Turnitin Originality Report

je200239p by Suryadi Ismadji

From paper 2 (Hippo-hippo 02)

Processed on 16-Feb-2018 14:39 WIB
ID: 916894511
Word Count: 3065

Similarity Index	Similarity by Source	
19%	Internet Sources:	9%
	Publications:	16%
	Student Papers:	6%

sources:

1 2% match (Internet from 02-Jan-2017)
https://www.benthamopen.com/ABSTRACT/TOCENGJ-10-18

2 2% match (student papers from 27-Jan-2012)
Submitted to iGroup on 2012-01-27

3 1% match (Internet from 30-Aug-2017)
https://brage.bibsys.no/xmlui/bitstream/handle/11250/2437779/PhD_Thesis.pdf?isAllowed=y&sequence=2

4 1% match (publications)
Lin, H.m.. "Solubilities of disperse dyes of blue 79:1, red 82 and modified yellow 119 in supercritical carbon dioxide and nitrous oxide", The Journal of Supercritical Fluids, 200412

5 1% match (publications)
Hugo Segura. "Phase Equilibria in the Systems Cyclohexane + 2,2,4-Trimethylpentane and Ethyl 1,1-Dimethylethyl Ether + Cyclohexane + 2,2,4-Trimethylpentane at 94.00 kPa", Journal of Chemical & Engineering Data, 07/2000

6 1% match (publications)
Vandana Sharma, Suresh Walia, Jitendra Kumar, Muraleedharan G. Nair, Balraj S. Parmar. "An Efficient Method for the Purification and Characterization of Nematicidal Azadirachtins A, B, and H, Using MPLC and ESIMS", Journal of Agricultural and Food Chemistry, 2003

7 1% match (publications)
Garlapati, C.. "Solubilities of solids in supercritical fluids using dimensionally consistent modified solvate complex models", Fluid Phase Equilibria, 20090915

8 1% match (publications)
Renzo Carta. "Solubilities of l-Cystine, l-Tyrosine, l-Leucine, and Glycine in Their Water Solutions", Journal of Chemical & Engineering Data, 05/1999

9 1% match (publications)
Hiroyuki Matsuda, Sho Matsumoto, Kenta Kaguragi, Kiyofumi Kurihara, Katsumi Tochigi, Kazuo Tomono. "Determination and correlation of solubilities of famotidine in water+co-solvent mixed solvents", Fluid Phase Equilibria, 2011

10 1% match (Internet from 01-Oct-2012)

http://jchpe.ir/jufile?
c2hvd1BERj0xNTE0Jl9hY3Rpb249c2hvd1BERiZhcnRpY2xlPTE1MTQmX29iPSZmaWxlTmFtZT1mdWxsX3RleHQu

---

11 1% match (Internet from 25-Nov-2017)
https://kanazawa-u.repo.nii.ac.jp/?
action=repository_action_common_download&attribute_id=31&file_no=1&item_id=36169&item_no=1

---

12 1% match (publications)
Zhen Yao. "Solubility of Subcritical and Supercritical Propylene in Semicrystalline Polypropylene", Journal of Chemical & Engineering Data, 04/14/2011

---

13 1% match (publications)
Asiabi, Hamid, Yadollah Yamini, Farzad Latifeh, and Alireza Vatanara. "Solubilities of four macrolide antibiotics in supercritical carbon dioxide and their correlations using semi-empirical models", The Journal of Supercritical Fluids, 2015.

---

14 1% match (Internet from 01-Oct-2016)
https://pt.scribd.com/document/73719826/10-1-1-116

---

15 1% match (student papers from 23-Oct-2012)
Submitted to Michigan Technological University on 2012-10-23

---

16 1% match (Internet from 15-Jan-2018)
http://pubs.rsc.org/en/content/articlepdf/2015/ra/c5ra15419g?page=search

---

17 1% match (publications)
Tang, Zhao, Jun-su Jin, Ze-ting Zhang, and Hong-tao Liu. "New Experimental Data and Modeling of the Solubility of Compounds in Supercritical Carbon Dioxide", Industrial & Engineering Chemistry Research, 2012.

---

18 1% match (publications)
Bera, Achinta, Ajay Mandal, Keka Ojha, and T. Kumar. "Water Solubilization Capacity and Conductance Behaviors of Anionic and Cationic Microemulsion Systems", Journal of Chemical & Engineering Data, 2011.

paper text:

pubs.acs.org/jced

6**Solubility of Azadirachtin in Supercritical Carbon Dioxide at Several Temperatures Suryadi Ismadji,*,† Yi-Hsu Ju,‡ Felycia Edi Soetaredjo,† and Aning Ayucitra†**

1**†Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia ‡Department of Chemical Engineering, National Taiwan University of Science and**

Technology, 43, sec. 4 Keelung Rd., Taipei, 106 Taiwan ABSTRACT: The solubility data of azadirachtin **in supercritical carbon dioxide were measured**

at several temperatures (308.15, 313.15, 318.15, 323.15, 328.15, and 333.15 K) and at pressure between (10 and 26) MPa. The measurement of solubility data

16**was conducted in** static **mode. The** experimental results **were correlated by**

Chrastil model and Del valle and Aguilera equation. Chrastil model can represent the experimental data well and give a reasonable value for fitting parameters. ’ INTRODUCTION Azadirachtin is a chemical compound belonging to the limo- noids and one of more than 70 limonoids produced by the neem tree. Azadirachtin has a complex structure, and the IUPAC name of this compound is dimethyl (2aR,3S,4S,R,S,7aS,8S,10R,10aS, 10bR)-10-(acetyloxy)- 3,5-dihydroxy-4-[(1S,2S,6S,8S,9R,11S)-2-hydroxy-11-methyl-5,7,10-trioxatetracyclo[6.3.1.02,6.09,11]dodec-3- en-9-yl]-4-methyl-8-{[(2E)-2-methylbut-2-enoyl]oxy}octahydro- 1H-furo[30,40:4,4a]naphtho[1,8-bc]furan-5,10a(8H)-dicarboxylate. The molecular structure of azadirachtin is given in Figure 1. Azadirachtin has an insecticidal effect; therefore, it can be used as a natural insecticide.1 5 Azadirachtin and related limonoids are obtained from neem seeds by solvent extraction followed by several steps of separation and purification to obtain a high purity product. Purification of azadirachtin from the extract or oil can be conducted using various methods such solvent precipitation,6 and combination of several chromatography techniques.7 10 Ex- traction of azadirachtin using supercritical fluid technology has also been explored,11 13 but this technique did not give complete recovery.14 The failure of supercritical extraction technology to recovery completely of azadirachtin from its extract may be due to incorrect operation condition because of the lack of information about the solubility of this substance

4**in supercritical carbon dioxide at various temperatures and pressures. The solubility**

of solids and liquids in supercritical fluids is very important information for the design of any supercritical extrac- tion processes.15 Currently, there is no information about the solubility of azadirachtin in supercritical carbon dioxide available in the literature.

14**In this study,** solubilities **of** azadirachtin **in** supercritical **carbon dioxide** were measured **at several**

tempera- tures in a range of pressures from (10 to 26) MPa. The experimental data were then correlated by the Chrastil equation and its modified form. ’ MATERIAL AND METHODS Material. Azadirachtin is a microcrystalline powder with a melting point of 447.15 K and 1.4.14 Azadirachtin

16**used in this study** was **obtained as** a analytical standard **from Sigma-Aldrich**

r 2011 American Chemical Society (CAS no: 11141-17-6) and used without any further purification. Food grade carbon dioxide obtained from Aneka Gas Pty Ltd. was used as the supercritical solvent and supplied as liquid CO_2 with a mole fraction purity of 0.999. ’ EXPERIMENTAL PROCEDURE The schematic diagram of supercritical equipment

9**used in this study to** obtain the **solubility data** of azadirachtin **is given in** Figure **2.**

The supercritical equipment consists of a high pressure pump (Eldex AA-100-S-2-CE, U.S.A.), a pressure transducer (Druck PTX 611, U.S.A.) with a digital process indicator (Druck DPI 280, U.S.A.), a heater and temperature controller (oven Memmert, Germany), a vacuum pump (GAST DOA-P504 BN, U.S.A.), a volume calibrator (ZEAL DM3B, U.K.), and an equilibration column (Swagelok, U.S.A.). All fitting and tubing used in the system are made of stainless steel (Swagelok, U.S.A.). The maximum working pressure and temperature of the super- critical system are 30 MPa and 373.15 K, respectively.

11**The uncertainties of the** pressure **and** temperature **measurements were (0.** 01 MPa **and** (1 K, **respectively.** To measure **the**

solubility of azadirachtin in supercritical CO2, the following procedure was employed:15 the sample holder in the equilibration column was loaded with azadirachtin. The system was evacuated using a vacuum pump (GAST DOA- P504 BN, U.S.A.) to remove air, and then the system was heated until the desired temperature was reached. Subsequently, the liquid CO2 was pumped to the equilibration column using a high pressure pump (Eldex AA-100-S-2-CE, U.S.A.). During the experiments, valves

15**V-3, V-4, and V-5 were closed,**

while

15**valves V-1 and V-2 were opened.** After equilibrium of **the**

desired temperature and pressure was achieved (4 h), the sampling tube was disconnected from the system by closing valve V-2.15 The sample in the sampling tube was released to the collector containing

18**Special Issue: Kenneth N. Marsh Festschrift Received: March** 9, **2011 Accepted: April 22, 2011 Published:** April 29, **2011**

a known amount of methanol to completely separate azadirachtin and carbon dioxide. At least three replicated samples

4**were taken at** an **experimental condition,** and **the** equilibrium composition **was** determined **by averaging** the **replications. The uncertainty of** each measurement **was**

within (2 %. The concentration of azadirachtin in methanol was determined by HPLC technique. ’ RESULTS AND DISCUSSIONS The densities of

4**supercritical carbon dioxide at** various pres- sures **and temperatures**

are calculated from the Stryjek and Vera modification of the Peng Robinson equation of state,16 and the results

6**are reported in Table 1. The** solubilities **of azadirachtin**

in supercritical CO2 at various pressures and temperatures are given in Table 2. At 10 MPa, the solubility of azadiracthin decreases with increases of temperature. At pressures above 10 MPa, as the temperature increases, the solubility of the compound also increases. This phenomenon indicates that a crossover pressure region is present in the system.

10**Below the crossover region, the effect of density is more dominant than vapor pressure, indicated by** a **decrease of solubility as the temperature increases,**

whereas above crossover region, the effect of vapor pressure is more dominant (solubility of azadiracthin increases with increases of temperature). Plots of solubility data of azadiracthin in super- critical carbon dioxide

14**as a function of temperature** are given **in Figure 3. The** experimental **solubility**

data were correlated by several semi empirical models. The density-based correlation method is Figure 1. Molecular structure of azadirachtin. widely

17**used to correlate the** experimental **solubility data. This**

approach was developed based on the common observation that the logarithm of the solubility is linearly dependent on the density. Chrastil17 developed a semiempirical model based on this approach; his model has the form as follows: y2 ¼ Fk expða=T þ bÞ ð1Þ where y2

11**is the solubility of the solute in** gas, F **is the density of**

gas, k is

7**an association number, a** is a **function of the enthalpy of solvation and enthalpy of vaporization,** and b is **a function of the association number and molecular weights of the solute and supercritical**

fluids. The fitting of the solubility experimental data was conducted at each temperature using nonlinear least-squares technique by minimizing the sum of squared errors as objective function !1=2 ð∑y2ðexpÞ y2ðcalÞÞ2 SSE ¼ N ð2Þ Here y2(exp) is the actual solubility of azadiracthin in supercritical CO2, y2(cal) is the calculated solubility,

17**and N is the number of experimental data. The**

nonlinear squares technique involves an Table 1. Density of Supercritical CO2 at Various Pressures and Temperatures p F/kg 3 m 3 MPa

3**308.15 K 313.15 K 318.15 K 323.15 K 328.15 K 333.15 K**

10 12 14 16 18 20 22 24 26 655 726 773 809 838 863 885 905 922 568 463 669 605 727 678 769 728 803 767 831 798 856 825 877 849 896 870 378 327 537 472 627 574 685 642 729 691 765 730 794 763 820 791 843 816 294 417 523 598 653 696 732 762 788 Figure 2. Schematic diagram of supercritical equipment 1. Liquid CO2 cylinder. 2. High pressure pump system. 3. Equilibration cylinder. 4. High pressure transducer. 5. Sampling tube. 6. Temperature controller. 7. Low pressure transducer. 8. Collecting tank. 9. Vacuum pump. 10. Volume calibrator. 11. Helium cylinder. Table 2. Experimental Solubility Data of Azadiracthin in Supercritical Carbon Dioxide p 106 y2 MPa

3**308.15 K 313.15 K 318.15 K 323.15 K 328.15 K 333.15 K**

10 12 14 16 18 20 22 24 26 2.1 2.6 3.0 3.4 3.6 4.1 4.3 4.5 4.8 1.9 1.6 2.9 3.1 3.6 4.2 4.2 4.8 4.6 5.7 5.1 6.3 5.5 6.8 5.8 7.3 6.1 7.8 1.3 1.2 3.1 3.0 4.6 5.0 5.8 6.6 6.8 8.0 7.6 9.1 8.4 10.2 9.1 11.3 9.8 12.2 1.2 2.9 5.3 7.4 9.3 10.9 12.4 13.7 14.9 Figure 3. Solubility of azadirachtin on supercritical CO2 as function of pressure. b, Experimental data

8**at 308.15 K; 4,** experimental **data at** 313 **.15 K;**

9, experimental data at 318

5**.15 K; O, experimental data at** 323 **.15 K;** 2, **experimental data**

at 328

12**.15 K;** 0, **experimental data at** 333 **.15 K.**

iterative curve fitting procedure. In this procedure, an initial set of estimates for the parameters in the equation must be provided, and then calculation of a point by point sum of squares (eq 2) for each iteration will be conducted. The algorithm will modify each parameter value until it satisfies the convergence criteria to obtain a final solution. Figure 4 shows

13**that the Chrastil equation can represent the experimental solubility data of** azadiracthin **in** supercritical CO2 very **well.**

The advantage of using the Chrastil equation is the model does not require any physical chemical property data of the solute. Therefore this equation is applicable in most cases. The optimal parameters from the fitting of the Chrastil model are given in Table 3. The parameters of k, a, and b for the system of CO2(1) þ azadiracthin (2) are almost constant as indicated in Table 3. As mentioned before, k is an association number. Therefore this value should be specific for a given system, and the parameter of k obtained from this study is consistent. The parameter a is a function of the enthalpy of solvation and enthalpy of vaporization, and this parameter should increase with the increase of temperature; however, since the solubilities of azadiracthin in supercritical CO2 are very small (Table 2), changes in the enthalpy of salvation and enthalpy of vaporization Figure 4. Experimental solubility data as a function of density (shown in logarithmic scale) and those estimated from the Chrastil equation (eq 1) by minimizing eq 2. b, Experimental data

8**at 308.15 K; 4,** experimental **data at** 313 **.15 K;**

9, experimental data at 318

5**.15 K; O, experimental data at** 323 **.15 K;** 2, **experimental data**

at 328

12**.15 K;** 0, **experimental data at** 333 **.15 K;**

—, Chrastil model. Table 3. Fitted Chrastil Equation Parameters for CO2 (1) þ Azadirachtin (2) T parameter SSE K k a b % 308.15 313.15 318.15 323.15 328.15 333.15 2.511 2.551 2.534 2.535 2.551 2.541 6270.1 6303.3 6275.4 6260.1 6264.6 6246.2 9.052 9.213 9.191 9.244 9.325 9.308 0.18 0.14 0.17 0.09 0.15 0.17 are not considered by this equation. Therefore this parameter in the system of CO2(1) þ azadiracthin (2) remains constant. The last parameter b

9**is a function of the association number and the molecular weights of the solute and**

supercritical fluids. Since the molecular weight of azadiracthin is constant and the association number of the solute is specific for each solute, this parameter should not be influenced by temperature. The fitting values of the parameter b at different temperatures are essentially constant, which is consistent with the physical meaning of this parameter. Del Valle and Aguilera18 proposed another density-based model based on Chrastil's equation. Their model considered the change in the enthalpy of vaporization with temperature y2 ¼ Fk0 exp b0 þ a0 T þ d T 2 ð3Þ The meaning of the parameters k0, b0, and a0 is similar to that of the parameters in the Chrastil model. The parameter d0 is a parameter associated with the change in enthalpy of vaporization.

13**This equation can represent the experimental data well,**

as shown in Figure 5. The parameters of eq 3 obtained from fitting experimental data are given in Table 4. Even if this equation can fit the experimental data well, however, considerably varying values of parameters b0, a0, and d were obvious. This inconsistency indicates a drawback in using this equation to correlate the solubility data of Figure 5. Experimental solubility data as a function of density (shown in logarithmic scale) and those estimated from the Del Valle and Aguilera model (eq 3) by minimizing eq 2. b, Experimental data

8**at 308.15 K; 4,** experimental **data at** 313 **.15 K;**

9, experimental data at 318

5**.15 K; O, experimental data at** 323 **.15 K;** 2, **experimental data**

at 328

12**.15 K;** 0, **experimental data at** 333 **.15 K;**

—, Del Valle and Aguilera model. Table 4. Fitted Del Valle and Aguilera Model Parameters for CO2 (1) þ Azadirachtin (2) T parameter SSE K k0 a0 b0 d % 308.15 313.15 318.15 323.15 328.15 333.15 2.511 2.550 2.534 2.535 2.551 2.541 19.31 42.73 36.13 10.49 14.60 9.13 12590 20101 4808 3408 2041 3773 745353 772497 799470 791069 817174 843531 0.18 0.14 0.18 0.13 0.15 0.16 azadiracthin in supercritical carbon dioxide. The deviations of experimental data to the models of Del Valle Aguilera and Chrastil are close as indicated in Tables 3 and 4. As mentioned before, the Del Valle and Aguilera model was developed based on the Chrastil model; therefore, this model will give a similar trend to the Chrastil equation in predicting the experimental data. ’ CONCLUSION New

1**solubility data of** azadirachtin **in supercritical carbon dioxide were**

obtained in this study. The solubility data were correlated by the Chrastil model and teh Del Valle and Aguilera equation. The Chrastil model can represent the experimental data well and give a reasonable value of the fitting parameters. ’ AUTHOR INFORMATION Corresponding Author *E-mail: suryadiismadji@yahoo.com. Tel.: þ62313891264. Fax: þ62313891267. Funding Sources This work was supported by Directorate General of Higher Education, Indonesia Ministry of Education through Competency Grant 2010. ’ REFERENCES (1) Denardi, S. E.; Bechara, G. H.; Oliveira, P. R. D.; Camargo- Mathias, M. I. Azadirachta indica A. Juss (neem) induced morphological changes on oocytes of Rhipicephalus sanguineus (Latreille, 1806) (Acari: Ixodidae) tick females. Exp. Parasitol. 2010, 126, 462–70. (2) McKenzie, N.; Helson, B.; Thompson, D.; Otis, C.; McFarlane, J.; Buscarini, T.; Meating, J. Azadirachtin: An effective systemic insecti- cide for control of agrilus planipennis (Coleoptera: Buprestidae). J. Econ. Entomol. 2010, 103, 708–717. (3) Cherry, R.; Nuessly, G. Repellency of the biopesticide, azadir- achtin, to wireworms (Coleoptera: Elateridae). Fla. Entomol. 2010, 93, 52–55. (4) Lu, H.-Y.; Liu, F.; Zhu, S.-D.; Zhang, Q. Effects of azadirachtin on rice plant volatiles induced by Nilaparvata lugens. Chin. J. Appl. Ecol. 2010, 21, 197–202. (5) Ganguly, S.; Bhattacharya, S.; Mandi, S.; Tarafdar, J. Biological detection and analysis of toxicity of organophosphate- and azadirachtin- based insecticides in Lathyrus sativus L. Ecotoxicology 2010, 19, 85–95. (6) Melwita, E.; Ju, Y. H. Separation of azadiracthin and other limonoids from crude neem oil via solvent precipitation. Sep. Purif. Technol. 2010, 74, 219–224. (7) Yamasaki, R. B.; Klocke, J. A.; Lee, S. M.; Stone, G. A.; Darlington, M. V. Isolation and purification of azadiracthin from neem (Azadiractha indica) seeds using flash chromatography and high perfor- mance liquid chromatography. J. Chromatogr. 1986, 356, 220–226. (8) Govindachari, T. R.; Sandhya, G.; Raj, S. P. G. Simple method for the isolation of azadirachtin by preparative high-performance liquid chromatography. J. Chromatogr. 1990, 513, 389–391. (9) Schroeder, D. R.; Nakanishi, K. A simplified isolation procedure for azadiracthin. J. Nat. Prod. 1987, 50, 241–244. (10)

Sharma, V.; Walia, S.; Kumar, J.; Nair, M. G.; Parmar, B. S. An efficient method for the purification and characterization of nematicidal azadirachtins A, B, and H using MPLC and ESIMS. J. Agric. Food Chem. 2003, 51, 3966–3997. (11) Ambrosino, P.; Fresa, R.; Fogliano, V.; Monti, S. M.; Ritieni, A. Extraction of azadirachtin a from neem seed kernels by supercritical fluid and its evaluation by HPLC and LC/MS. J. Agric. Food Chem. 1999, 47, 5252–5256. (12) Johnson, S.; Morgan, E. D. Supercritical fluid extraction of oil and triterpenoids from Neem seeds. Phytochem. Anal. 1997, 8, 228–232. (13) Brooks, M. W.; Roy, S.; Uden, P. C.; Vittum, P. The extraction and determination of azadirachtin from soil and insects by supercritical fluid extraction. J. Test. Eval. 1996, 24, 149–153. (14) Morgan, E. D. Azadirachtin, a scientific gold mine. Bioorg. Med. Chem. 2009, 17, 4096–4105. (15) Ismadji, S. Solubility of methyl salicylate in supercritical carbon dioxide at several temperatures. J. Chem. Eng. Data 2008, 53, 2207–2210. (16) Stryjek, R.; Vera, J. H PRSV: An Improved Peng Robinson Equation of State for Pure Compounds and Mixtures. Can. J. Chem. Eng. 1986, 64, 323–333. (17) Chrastil, J Solubility of solids and liquids in supercritical gases. J. Phys. Chem. 1982, 86, 3016–3021. (18) del Valle, J. M.; Aguilera, J. M. An improved equation for predicting the solubility of vegetable oils in supercritical CO2. Ind. Eng. Chem. Res. 1988, 27, 1551–1553.

2**ARTICLE Journal of Chemical & Engineering Data ARTICLE Journal of Chemical & Engineering Data ARTICLE Journal of Chemical & Engineering Data ARTICLE** 4396 **dx.doi.org/10.1021/** je200239p | **J. Chem. Eng. Data 2011, 56,** 4396–4399 4397 **dx.doi.org/10.1021/** je200239p **|J. Chem. Eng. Data 2011, 56,** 4396–4399 4398 **dx.doi.org/10.1021/** je200239p **|J. Chem. Eng. Data 2011, 56,**

4396–4399 4399 dx.doi.org/10.1021/je200239p |J. Chem. Eng. Data 2011, 56, 4396–4399