31) Zhang, M.; Dou, M.; Wang, M.; Yu, Y. Study on the solubility parameter of supercritical carbon dioxide system by molecular dynamics simulation. *J. Mol. Liq.* 2017, 248, 322−329.
(32) Bogdanovic, A.; Tadic, V.; Ristic, M.; Petrovic, S.; Skala, D. Optimization of supercritical CO₂ extraction of fenugreek seed (Trigonella foenum-graecum L.) and calculating extracts solubility. *J. Supercrit. Fluids* 2016, 117, 297−307.
(33) Wai, C. M.; Wang, S. J.; Yu, J.-J. Solubility parameters and solubilities of metal dithiocarbamates in supercritical carbon dioxide. *Anal. Chem.* 1996, 68, 3516−3519.
(34) Cipollina, A.; Anselmo, R.; Scialdone, O.; Filardo, G.; Galia, A. Experimental P-T-p measurements of supercritical mixtures of carbon dioxide, carbon monoxide, and hydrogen and semiquantitative estimation of their solvent power using the solubility parameter concept. *J. Chem. Eng. Data* 2007, 52, 2291−2297.
(35) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* 1996, 25, 1509−1596.
(36) Williams, L. L. In *Hansen Solubility Parameters. A User’s Handbook*, 2nd ed.; Hansen, C. M., Ed.; Taylor & Francis: Hoboken, NJ, 2007; Chapter 10.
(37) Huang, F.-H.; Li, M.-H.; Lee, L. L.; Starling, K. E.; Chung, F. T. H. An Accurate Equation of State for Carbon Dioxide. *J. Chem. Eng. Jpn.* 1985, 18, 490−496.
(38) Marcus, Y. Solubility parameters of permanent gases. *J. Chem. 2016, 2016, 4701919.