AJChE 2007, Vol. 7, No. 2, 127-136

Phase Equilibrium Study in Supercritical Fluid Extraction of Ethanol to Octane Mixture Using CO_2

R. Davarnejad
K. M. Kassim
A. Zainal
Suhairi A. Sata
School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia
14300 Nibong Tebal, Penang, Malaysia
Email: chzahmad@eng.usm.my

Solubility data was measured for carbon dioxide with ethanol and octane using a phase equilibrium loading re-circulating high-pressure type apparatus at a pressure up to 100.75 bar and a temperature of 348.15K for ethanol and octane mixture involved with 25% ethanol and 75% octane. Experimental data was compared with the calculated regular solution theory data. A procedure is employed to each phase by applying activity coefficient expressions based on regular solution theory. Calculations along these lines are described and the physical bases for applying this method under the relevant conditions are discussed. The regular solution theory approach has been found to be encouraging for the prediction of phase equilibria solubilities though the interaction parameters must be regarded as pressure dependent.

Keywords: Activity coefficient, CO2 solvent, ethanol and octane, phase equilibria, regular solution theory, *and* supercritical extraction.

INTRODUCTION

Many researchers have proven that carbon dioxide is chemically reactive toward alcohols and general oxygen-containing compounds and it also produces weak complexation in condensed mixtures of these substances (Hildebrand and Scott 1964; Gupta, Lesslie, and King 1973; Kassim and Davarnejad 2006a,b; Kassim, Davarnejad, and Zainal 2008; Davarnejad et al. 2008a).

However, percentage of octane and ethanol extraction by high pressure CO_2 solvent increases with a decrease of pressure in the binary systems of CO_2-octane and CO_2-ethanol, respectively, but extraction percentage of ethanol is more than octane at the same conditions (Kassim, Davarnejad, and Zainal 2008). Furthermore, the azeotrope of the ethanol-octane systems occurs at around a ratio of ethanol: octane = 84:16 (Kassim and Davarnejad 2006), similar to the chosen ethanol-octane ratio in this study.

Recently some researchers have theoretically studied mutual solubilities of some natural hydrocarbons from petroleum production as a function of pressure (Pires, Mohamed, and Mansoori 2001, Benmekki and Mansoori 1987). They predicted equilibrium data for binary water-hydrocarbon, alcohol-hydrocarbon, and other complex mixture systems by applying associating fluid equations of state.

In addition, Browarzik (2004) theoretically studied vapor-liquid equilibrium for ethanol-octane system and the other binary systems containing alkane-alkanol. The research for the case of ethanol-octane system was conducted at temperatures of 75ºC and 45ºC.

According to this case, two closed loops were observed at temperatures of 45ºC and 75 ºC. The former was at a pressure less than 0.2 bar whereas the later was at pressure between 0.2 bar and 0.9 bar. An azeotrope point was observed at the ethanol mole fraction of 0.864 for this mixture in both of the loops. On the other hand, these results were supported by experimental data reported by Goral et al. (1998).

Gupta, Lesslie, and King (1973) have studied the solubilities of ethanol in compressed CO_2 at pressures ranging from 10 to 60 bar and at temperatures of 25, 50, and 75 ºC. They clearly showed that temperature increased ethanol solubility in CO_2. Furthermore, solubility decreased with increasing pressure of CO_2.

The solubilities of octane in CO_2 at temperatures of 17 ºC and 38 ºC and pressures up to 36.7 bar were studied by Wang, Lang, and Guo (1996). They concluded that solubility decreased with increasing pressure. Furthermore, temperature increased octane solubility in CO_2 at similar pressures.

Therefore, the objective of this study is to predict mutual solubilities for a system consisting of 0.33 mole ratio of octane to ethanol as heavy component with supercritical and slightly subcritical carbon dioxide solvent. The data was then calculated from regular solution equations. The equations are described in details by King et al. (1983). The main reason for using the regular solution theory is that the estimation of some of the parameters required for these calculations would be difficult to obtain if the solute was a complex substance; furthermore, little information was known apart from its structural formula.

Hence, an alternative procedure which, apart from these objectives, was to apply the activity coefficient expressions of the regular solution equations type to each phase. Calculations along these lines were described and the physical bases for applying these methods under the relevant conditions were discussed. Some of the interaction parameters required for the calculation of activity coefficients can be calculated from the experimental data for some equilibria systems mentioned in the literature (Francis 1954, Schneider et al. 1967). The other information regarding these equations can be obtained from another reference (Fredenslund, Gmehling, and Rasussen 1977). These parameters are independent of temperature and related to the pressure (Smith and Van Ness 1987, Kassim and Davarnedjan 2006a.b, Davarnejad et al. 2008). The method of extracting the parameters has been described in Kassim and Davarnedjan (2006a,b) and King et al.(1984). By putting together all the information obtained from the aforementioned references and applying the regular solution equations for activity coefficients to calculate Gibbs function relationships, the mutual solubility data for the phases will be calculated eventually.

In this study, two-phase equilibrium data was experimentally obtained and was theoretically modeled using regular solution theory equations.

EXPERIMENTAL

Materials

A solution of ethanol (99.9 %, J.T. Baker) and octane (99.8 %, J.T. Baker) containing

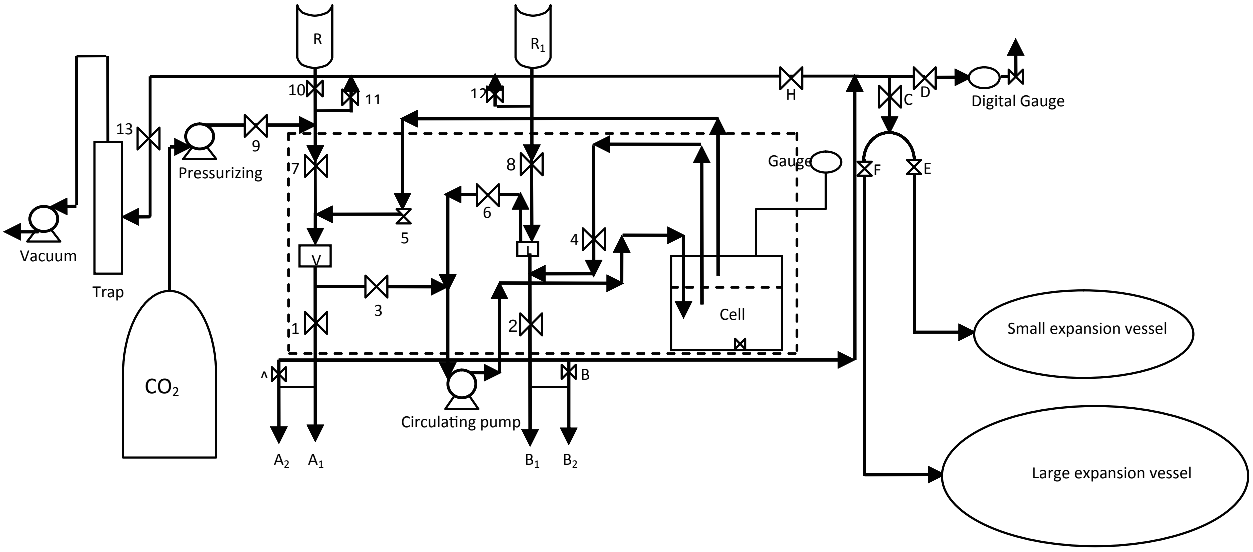

Figure 1. Supercritical Fluid Extraction Equilibria Apparatus

25% ethanol and 75% octane was utilized for the supercritical extraction process using CO_2 (99.99%) purchased from MOX Factory. The extracted samples from the apparatus were analyzed by gas chromatography (GC).

Experimental Procedure

The equipment used was the phase equilibrium re-circulation high-pressure type apparatus as shown in Figure 1 (fabricated by Alpha Dynamic Sdn. Bhd).

In this apparatus, the attainment of equilibrium was further assisted by magnetic stirrer which was installed in the equilibrium vessel. All units of the apparatus—that is, the equilibrium cell (volume 500cm^3), the joining tubes, vapor and liquid sample bombs (volume 50 and 40 cm^3), couplings, and valves—were made of stainless steel and designed to withstand a working pressure of 500 bar. The part of the equipment shown within the dash line was immersed in an air bath. The temperature in the equilibrium cell was measured using a digital thermocouple.

When the cell and the circuit were under vacuum, the heavy component under study (ethanol-octane as feed) was fed into the equilibrium cell. This was accomplished by first filling the reservoir (R_1) with about 120cm^3 of this liquid. The liquid heavy component was then allowed to go directly into the cell by turning on valve 8 and turning off valve 6. Having charged the cell with the heavy component, CO_2 at cylinder pressure was admitted to the cell. A high pressure pump connected between the cylinder containing the contacting CO_2 and the cell was then switched on to pressurize the cell. In the filling process, the heaters for the cell, the air bath, and also the bath fan were switched on. As the cell was brought to the desired pressure, valves 6 and 3 were turned off, and the cell was carefully brought to the desired temperature. This was accomplished using a fine control on the heater outputs, which were gradually increased to obtain the required temperature.

Equilibration and sampling would be achieved when the required temperature (by controlling and observing the temperature indicator) and pressure (by controlling and observing the pressure gauge) were reached and remained constant (equilibrium condition); the pneumatic re-circulating pump and the magnetic stirrer were turned on at the same time. Then, valve 6 was opened and, after a few seconds, valve 3 was also opened. The reason for this was to avoid any droplets of solvent passing through the vapor sample bomb flow section. The pump and stirrer were left on for about 30min, to ensure that equilibrium would be achieved. When equilibrium was resumed, the pump and stirrer were turned off and internal valves 3, 5, 4, and 6 were kept open. The phases were then allowed to stand in contact with each other for about 30min to allow the bubbles in the liquid to become disengaged. After the 30-min period, the vapor sample bomb and the liquid sample bomb were isolated by turning off valves 3 and 5 (for the vapor sample bomb) and valves 4 and 6 (for the liquid sample bomb). Samples of the gas and liquid phases were then extracted from the vapor bomb and the liquid bomb through valves 1 and 2, respectively.

The samples taken from A and B were the vapor and liquid samples which were analyzed by GC (Perkin Elmer) equipped with a capillary GC column (length × I.D. 30m × 0.32mm, d_f 1.00 μm, Supelco brand).

In terms of uncertainty, the validity of the experimental data was already proposed by King et al. (1983). The experimental data were produced based on the average of the two repeat runs performed for each data point. The repeat runs ensured that the experiments could be repeated within an experimental error of ±2%.

RESULTS AND DISCUSSION

The mutual solubility of CO_2-ethanol-octane ternary system was studied at temperature of 75 ºC and at various pressures. The composition of the equilibrium phases was noted at each pressure. The mole fractions of ethanol in the liquid and vapor phases on a carbon dioxide free basis were calculated by applying a set of equations which were developed by Davarnejad et al. (2008 a,b). The results obtained are found in Table1.

THERMODYNAMIC MODEL

The regular solution theory was adopted as a model for this system based on the activity coefficients. The applied model with fundamental

Table 1. CO2-Ethanol-Octane System, Composition of the Equilibrium Vapor and Liquid Phase for an Ethanol/Octane Feed Ratio of 25:75 at 75ºC and at Various Pressures

Pressure (bar)	Vapor phase, ethanol mole fraction on CO_2 free basis	Liquid phase, ethanol mole fraction on CO_2 free basis	Vapor phase, CO_2 mole fraction	Liquid phase, CO_2 mole fraction
100.75	0.4450	0.2496	0.9725	0.9175
100.00	0.4450	0.2497	0.973	0.9120
97.00	0.4525	0.2496	0.9729	0.8911
92.75	0.4650	0.2498	0.9728	0.8522
85.00	0.4860	0.2497	0.9733	0.7805
75.00	0.5150	0.2496	0.9732	0.7011
60.00	0.5575	0.2498	0.9720	0.5521
50.00	0.5900	0.2498	0.9707	0.4811
31.50	0.655	0.2496	0.9658	0.2851

Table 2. Interaction Parameters Based on the Experimental Data Extracted from Literature (Schneider et al. 1967, King et al. 1984) at 25ºC

P (bar)	$a_{CH3/CO2}$	$a_{CO2/CH3}$	$(x^E_{CO2})^{model}$	$(x^S_{CO2})^{model}$
100.75	640.5753	89.4743	0.9516	0.8348
100.00	640.3018	89.5782	0.9519	0.8344
97.00	639.1897	89.9994	0.9751	0.6282
92.75	637.5649	90.6118	0.9754	0.6287
85.00	634.4533	91.7773	0.9570	0.8248
75.00	630.1543	93.3783	0.9600	0.8184
60.00	623.1058	95.9983	0.9642	0.8091
50.00	618.0068	97.9008	0.9667	0.8031
31.50	607.7301	101.7784	0.9710	0.7922

$a_{CO2/OH}$ = 855.51 calculated from CO_2-heptylalcohol system (Francis, 1954).
$a_{OH/CO2}$ = 3000 calculated from CO_2-heptylalcohol system (Francis, 1954).

thermodynamic roots have been described in detail in the literature (Davarnejad et al. 2008 a; Davarnejad et al. 2008 b).

Interaction parameters as function of pressure were calculated by using the procedure and equations mentioned in the literature (Davarnejad et al. 2008a,b). These data were used to predict the mutual miscibility of the CO_2-ethanol-octane system at a temperature of 75ºC and at various pressures as shown in Table 2.

Two-phase equilibrium data based on the experiment and model related to the pressure and at temperature of 75ºC are shown in figures 2 and 3, respectively.

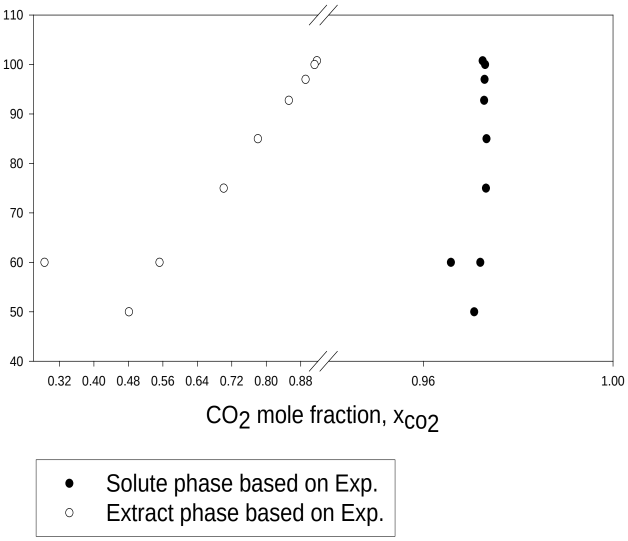

Figure 2. Two-Phase Equilibrium Data Based on the Experiment for CO2 Component

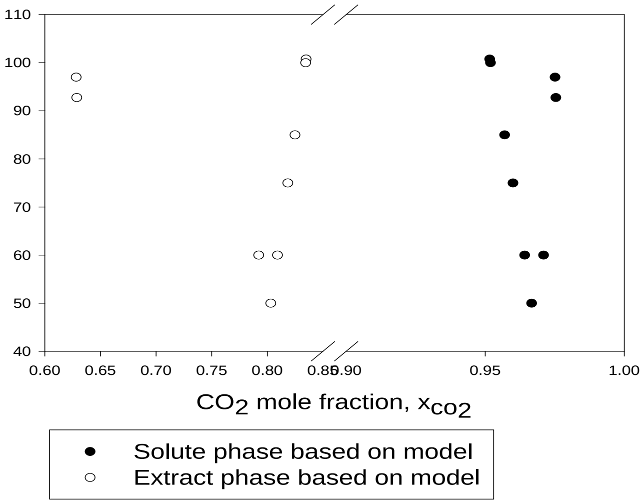

Figure 3. Two-Phase Equilibrium Data Based on Regular Solution Model for CO2 Component

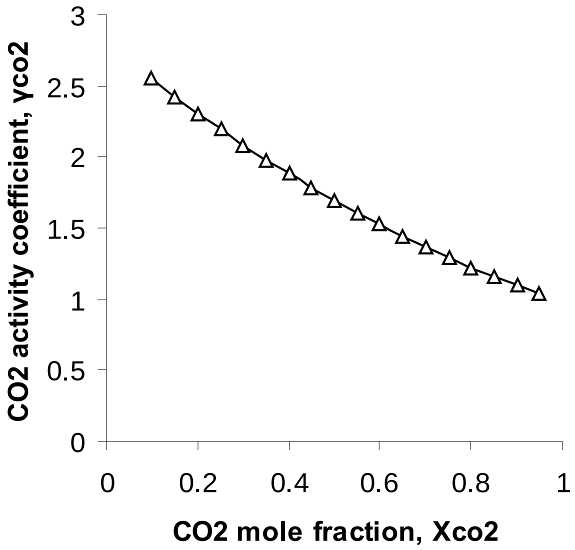

Fig. 4. CO_2 activity coefficient (γCO_2) against CO_2 mole fraction (xCO_2) at constant temperature of 75 ºC and at pressure of 100 bar

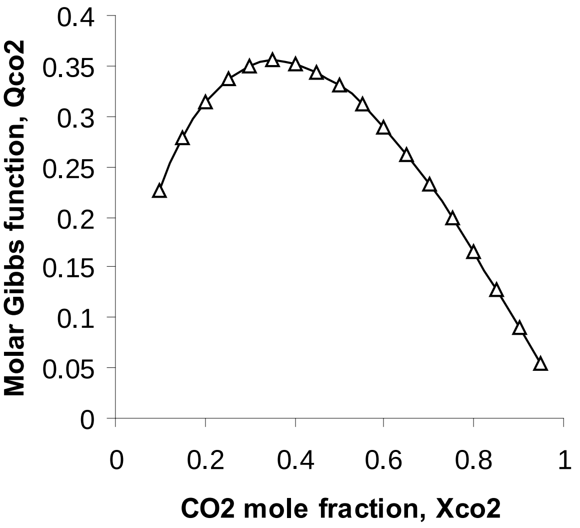

Fig. 5. Molar Gibbs function for CO_2 (Gmixingm) against CO_2 mole fraction (xCO_2) at constant temperature

Figure 4 shows the CO_2 activity coefficient, γ_{CO2}, against CO_2 mole fraction, x_{CO2}, at a constant temperature of 75ºC and at a pressure of 100 bar. Activity coefficients for the other pressures are shown in Table 3. Figure 5 shows that the molar Gibbs function of CO_2, G^{mixing}_m, against CO_2 mole fraction, x_{CO2}, at constant temperature of 75ºC and at pressure of 100 bar. G^{mixing}_m varies similarly to a function having a parabolic profile and marks its maximum at $x_{CO2} = 0.35$.

Meanwhile, Figure 6 shows that the first derivative of the G^{mixing}_m curve which has a logarithmic profile. It deceases continuously when the CO_2 mole fraction increases up to 1. Of course, this derivative is null at $x_{CO2} = 0.35$.

Figure 7 shows the solubility parameter, d^2Q_{CO2}/dx^2_{CO2}, (second derivative of the molar Gibbs function) against CO_2 mole fraction, x_{CO2}, at constant temperature of 75ºC and at pressure of 100 bar. It clearly shows the partial miscibility

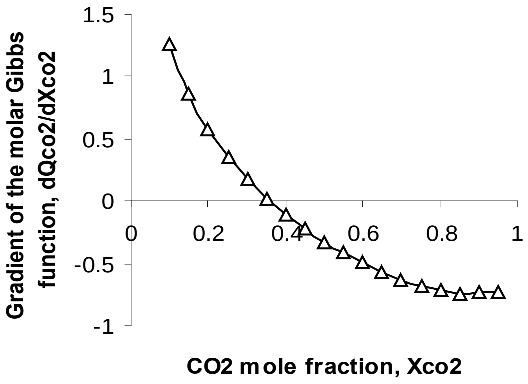

Figure 6. Gradient of the Molar Gibbs Function for CO_2 (dG^{mixing}_m/dx_{CO2}) against CO_2 Mole Fraction (x_{CO2}) at Constant Temperature of 75ºC and at Pressure of 100 bar

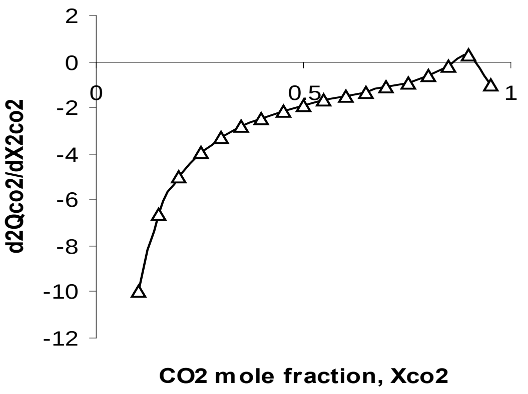

Figure 7. Second Derivative of the Molar Gibbs Function for CO_2 ($d^2G^{mixing}_m/dx^2CO^2$) against CO_2 Mole Fraction (x_{CO2}) at Constant Temperature of 75ºC and at Pressure of 100 bar

Table 3. CO_2 Activity Coefficient (γ_{CO2}) against CO_2 Mole Fraction (x_{CO2}) at a Constant Temperature of 75ºC and at Various Pressures

x_{CO2}	γ_{CO2} 31.5 bar	γ_{CO2} 50 bar	γ_{CO2} 60 bar	γ_{CO2} 75 bar	γ_{CO2} 85 bar	γ_{CO2} 92.75 bar	γ_{CO2} 97 bar	γ_{CO2} 100 bar	γ_{CO2} 100.75 bar
0.1	2.4210	2.4626	2.4833	2.5122	2.5298	2.5425	2.5491	2.5537	2.5548
0.15	2.3189	2.3531	2.3701	2.3937	2.4080	2.4184	2.4237	2.4274	2.4283
0.20	2.2197	2.2475	2.2613	2.2802	2.2916	2.2999	2.3041	2.3070	2.3077
0.25	2.1236	2.1456	2.1565	2.1714	2.1803	2.1867	2.1900	2.1923	2.1928
0.30	2.0303	2.0474	2.0557	2.0671	2.0739	2.0787	2.0812	2.0829	2.0833
0.35	1.9398	1.9525	1.9587	1.9671	1.9720	1.9755	1.9773	1.9785	1.9788
0.40	1.8521	1.8610	1.8654	1.8712	1.8745	1.8769	1.8781	1.8789	1.8791
0.45	1.7669	1.7727	1.7755	1.7791	1.7812	1.7827	1.7834	1.7839	1.7840
0.50	1.6842	1.6875	1.6889	1.6908	1.6919	1.6926	1.6929	1.6931	1.6932
0.55	1.6040	1.6051	1.6055	1.6060	1.6062	1.6063	1.6063	1.6063	1.6063
0.60	1.5259	1.5254	1.5251	1.5245	1.5241	1.5237	1.5235	1.5233	1.5233
0.65	1.4500	1.4483	1.4474	1.4460	1.4451	1.4445	1.4441	1.4438	1.4438
0.70	1.3760	1.3735	1.3722	1.3704	1.3692	1.3684	1.3679	1.3676	1.3675
0.75	1.3038	1.3009	1.2995	1.2974	1.2961	1.2952	1.2947	1.2943	1.2943
0.80	1.2332	1.2303	1.2289	1.2269	1.2257	1.2247	1.2242	1.2239	1.2238
0.85	1.1643	1.1618	1.1605	1.1588	1.1577	1.1570	1.1566	1.1563	1.1562
0.90	1.0976	1.0958	1.0949	1.0937	1.0930	1.0924	1.0922	1.0920	1.0919
0.95	1.0364	1.0357	1.0353	1.0348	1.0345	1.0342	1.0341	1.0340	1.0340

zone. The sign of the second derivative of G^{mixing}_{m} changes at x_{CO2} = 0.9. The solubility parameter data for the other pressures is shown in Table 4 and the interaction parameters are obtained from Table 2 and also from the literature (Fredenslund, Gmehling, and Rasussen 1977).

The solubility parameter shows a negative range for a completely miscible system. If the system is partially miscible, this parameter shows a positive range. Hence, the results based on the regular solution model predict that the studied system is completely miscible in the whole of CO_2 mole fractions except at x_{CO2}=0.9 to which the current system is partially miscible for all of the operating pressures. Furthermore, this system is miscible partially at x_{CO2}=0.95 and at pressure of 31.5 bar.

CONCLUSIONS

In this study, the solubility data based on the regular solution theory with the differing shapes of the molecules and random mixing assumption was obtained and compared with the experimental data. The model used in the present work was one of the fundamental

Table 4. Solubility Parameter, d^2Q_{CO2}/dx^2_{CO2}, for CO_2 against CO_2 Mole Fraction (x_{CO2}) at Constant Temperature of 75ºC and at Various Pressures

x_{CO2}	d^2Q_{CO2}/dx^2_{CO2} 31.5 bar	d^2Q_{CO2}/dx^2_{CO2} 50 bar	d^2Q_{CO2}/dx^2_{CO2} 60 bar	d^2Q_{CO2}/dx^2_{CO2} 75 bar	d^2Q_{CO2}/dx^2_{CO2} 85 bar	d^2Q_{CO2}/dx^2_{CO2} 92.75 bar	d^2Q_{CO2}/dx^2_{CO2} 97 bar	d^2Q_{CO2}/dx^2_{CO2} 100 bar	d^2Q_{CO2}/dx^2_{CO2} 100.75 bar
0.10	-10.1591	-10.1056	-10.0786	-10.0408	-10.0175	-10.0005	-9.9916	-9.9855	-9.9840
0.15	-6.8220	-6.7682	-6.7411	-6.7033	-6.6801	-6.6631	-6.6543	-6.6482	-6.6467
0.20	-5.1505	-5.0964	-5.0693	-5.0315	-5.0083	-4.9915	-4.9826	-4.9766	-4.9751
0.25	-4.1442	-4.0899	-4.0627	-4.0251	-4.0020	-3.9853	-3.9765	-3.9706	-3.9691
0.30	-3.4693	-3.4149	-3.3878	-3.3504	-3.3275	-3.3109	-3.3023	-3.2963	-3.2949
0.35	-2.9823	-2.9280	-2.9011	-2.8639	-2.8413	-2.8249	-2.8164	-2.8106	-2.8091
0.40	-2.6108	-2.5569	-2.5302	-2.4935	-2.4713	-2.4552	-2.4468	-2.4411	-2.4397
0.45	-2.3138	-2.2606	-2.2344	-2.1984	-2.1767	-2.1610	-2.1529	-2.1473	-2.1459
0.50	-2.0655	-2.0134	-1.9879	-1.9530	-1.9320	-1.9169	-1.9091	-1.9037	-1.9024
0.55	-1.8476	-1.7974	-1.7730	-1.7397	-1.7197	-1.7054	-1.6979	-1.6929	-1.6917
0.60	-1.6450	-1.5979	-1.5750	-1.5441	-1.5256	-1.5124	-1.5056	-1.5010	-1.4999
0.65	-1.4426	-1.4004	-1.3800	-1.3527	-1.3365	-1.3250	-1.3191	-1.3151	-1.3141
0.70	-1.2216	-1.1871	-1.1708	-1.1491	-1.1365	-1.1276	-1.1231	-1.1201	-1.1194
0.75	-0.9535	-0.9323	-0.9226	-0.9102	-0.9033	-0.8988	-0.8965	-0.8951	-0.8947
0.80	-0.5908	-0.5929	-0.5949	-0.5988	-0.6021	-0.6049	-0.6065	-0.6078	-0.6081
0.85	-0.0532	-0.1003	-0.1245	-0.1594	-0.1816	-0.1983	-0.2073	-0.2136	-0.2151
0.90	0.7205	0.5765	0.5046	0.4038	0.3412	0.2951	0.2706	0.2537	0.2495
0.95	0.2458	-0.1477	-0.3417	-0.6102	-0.7751	-0.8956	-0.9591	-1.0028	-1.0136

thermodynamic theories. In this treatment, the interaction between the individual groups constituting the molecules was considered. From this work, a table of group interaction parameters was generated, together with the parameters, which described the size and shape of the molecules that proves possible to predict the vapor-liquid equilibria from a knowledge of the structural formula of the constituent molecular species. From the separations point of view, considerable separation was not achieved in this ratio of ethanol and octane mixture using supercritical carbon dioxide.

ACKNOWLEDGMENTS

Our real gratitude goes to Professor Hatem Ksibi who helped and guided us. This work was financially supported by Ministry of Science, Technology and Innovations, Malaysia (IRPA Grant No: 6012616).

REFERENCES

Benmekki, E.H., and Mansoori, G.A. (1987). "Phase equilibrium calculations of highly polar systems," *Fluid Phase Equilibria*, *32,* 139-149.

Browarzik, D. (2004). "Phase-equilibrium calculations for *n*-alkane + alkanol systems using continuous thermodynamics," *Fluid Phase Equilibria, 217,* 125-135.

Davarnejad, R., Kassim, K.M., Zainal, A., and Suhairi, A.S. (2008a). "Mutual solubility study for 94.2:5.8 of ethanol to octane with supercritical carbon dioxide solvent," *J. Chinese Institute of Chemical Engineers*, *39,* 343-352.

Davarnejad, R. Kassim, K.M., Zainal, A., and Suhairi, A.S. (2008b). "Supercritical fluid extraction of carotenoid from microalgae with projected thermodynamic models," *Int. J. Engineering*, *21,* 117-126.

Francis, A.W. (1954). "Ternary systems of liquid carbon dioxide," *J. Phys. and Chem.*, 58, 1099-1114.

Fredenslund, A., Gmehling, J., and Rasussen, P. (1977). *Vapor-Liquid Equilibria Using UNIFAC.* Elsevier, Amesterdam-Oxford-New York.

Goral, M., Maczynski, A., Bok, A., Oracz, P., and Skrzecs, A. (1998). *Vapor-Liquid Equilibria.* Vol. 3, Alcohols + Aliphatic Hhydrocarbons. Thermodynamic Data Center, Warszawa.

Guggenheim, E.A. (1952). *Mixtures.* Oxford University Press, UK.

Gupta, S.K., Lesslie, R.D., and King, A.D. (1973). "Solubility of alcohols in compressed gases. A comparison of vapor-phase interactions of alcohols and homomorphic compounds with various gases. I. Ethanol in compressed helium, hydrogen, argon, methane, ethylene, ethane, carbon dioxide and nitrous oxide," *J. Phys. Chem.*, *77,* 2011-2015.

Hildebrand, J.H. and Scott, R.L. (1964). *The Solubility of Nonelectrolytes.* Dover Publications, New York.

Hildebrand, J.H., Prausnitz, J.M., and Scott, R.L. (1970). *Regular and Related Solutions, The Solubility of Gases, Liquids and Solids.* Van Nostrand Reinhold, New York.

Kassim, K.M., and Davarnejad, R. (2006, November 13-15). Mutual solubilities prediction for some oils derivatives with supercritical and slightly subcritical carbon dioxide solvent. First International Conference on Environment. Park Royal Hotel, Malaysia.

Kassim, K.M., and Davarnejad, R. (2006, December 19-21). Supercritical fluid extraction of carbon dioxide solvent used with different ratios of ethanol/octane systems. 20th Symposium of Malaysian Chemical Engineers, UITM University, Kuala Lumpur, Malaysia.

Kassim, K.M., Davarnejad, R., and Zainal, A. (2008). "Phase equilibrium studying for the supercritical fluid extraction process using carbon dioxide solvent with 1.35 mole ratio of octane to ethanol mixture," *Chem. Eng. J.*, *140,* 173-182.

King, M.B., Alderson, D.A., Fallah, F.H., Kassim, K.M., Kassim, D.M., Sheldon, J.R,. and Mahmud, R.S. (1983). *Chemical Engineering at Supercritical Fluid Conditions.* Chapter 1. In: Paulaitis, M.E., Penninger, J.M.L., Gray, R.D. Jr., and Davidson, P. editors. Ann Arbor Science, Ann Arbor, MI.

King, M.B., Kassim, K.M., Bott, T.R., Sheldon, J.R., and Mahmud, R.S. (1984). "Prediction of mutual solubilities of heavy components with supercritical and slightly subcritical solvents: The role of equations of state and some applications of a simple expanded lattice model at subcritical temperatures," *Ber. Bunsenges Phys. Chem.*, *88,* 812-820.

King, M.B. (1969). *Phase Equilibrium in Mixtures.* Pergamon Press, UK.

Pires, A.P., Mohamed, R.S., Mansoori, G.A. (2001). "An equation of state for property prediction of alcohol-hydrocarbon and water-hydrocarbon systems," *J. Petrol. Sci. & Eng.*, *32,* 103-114.

Schneider, G., Alwani, Z., Horvath, E., and Frank, U. (1967). "Phase equilibriums and critical phenomena in binary mixed systems to 1500 bars carbon dioxide with n-octane, n-undecane, n-tridecane, and n-hexadecane," *Chem. Ing. Tech.*, *39,* 649-656.

Smith, J.M., and Van Ness, H.C. (1987). *Introduction to Chemical Engineering Thermodynamics.* 4th ed. McGraw-Hill, New York. 294.

Wang, L.S., Lang, Z.X., and Guo, T.M. (1996). "Measurement and correlation of the diffusion coefficients of carbon dioxide in liquid hydrocarbons under elevated pressures," *Fluid Phase Equilibria, 117,* 364.