**A Novel Equation of State:**

**Determination and Validation for Dyes and Drugs Solubility Calculations in Supercritical Carbon Dioxide**

**Abstract**

Based on Pitzer correlations for the compressibility factor and virial equation of state, a new equation of state has been developed in this study, which is a function of total number of atoms present in the solute molecule, normal boiling point temperature and reduced temperature. Thirty dyes and sixty drugs solubility data, 2417 data points, have been collected from literature and compared with the Peng-Robinson EOS plus the two adjustable parameters van der Waals mixing rules, and the new proposed EOS. As the results show, the proposed EOS presents more accurate predictions for solubility data in Supercritical Carbon Dioxide.

**Keywords:**Carbon dioxide; Phase Equilibria; State equation; Supercritical fluid; Thermodynamics Process; Solubility.

**1. Introduction**

Supercritical fluid processes have been attracted considerable attentions in recent years. This technology is increasingly applied in chemical and petroleum, pharmaceutical, food, biotechnology, biomedical, nuclear, material and polymer processing industries [[1-18](#_ENREF_1)]. The need for automated, simpler, faster, non-destructive and selective methods for extraction preferably can be fulfilled by employing supercritical fluid technology using non-toxic extraction media, which are easily disposed of. Supercritical fluids have unique physical and chemical properties and usually low toxicity and this technology is an environment friendly one. By setting suitable operating condition (temperature, pressure and density) a desired selectivity can be obtained which leads to a variation in solvating power [[19](#_ENREF_19)].Supercritical fluids are categorized as rapid processes due to high diffusivity and lower viscosity. One of the most commonly used supercritical fluids is carbon dioxide. The critical temperature and pressure of carbon dioxide is relatively low, 304 K and 73.7 bar, respectively. Supercritical carbon dioxide is low in cost, nontoxic, and nonflammable, and the carbon dioxide can be recycled and has no environmental hazard [[20](#_ENREF_20), [21](#_ENREF_21)].

For the design of supercritical fluid process, there is a vital need to know about the solubility data and mathematical modeling of these solubility data [[22-25](#_ENREF_22)]. In fact, mathematical modeling provides better understanding of the process and also can be used for the prediction of solubility at interested pressures and temperatures. Mathematical modeling leads to different equations of solubility data in supercritical carbon dioxide. Generally, these models are classified into two groups: theoretical or semi-empirical equations (such as models based on equations of state), and empirical equations (such as density based equations).

Some researchers tend to use empirical correlations such as density-based correlations [[26-28](#_ENREF_26)] or the Ziger–Eckert semi-empirical correlations [[29](#_ENREF_29)]. These models are based on the simple error minimization and they use only density of pure supercritical carbon dioxide and operational pressure and temperature. Several equations have been presented by different authors, covering from three to six parameters, which are necessary to determine solutes solubility. But these empirical correlations require accurate experimental solubility data in order to obtain the best coefficients of the models.

On the other hand, using theoretical models such as cubic equation of state require the knowledge of the solute (dyes here) properties including critical properties, acentric factor, molar volumes and sublimation pressure. These properties should be calculated using some group contribution method if these data are unavailable in the literature [[30](#_ENREF_30)].

Based on Pitzer correlations [[31](#_ENREF_31)] for the compressibility factor and virial equation, a new equation of state has been developed in this study as the supercritical fluids are assumed like a gas in modeling. The new equation is a function of n, total number of atoms present in the solute molecule, and Tb, normal boiling point temperature and reduced temperature. Solubility data of thirty dyes and sixty drugs are collected from literature and correlated with the Peng-Robinson EOS [[32](#_ENREF_32)] plus the two adjustable parameters van der Waals mixing rules, and the proposed EOS. Two types of components i.e. dyes and drugs are used to ensure the generality of the obtained EOS. As the results show, the proposed EOS presents more accurate predictions for solubility data in Supercritical Carbon Dioxide.

**2. Theoretical**

**2.1. Peng-Robinson EOS (PR EOS)**

The solubility of a solute at equilibrium with a supercritical fluid can be calculated using Eq. 1.

 (1)

In solubility calculation using Eq. 1, an equation of state is used to calculate the fugacity coefficient which representing the non-ideality of the fluid phase. Here  is the saturation pressure of solute, which can be measured experimentally or calculated using some estimation methods from literature.  is the molar volume of the solute.

The Peng-Robinson equation of state (PR-EOS) which is commonly used in studies is defined as follows.

 (2)

 (3)

 (4)

 (5)

For a binary mixture the PR-EOS needs some mixing rules. In this study we employed the van der Waals (vdW) mixing rules, with two adjustable parameters, kij and lij (vdW2).

 (6)

 (7)

kij and lij are the binary interaction parameters which are obtained by fitting experimental data and through minimization of an objective function. The fugacity coefficient for a component i in a mixture is given by Prausnitz using mixing rules as follows[[33](#_ENREF_33)].

 (8)

Here yj is the mole fraction of component j.

**2.2. Theory of Proposed Equation of State**

For development of the new EOS, Berlin virial EOS which is power series in pressure has been used preferably.

 (9)

Where coefficients,  and etc. are virial equivalent coefficients.

 (10)

Pitzer and Curl[[34](#_ENREF_34)] proposed a correlation for  (=) as follows.

 (11)

Here the function  represents the reduced second virial coefficient for simple fluid, i.e. ω=0 and the function  is a correlation represents the effect of eccentricity. These two functions were obtained from experimental data and modified by[[35](#_ENREF_35)]. Pitzer et al. proposed a second correlation for [[31](#_ENREF_31)].

 (12)

Where  and  are function of Tr only and given by following equations.

 (13.a)

 (13.b)

Orbey and Vera [[36](#_ENREF_36)] expressed the reduced temperature depended coefficients of a Pitzer type correlation for , which itself is related to third virial coefficient through , as illustrated for B as follows.

 (14.a)

 (14.b)

So following equations can be obtained for  and.

 (15)

 (16)

As mentioned previously,,,  and  are functions of reduced temperature only. According to Lee and Kessler equation for acentric factor, it can be seen that ω is a function of critical temperature and pressure, and also normal boiling point temperature. As critical properties such as critical temperature and pressure for all materials always can’t be measured experimentally or their values aren’t available in literature, one has to use some group contribution methods like Joback and Reid method for calculation of their value. In fact, Group Contribution Methods relate these critical properties to chemical structure of materials [[37](#_ENREF_37)]. Thus, From the work of Joback and Reid, it’s can be shown that critical temperature and pressure, themselves, are a function of total number of atoms present in material, n, and normal boiling point temperature, Tb, in the form of following equation.

 (17)

Here is the critical property of interest. ,  and  are constants for each critical property of interest. So far, we qualitatively found that acentric factor and critical temperature and pressure, and consequently virial coefficients, can be expressed as functions of n and Tb. Finding these desired functions, new functions can be found for virial coefficients of Eq. 9 by introducing Eq. 15 and 16 into it and the new EOS is obtained. The experimental data of 30 dyes and 60 drugs were used to formulate the critical temperature in the form of Eq. 17 and finding its coefficients. Where there’s an absent of experimental normal boiling point temperature data, one can use some group contribution method for estimation of Tb. Equation 18 shows this new obtained relation in this work for Tc (**R2>0.99**). The reason for such replacement is that the need for complicated calculations of chemical structure and arrangement of bonds and groups could be resolved in this way. Then the applicability of obtained new equation for Tc calculation, Eq. 18, for other materials was validated using the available data of 60 drugs and it found that the Eq. 18 can be used for other materials also.

 (18)

In development of the new EOS, M is defined as the ratio of P and T (), the operating parameter of new EOS. The definition is with regard to the appearance of the reciprocal of T in Eq. 15 and 16 and P in corresponding term in Eq. 9. So by this definition, T and P are merged as the new parameter M. This definition also makes the estimation of Pc possible as formulation of critical pressure in the form of Eq. 17 will never result in constant coefficients. The critical pressure appears in nominator of the critical M, Mc. So by finding the functionality of Mc to n and Tb, the critical pressure can be determined indirectly, in other words Pc can be calculated by multiplying Tc into the Mc. Equation 19 is derived and validated in the way described above for Tc in this work (**R2>0.99**).

 (19)

So the critical value of M, Mc, together with Eq. 18 can be used to estimate the critical pressure. Moreover ω can be calculated using following new proposed equation in this paper (**R2>0.98**).

 (20)

Inserting Eq. 15 and 16 into Eq. 9, the general form of new EOS is formed as Eq. 21. Separating the new parameter M in each term, what remains is the general coefficient of new EOS, A (1) and A (2).

 (21)

The coefficients A (1) and A (2) are formulated in a Pitzer like form as shown Eq. 22 and 22.

 (22)

 (23)

Here A (1) and A (2) are two different functions of new independent variables n and Tb, and as well as Tr, structural parameters. For development of these two coefficients of new EOS and their parameters, the obtained equations for critical properties, acentric factor, and the new parameter M are used and the coefficients of these parameters are found. Then the drugs data are used for evaluation of applicability and generality of coefficients and formulas for using for materials other than the dyes. The obtained functions of these parameters as a function of new independent variable Tb and n are (All with **R2>0.99**).

 (24)

 (25)

 (26)

And for A (2) we have also

 (27)

 (28)



 (29)



Although that choosing coefficients A (1) and A (2) in a Pitzer like form leads to these complicated relationships (Eq. 24-29), but attentions would be given to the accuracy that can be achieved using this EOS with these parameters which will be shown in **section 4**.

In order to use this new EOS for a binary mixture, Pseudo parameters are defined for the normal boiling temperature and the total number of atoms. Pseudo n and Tb can be obtained by solving following system of two equations for a binary mixture (Eq. 30-31). Using experimental solubility data, the value of Pseudo n and Tb can be obtained through solving the system of two equations formed employing an objective function, **OF**, and finding the best optimal value of the adjustable parameter Kij. Then the new EOS can be used for the binary mixture calculations with these calculated pseudo n and Tb.

 (30)

 (31)

Finally the fugacity coefficient of component i in the fluid mixture is expressed as.

 (33)

 (34)

Inserting relations in Eq. 34 into Eq. 33, we get the fugacity coefficient as following function.

 (35)

**3. Material and Methods**

Solubility data of thirty dyes and sixty drugs, a large number of solubility data more than 2417 data points, have been collected from literature [[10](#_ENREF_10), [11](#_ENREF_11), [38-](#_ENREF_38)91]. **Table 1** shows the details of these solubility data, references, temperature and pressure ranges, and number of data points for each system. All estimated critical properties and molecular weight of these dyes are listed in **Table 2**. These critical properties are calculated using proposed equations in this paper. In order to compare the accuracy of the new EOS with PR-EOS as a reference, it is assumed that all the experimental data are correct. The objective function, **OF**, has been minimized using experimental solubility data of each system of study by the well-known optimization method of genetic algorithm in MATLAB (R2009a) environment [92]. The reported AARD in Figures is Average absolute relative deviation and defined as following function, for comparison of calculated solubility values and experimental ones.

 (36)

Where  and  are calculated and experimental solubility of solute respectively. N is the number of experimental data points.

**4. Results and Discussion**

The Accumulative AARD% values of each system of dyes, in order of appearance in **Table 1**, for proposed EOS and PR-EOS are shown in **Fig.1**. As it can be seen, the new EOS has lower Accumulative AARD% values than PR-EOS. So, it can be concluded that the proposed EOS presented more accurate result for solubility prediction and correlation in supercritical carbon dioxide. Also as a key system (due to largest data points among other systems), **Fig. 2** shows the AARD% values corresponding to system 11, AC03, at a range of temperatures. Again it can be concluded that the new EOS is more successful in solubility correlation than PR-EOS. The performance of New EOS for Drugs data is shown in **Fig. 3**. We provide **Fig. 4** as pressure- composition graph of D2, showing the fitted isotherms at 308K and the experimental points used. Studies on applicability and generality of the new EOS on other solutes (60 Drugs solubility data, 1417 data points) show that the EOS will reveal even more accurate results if the Eq. 22 extended to third order in term of M (pressure to temperature ratio). This extension and derivation of practical thermodynamics relationships from this proposed EOS will be discussed later. It’s clear that the proposed EOS in this paper is able to predict and correlate the solubility of any solute in supercritical carbon dioxide.

**Figure 1.** The Accumulative AARD% values of each system, in order of appearance in Table 1, for proposed EOS and PR-EOS for Dyes.

**Figure 2.** The AARD% values corresponding to system 11, AC03, at a range of temperatures.

**Figure 3.** The Accumulative AARD% values of each system, in order of appearance in Table 1, for proposed EOS and PR-EOS for Drugs.

**Figure 4.** The pressure- composition graph for D2 at isotherm 308K.

**5. Conclusion**

In this study, solubility of thirty dyes and sixty drugs in supercritical carbon dioxide have been used for evaluation and assessment of the new proposed EOS accuracy in correlation of solubility data in supercritical fluids. The solubility data were correlated with two equation of state; PR-EOS together with two adjustable parameter van der Waals mixing and combining rules and Proposed EOS. As the results show the mean AARD for the new EOS is significantly lower than that obtained from PR-EOS. The new EOS presented more accurate prediction for solubility data in supercritical CO2.

**NOMENCLATURE**

α energy parameter of the cubic equation of state (Nm4mol-2)

A coefficients of new EOS

AARD average absolute relative deviation (%)

b volume parameter in the PR EOS and in the SRK EOS (m3mol-1)

A, B, C, D … virial coefficients

A’, B’, C’, D’, virial coefficients

EOS equation of state

GCM group contribution method

k coefficients of proposed EOS

kij binary interaction parameters

lij binary interaction parameters

M proposed EOS parameter

Mw molecular weight

N number of data points

n number of atoms

P pressure (Pa)

PR Peng-Robinson

R ideal gas constant (Jmol-1K-1)

T temperature (K)

ν molar volume (cm3mol-1)

vdW2 van der Waals mixing and combining rules with two adjustable parameters

y mole fraction

Z compressibility factor

Greek Symbols

α, β, γ coefficients of Equation (19)

φ fugacity coefficient

ω Pitzer’s acentric factor

Subscripts

1 solvent

2 solute

avg average

b boiling point

c critical property

i, j components

ps pseudo

r reduced

Superscripts

0, 1, 2 indices for new EOS coefficients

cal calculated

exp experimental

l liquid

SCF supercritical fluid

sat saturation

**References:**

1. V.F. Cabral, W.L.F. Santos, E.C. Muniz, A.F. Rubira, L. Cardozo-Filho. *The Journal of Supercritical Fluids* **40**, 163 (2007).

2. P. Dong, M. Xu, X. Lu, C. Lin. *Fluid Phase Equilibria* **297**, 46 (2010).

3. M.-W. Park, H.-K. Bae. *Journal of Supercritical Fluids* **22**, 65 (2002).

4. M.R. De Giorgi, E. Cadoni, D. Maricca, A. Piras. *Dyes and Pigments* **45**, 75 (2000).

5. M.P. Srinivasan, Y. Gu, R. Begum. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **198–200**, 527 (2002).

6. E.E. Said-Galiyev, Y.S. Vygodskii, L.N. Nikitin, R.A. Vinokur, M.O. Gallyamov, I.V. Pototskaya, V.V. Kireev, A.R. Khokhlov, K. Schaumburg. *Journal of Supercritical Fluids* **27**, 119 (2003).

7. O. Guney, A. Akgerman, J.M. Wong, K.P. Johnston, B. Subramaniam, R.A. Rajewski, K. Snavely. *AIChE Journal* **48**, 856 (2002).

8. B. Subramaniam, R.A. Rajewski, K. Snavely. *Journal of Pharmaceutical Sciences* **86**, 885 (1997).

9. B. Guzel, A. Akgerman. *The Journal of Supercritical Fluids* **18**, 247 (2000).

10. S.J. Macnaughton, I. Kikic, N.R. Foster, P. Alessi, A. Cortesi, I. Colombo. *Journal of Chemical & Engineering Data* **41**, 1083 (1996).

11. R. Murga, M.a.T. Sanz, S. Beltrán, J.L. Cabezas. *The Journal of Supercritical Fluids* **23**, 113 (2002).

12. N. Ajzenberg, F. Trabelsi, F. Recasens. *Chemical Engineering & Technology* **23**, 829 (2000).

13. K.E. Laintz, E. Tachikawa. *Analytical Chemistry* **66**, 2190 (1994).

14. G. Kateman, M. Sjostriim, K. Furton, L. Chen, R. Jaffe. *Rapid Determination of Uranium on Solid Matrices by Synergistic In Situ Chelation Supercritical Fluid Extraction and UV Absorption Spectroscopy* (1995).

15. Y. Meguro, S. Iso, H. Takeishi, Z. Yoshida. *Chem. Lett.* **24**, 365 (1995).

16. N.G. Smart, T.E. Carleson, S. Elshani, S. Wang, C.M. Wai. *Industrial & Engineering Chemistry Research* **36**, 1819 (1997).

17. S. Wang, C.M. Wai. *Environmental Science & Technology* **30**, 3111 (1996).

18. P. Dondeti, Y. Desai. *Supercritical fluid technology in pharmaceutical research*. J. Swarbrick, J.C. Boylan (Eds.), 18Marcel Dekker, New York (1999).

19. A. Tabernero, E.M.M. del Valle, M.Á. Galán. *The Journal of Supercritical Fluids* **52**, 161 (2010).

20. W. Saus. *SFD-Dry dyeing of polyester in CO2*. Sterling Publication LTD (1995).

21. J. Fasihi, Y. Yamini, F. Nourmohammadian, N. Bahramifar. *Dyes and Pigments* **63**, 161 (2004).

22. F.P. Lucien, N.R. Foster. *The Journal of Supercritical Fluids* **17**, 111 (2000).

23. B. H.K., H.B. K. *J. Korean. Inst. Chem. Eng.* **34**, 379 (1996).

24. U. Haarhaus, P. Swidersky, G.M. Schneider. *The Journal of Supercritical Fluids* **8**, 100 (1995).

25. S. Joung, H. Shin, Y. Park, K.-P. Yoo. *Korean Journal of Chemical Engineering* **15**, 78 (1998).

26. J. Chrastil. *The Journal of Physical Chemistry* **86**, 3016 (1982).

27. K. Bartle, A. Clifford, S. Jafar, G. Shilstone. *J. Phys. Chem. Ref. Data* **20**, 713 (1991).

28. J. Mendez-Santiago, A.S. Teja. *Industrial & Engineering Chemistry Research* **39**, 4767 (2000).

29. D.H. Ziger, C.A. Eckert. *Industrial & Engineering Chemistry Process Design and Development* **22**, 582 (1983).

30. S. Garnier, E. Neau, P. Alessi, A. Cortesi, I. Kikic. *Fluid Phase Equilibria* **158–160**, 491 (1999).

31. J. Smith, H.v. Ness, M. Abbott. *Introduction to Chemical Engineering Thermodynamics*. McGraw-Hill, New York (2005).

32. D.-Y. Peng, D.B. Robinson. *Industrial & Engineering Chemistry Fundamentals* **15**, 59 (1976).

33. J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo. *Molecular thermodynamics of fluid-phase equilibria*. Prentice-Hall (1998).

34. P.K. S., C.R. F. *Journal of American Chemical Society* **79**, 2369 (1957).

35. G. Tsonopoulos. *Amer. Instit. Chem. Eng. J.* **21**, 827 (1975).

36. H. Orbey, J.H. Vera. *AIChE Journal* **29**, 107 (1983).

37. K.G. Joback, R.C. Reid. *Chemical Engineering Communications* **57**, 233 (1987).

38. S.N. Joung, K.-P. Yoo. *Journal of Chemical & Engineering Data* **43**, 9 (1998).

39. S.-Y. Huang, M. Tang, S.L. Ho, Y.-P. Chen. *The Journal of Supercritical Fluids* **42**, 165 (2007).

40. B. Wagner, C.B. Kautz, G.M. Schneider. *Fluid Phase Equilibria* **158-160**, 707 (1999).

41. A.S. Özcan, A.A. Clifford, K.D. Bartle, D.M. Lewis. *Journal of Chemical & Engineering Data* **42**, 590 (1997).

42. J.W. Lee, M.W. Park, H.K. Bae. *Fluid Phase Equilibria* **173**, 277 (2000).

43. H.-D. Sung, J.-J. Shim. *Journal of Chemical & Engineering Data* **44**, 985 (1999).

44. H.-m. Lin, C.-Y. Liu, C.-H. Cheng, Y.-T. Chen, M.-J. Lee. *Journal of Supercritical Fluids* **21**, 1 (2001).

45. H.-m. Lin, C.-C. Ho, M.-J. Lee. *The Journal of Supercritical Fluids* **32**, 105 (2004).

46. K. Tamura, T. Shinoda. *Fluid Phase Equilibria* **219**, 25 (2004).

47. B. Guzel, A. Akgerman. *Journal of Chemical & Engineering Data* **44**, 83 (1998).

48. J.W. Lee, J.M. Min, H.K. Bae. *Journal of Chemical & Engineering Data* **44**, 684 (1999).

49. P. Coimbra, M.H. Gil, C.M.M. Duarte, B.M. Heron, H.C. de Sousa. *Fluid Phase Equilibria* **238**, 120 (2005).

50. Xing, Yang, Su, M. Huang, Ren. *Journal of Chemical & Engineering Data* **48**, 330 (2003).

51. A.R.C. Duarte, P. Coimbra, H.C. de Sousa, C.M.M. Duarte. *Journal of Chemical & Engineering Data* **49**, 449 (2004).

52. M. Asghari-Khiavi, Y. Yamini. *Journal of Chemical & Engineering Data* **48**, 61 (2002).

53. H. Sovová. *Journal of Chemical & Engineering Data* **46**, 1255 (2001).

54. H. Uchida, I. Usui, A. Fuchita, M. Matsuoka. *Journal of Chemical & Engineering Data* **49**, 1560 (2004).

55. I. Medina, J.L. Bueno. *Journal of Chemical & Engineering Data* **46**, 1211 (2001).

56. K. Matsuyama, K. Mishima, R. Ohdate, M. Chidori, H. Yang. *Journal of Chemical & Engineering Data* **48**, 1040 (2003).

57. A. Garmroodi, J. Hassan, Y. Yamini. *Journal of Chemical & Engineering Data* **49**, 709 (2004).

58. Z. Huang, Y.-H. Guo, G.-B. Sun, Y.C. Chiew, S. Kawi. *Fluid Phase Equilibria* **236**, 136 (2005).

59. J.W. Hampson, R.J. Maxwell, S. Li, R.J. Shadwell. *Journal of Chemical & Engineering Data* **44**, 1222 (1999).

60. R. Murga, M.T. Sanz, S. Beltrán, J.L. Cabezas. *Journal of Chemical & Engineering Data* **49**, 779 (2004).

61. E. Sahle-Demessie, U.R. Pillai, S. Junsophonsri, K.L. Levien. *Journal of Chemical & Engineering Data* **48**, 541 (2003).

62. M. Asghari-Khiavi, Y. Yamini, M.A. Farajzadeh. *The Journal of Supercritical Fluids* **30**, 111 (2004).

63. M. Sauceau, J.J. Letourneau, B. Freiss, D. Richon, J. Fages. *The Journal of Supercritical Fluids* **31**, 133 (2004).

64. G.I. Burgos-Solórzano, J.F. Brennecke, M.A. Stadtherr. *Fluid Phase Equilibria* **220**, 55 (2004).

65. A. Stassi, R. Bettini, A. Gazzaniga, F. Giordano, A. Schiraldi. *Journal of Chemical & Engineering Data* **45**, 161 (2000).

66. R. Murga, M.a.T. Sanz, S. Beltrán, J.L. Cabezas. *The Journal of Supercritical Fluids* **27**, 239 (2003).

67. Y. Yamini, J. Hassan, S. Haghgo. *Journal of Chemical & Engineering Data* **46**, 451 (2001).

68. N. Elvassore, K. Vezzù, A. Bertucco. *The Journal of Supercritical Fluids* **33**, 1 (2005).

69. M.D. Gordillo, M.A. Blanco, A. Molero, E. Martinez de la Ossa. *The Journal of Supercritical Fluids* **15**, 183 (1999).

70. T. Mu, B. Han, J. Zhang, Z. Li, Z. Liu, J. Du, D. Liu. *The Journal of Supercritical Fluids* **30**, 17 (2004).

71. S.S.T. Ting, D.L. Tomasko, N.R. Foster, S.J. Macnaughton. *Industrial & Engineering Chemistry Research* **32**, 1471 (1993).

72. A. Cortesi, I. Kikic, P. Alessi, G. Turtoi, S. Garnier. *The Journal of Supercritical Fluids* **14**, 139 (1999).

73. S.L.J. Yun, K.K. Liong, G.S. Gurdial, N.R. Foster. *Industrial & Engineering Chemistry Research* **30**, 2476 (1991).

74. S.J. Macnaughton, N.R. Foster. *Industrial & Engineering Chemistry Research* **33**, 2757 (1994).

75. W.J. Schmitt, R.C. Reid. *Journal of Chemical & Engineering Data* **31**, 204 (1986).

76. Z. Knez, M. Skerget, P. Sencar-Bozic, A. Rizner. *Journal of Chemical & Engineering Data* **40**, 216 (1995).

77. P. Alessi, A. Cortesi, I. Kikic, N.R. Foster, S.J. Macnaughton, I. Colombo. *Industrial & Engineering Chemistry Research* **35**, 4718 (1996).

78. S. Li, G.S. Varadarajan, S. Hartland. *Fluid Phase Equilibria* **68**, 263 (1991).

79. M. Johannsen, G. Brunner. *Fluid Phase Equilibria* **95**, 215 (1994).

80. M. Shamsipur, A.R. Karami, Y. Yamini, H. Sharghi. *The Journal of Supercritical Fluids* **32**, 47 (2004).

81. K. Khimeche, P. Alessi, I. Kikic, A. Dahmani. *The Journal of Supercritical Fluids* **41**, 10 (2007).

82. S. Maeda, K. Mishima, K. Matsuyama, M. Baba, T. Hirabaru, H. Ishikawa, K.-i. Hayashi. *Journal of Chemical & Engineering Data* **46**, 647 (2001).

83. H. Z., L. W.D., K. S., a.C. Y.C. *J. Chem. Eng. Data* **49**, 1323 (2004).

84. M.D. Gordillo, C. Pereyra, E.J. Martı́nez de la Ossa. *The Journal of Supercritical Fluids* **27**, 31 (2003).

85. M. Gordillo, C. Pereyra, E. Martinezdelaossa. *Dyes and Pigments* **67**, 167 (2005).

86. J. Lee, M. Park, H.K. Bae. *Fluid Phase Equilibria* **179**, 387 (2001).

87. M. Banchero, A. Ferri, L. Manna, S. Sicardi. *Fluid Phase Equilibria* **243**, 107 (2006).

88. M.D. Gordillo, C. Pereyra, E.J. Martínez de la Ossa. *Dyes and Pigments* **67**, 167 (2005).

89. T. Shinoda, K. Tamura. *Fluid Phase Equilibria* **213**, 115 (2003).

90. Z. Jinhua, X. Mingxian, L. Xueyan, L. Chunmian. *Chinese Journal of Chemical Engineering* **18**, 648 (2010).

91. J.M. Wong, K.P. Johnston. *Biotechnology Progress* **2**, 29 (1986).

92. M.A. Khansary, A. Hallaji Sani, Fluid Phase Equilib 365 (2014).