

Measurement of Solubility of Anthracene in Supercritical Carbon Dioxide by the Synthetic-Static Method Using *In-situ* UV-Visible Spectroscopy

Kozue Takahara*, Hirohisa Uchida**

*(Graduate School of Natural Science & Technology, Division of Natural System, Kanazawa University, Japan)

** (Faculty of Frontier Engineering, Institute of Science & Engineering, Kanazawa University, Kakuma-machi, Kanazawa-shi, Ishikawa 920-1192, Japan)

ABSTRACT

Solubilities of anthracene in supercritical carbon dioxide in the pressure range of 8–25 MPa at 313.2 and 333.2 K were measured by the synthetic-static method, in which saturation states, i.e. equilibrium pressures, were determined using an *in-situ* UV-visible spectroscopy under static conditions. The experimental solubilities of anthracene at the present conditions were in the range of 1×10^{-6} – 2×10^{-4} in mole fraction and the crossover pressure between the solubility at 313.2 K and that at 333.2 K was around 15 MPa. The experimental solubilities were in good agreement with the literature data obtained by the analytical methods including flow methods, recirculation methods, and spectroscopic methods with an average absolute deviation of lower than 10%. The present measurement method is very effective for the solubility measurement of organic compounds with very low solubility in supercritical carbon dioxide. The solubilities were correlated by the Chrastil equation, which is one of the semi-empirical equations. The present model gave good correlation results for the experimental data.

Keywords - Solubility, anthracene, supercritical carbon dioxide, synthetic method, modelling

Date of Submission: 19-08-2023

Date of acceptance: 21-08-2023

I. INTRODUCTION

Supercritical fluids have been given much attention as a new type of solvent and have been applied in various industries [1, 2]. In particular, carbon dioxide has been commonly used as a solvent for many industrial applications because it is environmentally benign, nonhazardous, and inexpensive and has a low critical temperature and a moderate critical pressure [1–3].

A knowledge of solubility data of solutes in supercritical carbon dioxide is very important to the understanding and design of processes with supercritical carbon dioxide [4–12]. For example, solubility data can be used to predict the applicability of crystallization processes using supercritical carbon dioxide such as the production of fine particles [7, 8, 11, 13, 14] and thin films [15–17] by rapid expansion of supercritical solutions (RESS) [18] and the production of thin films [10, 12, 19, 20] by supercritical fluids deposition (SCFD) [21, 22]. Therefore, the solubility must be determined and modeled in order to design effective processes. In particular, the pressure and temperature dependence of solubility must be understood. This will lead to engineers to optimize the operating

conditions of unit operations such as extractors, separators, transfer lines, and crystallizers.

There have been a number of different approaches developed for measuring of solubility of solutes in supercritical carbon dioxide [4, 21–24]. These methods can be divided into two major categories depending on how the compositions of the equilibrium phases are determined (analytically or not) and whether the mixture to be investigated has been prepared (synthesized) with precisely known composition or not: analytical methods and synthetic methods [4, 23–26]. The simplest, most straightforward and most commonly used methods of measuring solubility will be the analytical-flow method. In the method, the extractor is filled with solutes, and supercritical carbon dioxide continuously flows through the extractor. The solutes and solvent are then separated by density difference, and the concentration of the sampled solutes is analyzed by various techniques including chromatographic, spectroscopic, gravimetric, and other techniques. In the method, it is important to ensure that the solutes and solvent, i.e., supercritical carbon dioxide, achieve equilibrium while the solvent is flowing through the extractor. Therefore,

it is difficult to measure solubility in supercritical carbon dioxide by the method when the solutes loading in the extractor is very small, e.g., when the solutes cost is high, and when the sampling amount of solutes is small, e.g., when the solubility of the solutes is small, because accurately measuring the concentration of solutes is very difficult with techniques such as chromatography and gravimetry. The spectroscopic technique has been one of powerful tools to measure solubility of solutes in supercritical carbon dioxide. It requires no sampling of the solutes, which overcomes many drawbacks of the analytical-flow method. Various studies have been reported in the literature for the past years, either using ultraviolet (UV)-visible spectroscopy [27–29], infrared (IR) spectroscopy [30–32], near-infrared (NIR) spectroscopy [33, 34], Raman spectroscopy [35], and fluorescence spectroscopy [36]. These spectroscopic measurement techniques need a calibration curve or molar absorptivity prepared with supercritical carbon dioxide or several organic solvents. However, calibration curves and molar absorption coefficients prepared using supercritical carbon dioxide and various organic solvents are not applicable because they differ from the actual ones due to the density dependence of carbon dioxide [37] and differences in absorption peaks caused by solvatochromism when the solution has absorption in the visible region [38].

Ngo *et al.* [39] proposed a new synthetic method to measure the solubility of solutes in supercritical carbon dioxide, in which saturation states, i.e., equilibrium of the mixture, were determined using an *in-situ* UV-visible, IR, or fluorescence spectroscopy under static conditions. The method is the static method, in which the vessel is charged with a known amount of solutes and it was pressurized with carbon dioxide and stirred constantly. Equilibrium of the mixture was observed *in-situ* by periodically taking UV, IR, or fluorescence spectra of the solution. The pressure was raised stepwise until no further significant increase in the peak absorbance was observed. This meant that all solids had been dissolved in the fluid phase. The method is able to obtain solubility data without performing any calibration prior to the experiments or making any assumptions on the constancy of the molar absorptivity. They proposed that IR is suitable for measuring the solubility higher than 10^{-5} in mole fraction, UV is appropriate for solubility higher than 10^{-6} in mole fraction, and fluorescence is suitable for measuring the solubility of about 10^{-7} in mole fraction.

In the present work, solubilities of anthracene in supercritical carbon dioxide in the pressure range of 8–25 MPa and at the temperatures 313.2 and 333.2 K were measured by the synthetic-

static method using an *in-situ* UV-visible spectroscopy proposed by Ngo *et al.* [39]. Anthracene was used as a model acene because it is a promising material for fabricating several organic semiconductors [40–46] and blue OLEDs [47, 48]. Because the experimental determination of solubility of solutes in supercritical carbon dioxide is difficult, costly, and time consuming, it is advantageous to extend and complement the experimental data with some model. Therefore, the solubilities obtained were correlated by the Chrastil equation [49], a semi-empirical equation that has been reported to have the highest correlation accuracy for solutes solubility in supercritical carbon dioxide [50].

II. EXPERIMENTAL

2.1 Materials

Anthracene (supplied by Acros Organics of Thermo Fisher Scientific Inc.; the purity is > 99%; molecular weight is 178.23) was used as a solute. Fig. 1 shows the chemical structure of anthracene. High-purity CO₂ (its purity is > 99.99%, supplied by Showa Denko Gas Products Co., Ltd.) was used as a solvent and was supplied through a dryer, in which 5A molecular sieve particles were packed to remove impurities such as water.

2.2 Apparatus and Procedures

A static equilibrium apparatus was used in this work. A schematic diagram of the apparatus used in this work is shown in Fig. 2.

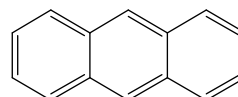


Fig. 1 Chemical structure of anthracene.

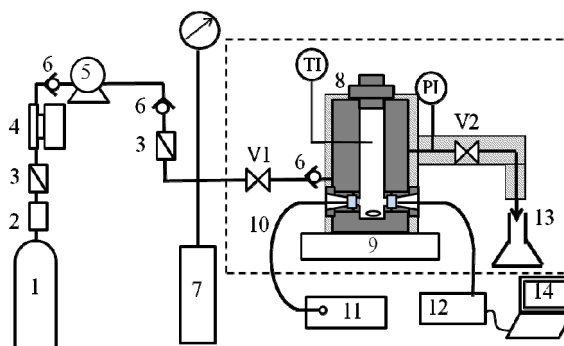




Fig. 2 Schematic diagram of the experimental setup: 1. CO₂ gas cylinder, 2. dryer, 3. filter, 4. cooling unit, 5. screw-type hand-pump, 6. stopper, 7. CO₂ reservoir, 8. high-pressure optical cell, 9. magnetic stirrer, 10. optical fibers, 11. UV-vis light source, 12. UV-vis spectrophotometer, 13. Glass trap, 14. personal computer,  heating jackets,  dark booth.

Known amounts of a solute were introduced into the high-pressure optical cell, having a direct path with two sapphire windows (8) (Taiatsu Techno Co.), in solid form (> 0.10 mg) or in toluene solution (< 0.01 mg). When the solute was added in the solution form, the toluene was evaporated in the cell at 313.2 K for 12 h. After loading, the cell was heated to a desired temperature by heating jackets. The pressurized carbon dioxide was then introduced into the cell to a desired pressure, and stirred constantly. The supercritical carbon dioxide was in contact with solid solute at the pressure and temperature. Equilibrium of the mixture was observed *in-situ* by periodically taking UV spectra of the solution (12) (Hamamatsu Photonics K.K. PMA-12, C10544-01). The spectral change of anthracene with increasing pressure of supercritical carbon dioxide is shown in Fig. 3. The pressure of carbon dioxide was increased up until there was no further increase in the peak absorbance. The absorbance was obtained using the average absorbance in the whole of peak wavelength to reduce a significant spectral shift, as shown in the following equation (1):

$$A_{\text{ave}} = \left(\int_a^b A(\lambda) d\lambda \right) / (b - a) \quad (1)$$

A_{ave} is the average absorbance calculated by integration of the absorbance in the wavelength range from a to b and $A(\lambda)$ is the absorbance at the wavelength λ . In a preliminary examination, we determined the values of a and b as 310 nm and 385 nm, respectively. The average absorbance was plotted versus the pressure as shown in Fig. 4. As the pressure increased, there was a large increase in solubility of the solute in supercritical carbon dioxide. Once all the solute in the cell dissolved, there was an abrupt change in the slope and the absorbance became almost constant. The pressure at saturation was then determined from the intersection of the two linear regions on the graph as shown in Fig. 4. For example, we can determine the saturation pressure is 9.08 MPa. Solubility can be calculated by the mass of solute in the cell, the fluid density at saturation, and the cell volume. The density of carbon dioxide was calculated from the Span-Wagner equation [51]. The solubility in mole fraction of the solute in supercritical carbon dioxide, y_2 was calculated by the following equation (2):

$$y_2 = \frac{w / M_s}{(V \times \rho / M_{\text{CO}_2}) + w / M_s} \quad (2)$$

where w is the mass of the solute, M_s and M_{CO_2} are the molar masses of the solute and carbon dioxide, respectively. V is the volume of the high-pressure optical cell, and ρ is the density of carbon dioxide at the experimental condition.

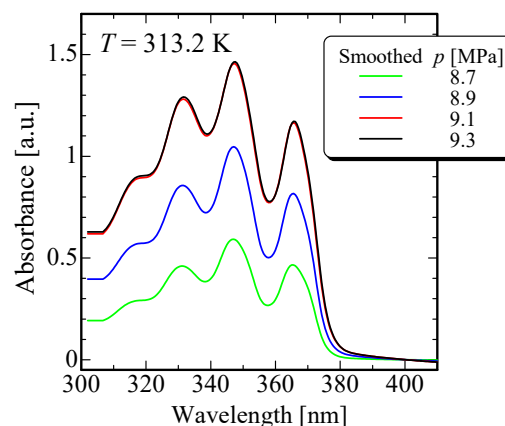


Fig. 3 Spectral change of anthracene with increasing pressure of supercritical carbon dioxide at 313.2 K.

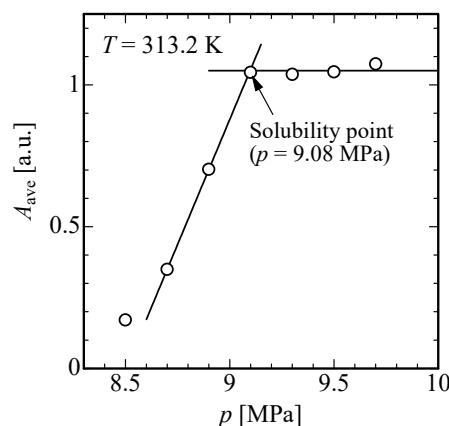


Fig. 4 UV absorbance of anthracene in supercritical carbon dioxide at 313.2 K as a function of pressure for 1.10 mg for anthracene.

III. RESULTS AND DISCUSSION

3.1 Experimental results

The experimental solubilities of anthracene in supercritical carbon dioxide at 313.2 and 333.2 K were shown in Fig. 5 and Table 1, and Fig. 6 and Table 2, respectively. As shown in Figs. 5 and 6, The experimental solubilities of anthracene at the present conditions were in the range from 1×10^{-6} to 2×10^{-4} in mole fraction and the crossover pressure between the solubility at 313.2 K and that at 333.2 K was around 15 MPa. The experimental solubilities were in good agreement with the literature data obtained by the analytical methods including the spectroscopic method [39], flow methods [54, 56, 58], and recirculation methods [53, 55] with an average absolute deviation of lower than 10%. The self-consistency of the measured solubility was evaluated using the following equation proposed by Méndez-Santiago and Teja [59]:

$$T \ln E = T \ln(y_2 p / p_2^{\text{sat}}) = A + Bp \quad (3)$$

where T is the equilibrium temperature, ρ is the density of carbon dioxide that was calculated by the Span-Wagner equation. A and B are the constants: $A = 834.7$ and $B = 0.1645$, and E is the enhancement factor. p is the equilibrium pressure and p_2^{sat} is the saturated vapor pressure of anthracene which was evaluated by the Antoine equation [60]. As shown in Fig. 7, the solubility data of anthracene at the present conditions collapsed to a straight line, when plotted as $T \ln E$ vs the density of carbon dioxide, so that the present data would be internally consistent. The present measurement method is very effective for the solubility measurement of organic compounds such as anthracene with very low solubility in supercritical carbon dioxide.

3.2 Correlation

The solubilities obtained were correlated by the following Chrastil equation [49]:

$$c = d^k \exp(a/T + b) \quad (4)$$

where c is the solute concentration; solubility, in supercritical carbon dioxide in $\text{kg} \cdot \text{m}^{-3}$, d is the density of carbon dioxide in $\text{kg} \cdot \text{m}^{-3}$ which was calculated by the Span-Wagner equation, T is an absolute temperature in K. The parameters, a , b and k are Chrastil parameters those were determined to give a good representation of the experimental solubility. The parameters were thus determined as $a = -5908 \text{ K}^{-1}$, $b = -17.55$ and $k = 5.2060$. The calculated solubilities of anthracene in supercritical carbon dioxide are shown in Fig. 8. The present model gave good correlation results for all of the experimental solubilities of anthracene in supercritical carbon dioxide.

IV. CONCLUSION

The experimental solubilities of anthracene at the present conditions were in the range of 1×10^{-6} to 2×10^{-4} in mole fraction and those were in good agreement with the literature data with an average absolute deviation of lower than 10%. The present technique, i.e., synthetic-static method using *in-situ* UV spectroscopy, enables high-precision solubility measurement of organic compounds with low solubility using only a small amount of solutes without using a calibration curve or molar absorptivity. The solubilities were correlated by the Chrastil equation and the present models gave good correlation results for the experimental data.

Acknowledgements

The authors acknowledge Dr. T. Momose (Kumamoto University, Japan) for allowing us to use the UV-vis spectrophotometer.

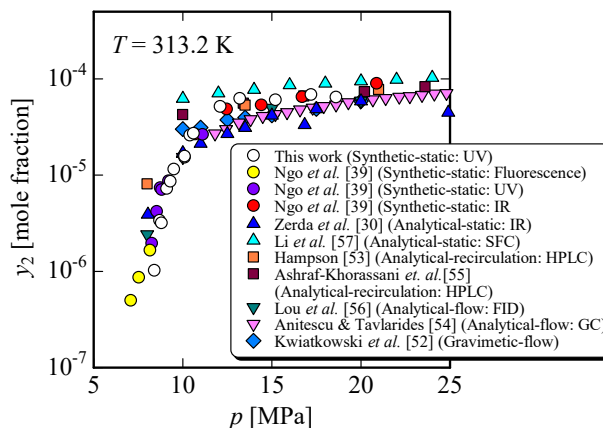


Fig. 5. Comparison of experimental results and literature data of solubility of anthracene in supercritical carbon dioxide at 313.2 K.

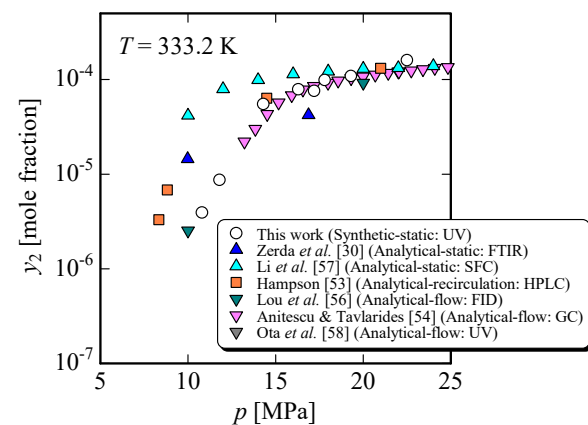


Fig. 6. Comparison of experimental results and literature data of solubility of anthracene in supercritical carbon dioxide at 333.2 K.

Table 1 Experimental solubility data of anthracene in supercritical carbon dioxide at 313.2 K.

T [K]	p [MPa]	y_2 [mole fraction]
313.2	8.35	1.02×10^{-6}
	8.67	3.39×10^{-6}
	8.77	3.18×10^{-6}
	9.08	7.27×10^{-6}
	9.25	8.64×10^{-6}
	9.49	1.15×10^{-5}
	10.05	1.53×10^{-5}
	10.13	1.57×10^{-5}
	10.42	2.60×10^{-5}
	10.57	2.72×10^{-5}
	12.06	5.17×10^{-5}
	13.19	6.27×10^{-5}
	15.21	6.05×10^{-5}
	17.21	6.88×10^{-5}
	18.61	6.47×10^{-5}
21.19	7.08×10^{-5}	
24.25	8.79×10^{-5}	

Table 2 Experimental solubility data of anthracene in supercritical carbon dioxide at 333.2 K.

T [K]	p [MPa]	y ₂ [mole fraction]
333.2	10.76	3.93×10 ⁻⁶
	11.85	8.70×10 ⁻⁶
	14.33	5.50×10 ⁻⁵
	16.25	7.87×10 ⁻⁵
	17.17	7.59×10 ⁻⁵
	17.83	9.87×10 ⁻⁵
	19.26	1.09×10 ⁻⁴
	22.46	1.60×10 ⁻⁴

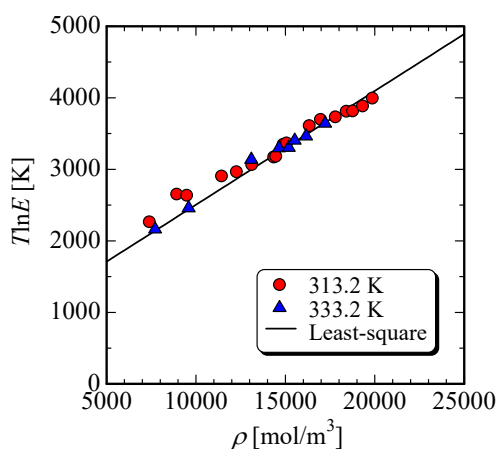


Fig. 7. Self-consistency of the experimental solubility data of anthracene in supercritical carbon dioxide.

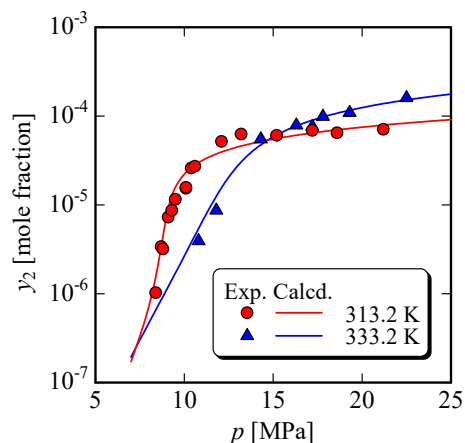


Fig. 8. Experimental and calculated solubility of anthracene in supercritical carbon dioxide.

References

- [1]. G. Brunner, Applications of supercritical fluids, *Annu. Rev. Chem. Biomol. Eng.*, 1, 2010, 321–342.
- [2]. Ž. Knez, E. Markočič, M. Leitgeb, M. Primožič, M. Knez Hrnčič, and M. Škerget, Industrial applications of supercritical fluids: A review, *Energy*, 77, 2014, 235–243.
- [3]. G. Sodeifian, and M.M.B. Usefi, Solubility, extraction, and nanoparticles production in supercritical carbon dioxide: A mini-review, *ChemBioEng Rev.*, 10, 2022, 133–166.
- [4]. R.B. Gupta, and J.-J. Shim, *Solubility in supercritical carbon dioxide* (Boca Raton, CRC Press, 2007).
- [5]. M. Škerget, Ž. Knez, and M. Knez-Hrnčič, Solubility of solids in sub- and supercritical fluids: A review, *J. Chem. Eng. Data*, 56, 2011, 694–719.
- [6]. Ž. Knez, D. Cör, and M. Knez Hrnčič, Solubility of solids in sub- and supercritical fluids: A review 2010–2017, *J. Chem. Eng. Data*, 63, 2018, 860–884.
- [7]. G.-T. Liu, and K. Nagahama, Solubility and RESS experiments of solid solution in supercritical carbon dioxide, *J. Chem. Eng. Japan*, 30, 1997, 293–301.
- [8]. M. Charoenchaitrakool, F. Dehghani, and N.R. Foster, Micronization by rapid expansion of supercritical solutions to enhance the dissolution rates of poorly water-soluble pharmaceuticals, *Ind. Eng. Chem. Res.*, 39, 2000, 4794–4802.
- [9]. A. Diefenbacher, and M. Türk, Phase equilibria of organic solid solutes and supercritical fluids with respect to the RESS process, *J. Supercrit. Fluids*, 22, 2002, 175–184.
- [10]. H. Uchida, K. Sekino, Y. Hayakawa, and S. Koda, Solubility of titanium diisopropoxide bis(dipivaloylmethanate) complex in supercritical carbon dioxide and its effect on supercritical fluid deposition process, *J. Supercrit. Fluids*, 66, 2012, 59–65.
- [11]. M. Türk, *Particle formation with supercritical fluids: Challenges and limitations* (Amsterdam, Elsevier, 2014).
- [12]. T. Momose, A. Kondo, T. Kamiya, H. Yamada, J. Ohara, Y. Kitamura, H. Uchida, Y. Shimogaki, and M. Sugiyama, Solubility of bis-(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) in mixed supercritical CO₂ and H₂ systems for application in supercritical fluid deposition of Cu, *J. Supercrit. Fluids*, 105, 2015, 193–200.
- [13]. H. Kwak, J. Woo, S.Y. Bae, and H. Kumazawa, Preparation of anthracene fine particles by rapid expansion of a supercritical solution process utilizing supercritical CO₂, *Korean J. Chem. Eng.*, 21, 2004, 1245–1249.

- [14]. J. Sakabe, and H. Uchida, Nanoparticle size control of theophylline using rapid expansion of supercritical solutions (RESS) technique, *Adv. Powder Technol.*, 33, 2022, 103413.
- [15]. T. Fujii, and H. Uchida; Crystal growth of anthracene thin films on silicon by rapid expansion of supercritical solutions (RESS) using carbon dioxide, *J. Chem. Eng. Japan*, 48, 2015, 787–794.
- [16]. T. Fujii, Y. Takahashi, and H. Uchida, Effects of solution concentrations on crystal growth of anthracene thin films on silicon by rapid expansion of supercritical solutions (RESS) using carbon dioxide, *J. Chem. Eng. Japan*, 48, 2015, 795–803.
- [17]. T. Fujii, Y. Takahashi, and H. Uchida, Deposition of tetracene thin films on SiO₂/Si substrates by rapid expansion of supercritical solutions using carbon dioxide, *App. Phys. Exp.*, 8, 2015, 035504.
- [18]. R. Kumar, A.K. Thakur, N. Banerjee, and P. Chaudhari, A critical review on the particle generation and other applications of rapid expansion of supercritical solution, *Int. J. Pharm.*, 608, 2021, 121089.
- [19]. J.M. Blackburn, D.P. Long, A. Cabañas, and J.J. Watkins, Deposition of conformal copper and nickel films from supercritical carbon dioxide, *Science*, 294, 2001, 141–145.
- [20]. M. Haruki, Y. Hasegawa, N. Fukui, S. Kihara, and S. Takishima, Deposition of aromatic polyimide thin films in supercritical carbon dioxide, *J. Supercrit. Fluids*, 94, 2014, 147–153.
- [21]. A.H. Romang, and J.J. Watkins, Supercritical fluids for the fabrication of semiconductor devices: Emerging or missed opportunities?, *Chem. Rev.*, 110, 2010, 459–478.
- [22]. S.B. Barim, E. Uzunlar, S.E. Bozbag, and C. Erkey, Review–Supercritical deposition: A powerful technique for synthesis of functional materials for electrochemical energy conversion and storage, *J. Electrochem. Soc.*, 167, 2020, 04510.
- [23]. T.J. Bruno, Thermophysical property data for supercritical fluid extraction design, in T.J. Bruno, and J.F. Ely (Eds.), *Supercritical fluid technology: Reviews in modern theory and applications* (Boca Raton, CRC Press, 1991) 293–324.
- [24]. K. Aim, and M. Fermeglia, Solubility of solids and liquids in supercritical fluids, in G.T. Hefter, R.P.T. Tomkins (Eds.), *The experimental determination of solubilities* (Chichester, John Wiley & Sons, 2003) pp.493–555.
- [25]. R. Dohrn, S. Peper, and J.M.S. Fonseca, High-pressure fluid-phase equilibria: Experimental methods and systems investigated (2000–2004), *Fluid Phase Equilib.*, 288, 2010, 1–54.
- [26]. H.B. Rad, J.K. Sabet, and F. Varaminian, Study of solubility in supercritical fluids: Thermodynamic concepts and measurement methods – A review, *Braz. J. Chem. Eng.*, 36, 2019, 1367–1392.
- [27]. G.L. Röbbling, and E.U. Franck, Solubility of anthracene in dense gases and liquids to 200 °C and 2000 bar, *Ber. Bunsenges. Phys. Chem.*, 87, 1983, 882–890.
- [28]. M.J. Carott, and C. Wai, UV-visible spectroscopic measurement of solubilities in supercritical CO₂ using high-pressure fiber-optic cells, *Anal. Chem.*, 70, 1998, 2421–2425.
- [29]. M. Haruki, F. Kobayashi, K. Kishimoto, S. Kihara, and S. Takishima, Measurement of the solubility of metal complexes in supercritical carbon dioxide using a UV-vis Spectrometer, *Fluid Phase Equilib.*, 280, 2009, 49–55.
- [30]. T.W. Zerda, B. Wlegand, and J. Jonas, FTIR measurements of solubilities of anthracene in supercritical carbon dioxide, *J. Chem. Eng. Data*, 31, 1986, 274–277.
- [31]. Y. Iwai, M. Uno, H. Nagano, and Y. Arai, Measurement of solubilities of palmitic acid in supercritical carbon dioxide and entrainer effect of water by FTIR spectroscopy, *J. Supercrit. Fluids*, 28, 2004, 193–200.
- [32]. K. Dujarric, I.T. Coutinho, G.T. Mantuanelli, T. Tassaing, and M. Champeau, Solubility of aspirin, ketoprofen and R(-)-carvone in supercritical CO₂ in binary, ternary and quaternary systems: Effect of co-solutes, *J. Supercrit. Fluids*, 189, 2022, 105697.
- [33]. W.C. Andersen, R.E. Sievers, A.F. Lagalante, and T.J. Bruno, Solubilities of cerium(IV), terbium(III), and iron(III) β -diketonates in supercritical carbon dioxide, *J. Chem. Eng. Data*, 46, 2001, 1045–1049.
- [34]. A.H. Haines, D.C. Steytler, and C. Rivett, Solubility dependence of peracylated D-glucopyranoses in supercritical carbon dioxide on the structure of their acyl moieties, *J. Supercrit. Fluids*, 44, 2008, 21–24.
- [35]. I. Rodriguez-Meizoso, P. Lazor, and C. Turner, In situ Raman spectroscopy for the evaluation of solubility in supercritical

- carbon dioxide mixtures, *J. Supercrit. Fluids*, 65, 2012, 87–92.
- [36]. R.S. Addleman, M.J. Carrott, and C.M. Wai, Determination of solubilities of uranium complexes in supercritical CO₂ by on-line laser-induced fluorescence, *Anal. Chem.*, 72, 2000, 4015–4021.
- [37]. H. Inomata, Y. Yagi, M. Saito, and S. Saito, Density dependence of the molar absorption coefficient—Application of the beer-lambert law to supercritical CO₂—Naphthalene mixture, *J. Supercrit. Fluids*, 6, 1993, 237–240.
- [38]. J.K. Rice, E.D. Niemeyer, and F.V. Bright, Evidence for density-dependent changes in solute molar absorptivities in supercritical CO₂: Impact on solubility determination practices, *Anal. Chem.*, 67, 1995, 4354–4357.
- [39]. T.T. Ngo, D. Bush, C.A. Eckert, Spectroscopic measurement of solid solubility in supercritical fluids, *AIChE. J.*, 47, 2001, 2566–2572.
- [40]. A.N. Aleshin, J.Y. Lee, S.W. Chu, J.S. Kim, and Y.W. Park, Mobility studies of field-effect transistor structures based on anthracene single crystals, *Appl. Phys. Lett.*, 84, 2004, 5383–5385.
- [41]. A. Sarve, J. George, S. Agrawal, R.V. Jasra, and P. Munshi, Unidirectional growth of organic single crystals of naphthalene, anthracene and pyrene by isothermal expansion of supercritical CO₂, *RSC Adv.*, 10, 2020, 22480–22486.
- [42]. K. Thirupugalmani, G. Shanmugam, V. Kannan, and S. Brahadeeswaran, Rapid growth of thin and flexible organic semiconductor single crystal anthracene by solution growth technique for device fabrication, *J. Cryst. Growth*, 413, 2015, 67–70.
- [43]. J. Sannigrahi, D. Bhadra, and B.K. Chaudhuri, Crystalline graphite oxide/PVDF nanocomposite gate dielectric: Low-voltage and high field effect mobility thin-film transistor, *Phys. Status Solidi A*, 210, 2013, 546–552.
- [44]. A.A. Al-Ghamdi, A.N. Nawar, F. El-Tantrawy, S.J. Yagmour, and A. Azam, Design and electrical characterization of Au/Anthracene/p-Si/Al organic/inorganic heterojunction, *J. Alloys Compd.*, 622, 2015, 243–249.
- [45]. H. Kaçus, Ş. Aydoğan, D. Ekinçi, S.V. Kurudirek, and A. Türüt, Optical absorption of the anthracene and temperature-dependent capacitance-voltage characteristics of the Au/anthracene/n-Si heterojunction in metal-organic-semiconductor configuration, *Physica E*, 74, 2015, 505–509.
- [46]. M. Chen, L. Yan, Y. Zhao, I. Murtaza, H. Meng, and W. Huang, Anthracene-based semiconductors for organic field-effect transistors, *J. Mater. Chem. C*, 6, 2018, 7416–7444.
- [47]. M.-H. Ho, B. Balaganesan, and C. H. (Fred) Chen, Blue fluorescence and bipolar transport materials based on anthracene and their application in OLEDs, *Isr. J. Chem.*, 52, 2012, 484–495.
- [48]. A.M. Nawar, and I.S. Yahia, Fabrication and characterization of anthracene thin films for wide-scale organic optoelectronic applications based on linear/nonlinear analyzed optical dispersion parameters, *Opt. Mater.*, 70, 2017, 1–10.
- [49]. J. Chrastil, Solubility of solids and liquids in supercritical gases, *J. Phys. Chem.*, 86, 1982, 3016–3021.
- [50]. H. Uchida, Calculation methods for physical properties of supercritical carbon dioxide + solid solutes systems (in Japanese), *J. Soc. Sep. Process Engineers, Japan (Bunri gijutsu)*, 41, 2011, 149–162.
- [51]. R. Span, and W. Wagner, 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*, 25, 1982, 1509–1596.
- [52]. J. Kwiatkowski, Z. Lisicki, and W. Majewski, An experimental method for measuring solubilities of solids in supercritical fluids, *Ber. Bunsenges. Phys. Chem.*, 88, 1984, 865–869.
- [53]. J.W. Hampson, A recirculating equilibrium procedure for determining organic compound solubility in supercritical fluids. Anthracene in carbon dioxide, *J. Chem. Eng. Data*, 41, 1996, 97–100.
- [54]. G. Anitescu, and L.L. Tavlarides, Solubilities of solids in supercritical fluids—I. New quasistatic experimental method for polycyclic aromatic hydrocarbons (PAHs) + pure fluids, *J. Supercrit. Fluids*, 10, 1997, 175–189.
- [55]. M. Ashraf-Khorassani, M.T. Combs, L.T. Taylor, F.K. Schweighardt, and P.S. Mathias, Solubility study of sulfamethazine and sulfadimethoxine in supercritical carbon dioxide, fluoroform, and subcritical freon 134A, *J. Chem. Eng. Data*, 42, 1997, 636–640.
- [56]. X. Lou, H.-G. Janssen, and C.A. Cramers, Temperature and pressure effects on solubility in supercritical carbon dioxide and

- retention in supercritical fluid chromatography, *J. Chromatogr. A*, 785, 1997, 57–64.
- [57]. B. Li, W. Guo, and E.D. Ramsey, Measuring the solubility of anthracene and chrysene in supercritical fluid carbon dioxide using static solubility apparatus directly interfaced online to supercritical fluid chromatography, *J. Chem. Eng. Data*, 63, 2018, 651–660.
- [58]. M. Ota, Y. Hashimoto, M. Sato, Y. Sato, R.L.Smith Jr., and H. Inomata, Solubility of flavone, 6-methoxyflavone and anthracene in supercritical CO₂ with/without a co-solvent of ethanol correlated by using a newly proposed entropy-based solubility parameter, *Fluid Phase Equilib.*, 425, 2016, 65–71.
- [59]. J. Méndez-Santiago, and A.S. Teja, The solubility of solids in supercritical fluids, *Fluid Phase Equilib.*, 158–160, 1999, 501–510.
- [60]. R.M. Stephaneson, and S. Malanowski, *Handbook of the thermodynamics of organic compounds* (New York, Elsevier, 1987), p.390.