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Thermodynamic Model Used to Predict Supercritical Carbon Dioxide Separation of an Ethanol-Octane Mixture: Feasibility Studies

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Abstract

Mutual solubilities of a mixture containing 80.52% ethanol and 19.48% octane were measured in a carbon dioxide solvent using a high-pressure type phase equilibrium apparatus at pressures up to 100 bar and at a temperature of 75°C. Experimental results showed that a considerable separation was not achieved in the ethanol-octane ratio investigated in this work. The experimental data were then compared with the theoretical data which were obtained from the regular solution equations. Regular solution theory was employed for each phase by applying activity coefficient expressions. The regular solution theory approach has been found to be encouraging for the prediction of solubility data (vapor phase data) and also showed that the interaction parameters were dependent on pressure.

Keywords: Supercritical extraction, regular solution theory, ethanol-octane mixture, carbon dioxide solvent, miscibility.

1. 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 (Hempel and Seidel, 1898; Hildebrand and Scott, 1964; Gupta et al., 1973; Kassim and Davarnejad, 2006; Davarnejad et al., 2007; Davarnejad et al., 2008a; Kassim et al., 2008).

However, the percentage of octane and ethanol extraction at high CO_2 solvent pressures increases with a decrease in pressure in the binary systems of CO_2-octane and CO_2-ethanol, respectively, but the extraction percentage of ethanol is more than octane at the same conditions (Kassim et al., 2008). Furthermore, the azeotrope of the ethanol-octane systems occurs at an ethanol-octane ratio of around 84:16, similar to the ratio investigated in this study (Kassim and Davarnejad, 2006; Davarnejad et al., 2007; Davarnejad et al., 2008a; Kassim et al., 2008).

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

Browarzik (2004) theoretically studied vapor-liquid equilibrium for an ethanol-octane system and other binary systems containing alkane-alkanol. The research for the case of the ethanol-octane system was conducted at two temperatures of 75ºC and 45ºC. The results from this case show that there are two closed loops at temperatures of 45ºC and 75ºC, respectively. The former is at a pressure less than 0.2 bar whereas the latter is at a pressure between 0.2 bar and 0.9 bar. An azeotrope point was observed at an ethanol mole fraction of 0.864 for this mixture in both of the loops. These results are also supported by experimental data reported by Goral et al. (1998).

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

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

There are alkanes and alcohols in natural gases. From an industrial point of view, separation and purification processes for production of bio-fuels and other chemicals are crucial. Since some of these mixtures in certain temperatures and ratios form azetrope mixtures which can not be separated by normal distillation, methods for new separation techniques such as supercritical fluid extraction should be developed.

Supercritical fluid extraction process of ethanol-octane mixtures were studied recently (Kassim et al. 2008; Davarnejad et al. 2007; Davarnejad et al. 2008a). In the current work, the mutual feasibility of a system involving a 24.2% mole ratio of octane-to-ethanol (as heavy component) and using supercritical and slightly sub-critical carbon dioxide solvent was studied. Theoretical data were calculated from regular solution equations and compared with experimental data. These equations are described in detail by King et al. (1984). According to the previous thermodynamic models such as equations of state, the estimation of the required parameters for these calculations is difficult if the solute is a complex substance with little information known about the structural formula. An alternative procedure is calculating the activity coefficient

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from regular solution equations which can then be applied to each phase.

Calculations using the proposed theoretical method are defined and described in this paper, together with the physical basis for applying the model to the current system under relevant conditions. Some of the interaction parameters which are required for the calculation of activity coefficients can be calculated from the two-phase equilibrium data obtained from the literature such as Francis (1954) and Schneider et al. (1967). Other interaction parameters used in this work were generated by Fredenslund et al. (1977). These parameters are independent of temperature and dependent on pressure (King et al., 1984; Smith and Van Ness, 1987; Kassim et al., 2007; Davarnejad et al., 2007; Davarnejad et al., 2008a; Davarnejad et al., 2008b). The method of extracting parameters has been described in these mentioned references. The activity coefficient, Gibbs function relationships and eventually mutual solubility data are generated for two phase equilibrium conditions using regular solution equations.

2. Experimental

2.1. Materials

A mixture of ethanol (99.9 %, J.T. Baker) and octane (99.8 %, J.T. Baker) containing 80.52 % ethanol and 19.48 % octane was prepared for the supercritical extraction process, using CO_2 (99.99 %) which was purchased from Malaysian Oxygen (MOX) Sdn. Bhd. Extracted samples from the apparatus were analyzed by gas chromatography (GC).

2.2. *Experimental procedure*

A phase equilibrium re-circulation high-pressure type apparatus was used as shown in Figure 1. In this apparatus, the attainment of equilibrium was further assisted by a magnetic stirrer which was installed in the equilibrium vessel (extractor). All units of the apparatus including the equilibrium cell (volume 500 cm^3), the joining tubes, vapor and liquid sample bombs (V and L in Figure 1 with volumes 50 cm^3 and 40 cm^3, respectively), 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 dashed line was immersed in an air bath. The temperature in the equilibrium cell was measured using a thermocouple which was connected to a digital indicator.

When the cell and the circuit were under vacuum, the heavy component under study (ethanol + octane) was fed into the equilibrium cell. This was accomplished by first filling the reservoir (R_1) with about 120 cm^3 of this mixture. The 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 connecting the cylinder containing the contacting CO_2 and the cell was then switched on to pressurize the cell. In the filling process, heaters for the cell, air bath and bath fan were switched on. As the cell was brought to the desired pressure, valve 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. Equilibrium was achieved when the required temperature and pressure 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 to avoid any droplets of solvent passing through the flow section of the vapor sample bomb. The pump and stirrer were left on for about 30 minutes, to ensure that equilibrium had been achieved. When equilibrium was resumed, the pump and stirrer were turned off and internal valves 3, 5, 4 and 6 were kept opened. The phases were then allowed to stand in contact with each other for about 30 minutes to allow any bubbles in the liquid to become disengaged.

After a period of 30 minutes, 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. After each run, the remaining gas was vented via R by opening the related valves (Figure 1). The samples were analyzed by a GC (Perkin Elmer) which had been equipped with a capillary GC column (length × I.D. 30 m × 0.32 mm, d_f 1.00 µm, Supelco brand).

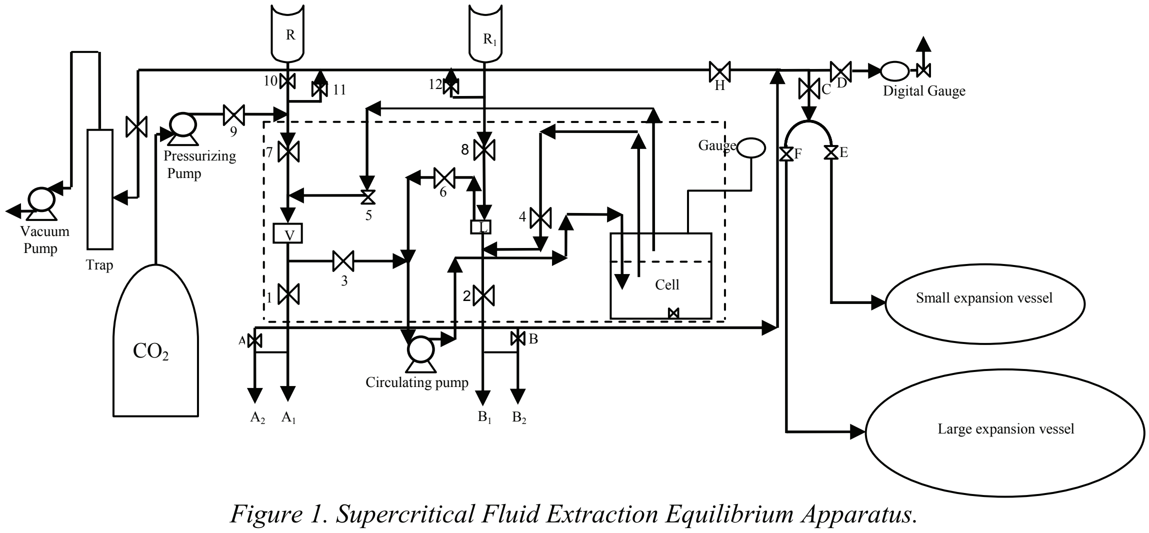

Figure 1. Supercritical Fluid Extraction Equilibrium Apparatus.

3. Calculations Procedures

3.1. Calculations Procedure based on Experiment:

The mutual solubility of CO_2 – ethanol/octane ternary system was studied at a 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 CO_2 free basis were calculated from the following equations:

$$X_1 = \frac{(nx_1)^L}{\left[(nx_1)^L + (nx_2)^L\right]} = \frac{\bar{R}}{1+\bar{R}} \tag{1}$$

$$Y_1 = \frac{(nx_1)^G}{\left[(nx_1)^G + (nx_2)^G\right]} = \frac{\bar{R}_1}{1+\bar{R}_1} \tag{2}$$

$$\bar{R} = (nx_1)^L / (nx_2)^L \tag{3}$$

$$\bar{R}_1 = (nx_1)^G / (nx_2)^G \tag{4}$$

The calculations for the mole fraction of CO_2 in the liquid phase, X, and in the vapor phase, Y, of this system were carried out using the following equations:

$$Y = \frac{(ny)^G}{\left[(nx)^G + (ny)^G\right]} \tag{5}$$

$$(1-X) = \frac{(nx)^L}{\left[(ny)^L + (nx)^L\right]} \tag{6}$$

The values of $(nx)^L$ and $(nx)^G$ were calculated from the relationship $(nx)^L$ or $(nx)^G$ = (weight of extracted heavy components) / ($x_A \times M_A + x_B \times M_B$). The molecular weight of ethanol, M_A, and octane, M_B, are 46.07 g. mole^{-1} and 114.23 g. mole^{-1}, respectively.

In order to calculate $(ny)^G$ and $(ny)^L$ it is necessary to consider the deviation from the perfect gas law pressure of about 1 bar which may be conveniently expressed by the following equation (Walas, 1985):

$$P\,V = n\,(RT + B_v\,P) \tag{7}$$

where P is pressure, V is system volume, n is number of moles of gas, and B_v is the second virial coefficient.

By applying Eq. (7) for two states before and after the expansion process for the vapor phase in each sample and applying several assumptions such as an isothermal and constant volume process during expansion and constant second virial coefficient (B_v), the following equation for the number of mole of gas in the vapor sample bomb is obtained:

$$\begin{aligned}(ny)^G &= V\left[\frac{P_2}{RT + B_vP_2} - \frac{P_1}{RT + B_vP_1}\right] \\ &= VP_2\left[\frac{1-\left(\frac{P_1}{P_2}\right)\left(\frac{RT + B_vP_2}{RT + B_vP_1}\right)}{(RT + B_vP_2)}\right]\end{aligned} \tag{8}$$

where P_1 and P_2 are expansion vessel pressure before and after expansion and V is the volume of the system (35 liters). The number of moles for CO_2 in the liquid sample bomb, $(ny)^L$, was calculated using exactly the same procedure as given above with a total volume of the expansion system taken as 7 liters.

Because the proportion of heavy component extracted into the vapor phase was comparatively small, the majority of it was maintained in the liquid phase throughout the tests. The mole fraction of ethanol in the liquid and vapor phases were calculated on a carbon dioxide free basis at the pressures studied. The results are given in Table 1.

The overall weight fraction of the heavy components for the ternary system can be calculated as:

$$X_w = \frac{m}{m + 44.01 \times n_G} \approx \frac{m}{44.01 \times n_G} \tag{9}$$

where n_G is number of molecules of CO_2 entering the expansion system and is given approximately by:

$$n_G = \frac{V \times \Delta P}{R \times T} \tag{10}$$

where V, T, ΔP, and m are volume and absolute temperature of the expansion system, pressure rise in the expansion system, and mass of the collected heavy component, respectively. The overall mole fraction of the heavy component in the vapor phase is likewise given by:

$$X_M = \frac{m/M}{m/M + n_G} \approx \frac{m}{M \times n_G} \tag{11}$$

where M is the molecular weight of the heavy component (or the average molecular weight of the heavy components in the case of the ternary system).

3.2. Calculation Procedure Based on Thermodynamics Model

The regular solution theory adopted as a model for this system is based on the activity coefficients by applying the following equations (King et al., 1984; Kassim et al., 2008; Davarnejad et al., 2007; Davarnejad et al., 2008a; Davarnejad et al., 2008b):

$$\begin{aligned}RT\ln\gamma_i &= \left(\frac{d\left(nG^{Excess}_{mixing}\right)}{dn_i}\right)_{T,P,n_{j\neq i}} \\ &= \left(\frac{d\left(nH^{Excess}_{mixing}\right)}{dn_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{d\left(nS^{Excess}_{mixing}\right)}{dn_i}\right)_{T,P,n_{j\neq i}}\end{aligned} \tag{12}$$

$$\ln\gamma_i = \left(\ln\gamma_i\right)^{Extract} + \left(\ln\gamma_i\right)^{Solute} \tag{13}$$

Further, Eq. (13) shows a summation of the molar excess enthalpy of mixing (residual or energy-related contribution) and the molar excess entropy of mixing (combinatorial or entropic contribution to the non-ideality of the mixture related to size and shape differences between molecules) (King et al., 1984). In this paper, residual and combinatorial contributions were assumed as vapor (extracted) phase and liquid (solute) phase properties, respectively.

$$\left(\ln\gamma_i\right)^{Extract} = \frac{1}{R\times T}\times\left(\frac{d\left(nH^{Excess}_{mixing}\right)}{dn_i}\right)_{T,P,n_{j\neq i}}$$
$$= \left(\frac{\phi^2\times V_{mi}}{R\times T}\right)\left(d_i-\zeta_{ij}d_j\right)^2+2l_{ij}d_id_j\zeta_{ij} \quad (14)$$

where

$$\zeta_{ij} = \left[\left(\frac{V_{mj}}{V_{mi}}\right)\left(\frac{q_i}{q_j}\right)\right]^{\frac{1}{2}} \quad (15)$$

$$d_i = \left[\frac{\left(U^0{}_{mi}-U_{mi}\right)}{V_{mi}}\right]^{\frac{1}{2}} \quad (16)$$

d_i is the well known "solubility parameter" of component *i*. U_{mi} and $U^0{}_{mi}$ are the molar internal energy of the compressed fluid component *i* and the same fluid at the same temperature but at a very low pressure. These parameters are calculated for component *j* as well. Eq. (14) may be compared with the expression based on the Van der Waals approach (Hildebrand et al., 1970):

$$\left(\ln\gamma_i\right)^{Extract} = \left(\frac{\phi_j^{v2}\times V_{mi}}{R\times T}\right)\left(\left(d_i-d_j\right)^2+2l_{ij}d_id_j\right) \quad (17)$$

Eq. (14) differs from Eq. (17) only in the term of ζ (which is usually close to unity) and in the replacement of the area function ϕ_j^v by the volume fraction:

$$\phi_j{}^v = \frac{\left(x_j\times V_{mj}\right)}{\left(x_i\times V_{mi}+x_j\times V_{mj}\right)} \quad (18)$$

where V_{mi} is the molar volume of the pure liquid *i*. For a non-spherical molecule of type *i*, the quantity q_i is defined such that Zq_i is the number of interactions made by a molecular of this type with surrounding molecules. A monomer has Z interactions with the nearest neighbor molecules (following X-ray diffraction information for simple fluids, Z is normally given a value of 10). q_i is the area function for the molecule. For a linear molecule (King, 1969; Guggenheim, 1952):

$$q_i = r_i-\left(\frac{2\times\left(r_i-1\right)}{Z}\right) \quad (19)$$

where r is the number of segments and it is calculated as a function of number of carbon atoms, for example n for alkanes:

$$r = 0.90+0.283\left(n-1\right) \quad (20)$$

Also, Eq. (14) can be arranged as follows:

$$\ln\gamma_i^{Extract} = \sum\nolimits_{k=1}^{N} v_k^{(i)}\left(\ln\Gamma_k-\ln\Gamma_k^{(i)}\right) \quad (21)$$

$$\ln\Gamma_k = Q_k\left[1-\ln\left(\sum\nolimits_m^N\theta_m\Psi_{mk}\right)-\sum_{m=1}^{N}\frac{\theta_m\Psi_{km}}{\sum\nolimits_{n=1}^{N}\theta_n\Psi_{nm}}\right] \quad (22)$$

where

$$\Psi_{mk} = Exp\left(-\frac{a_{mn}}{T}\right) \quad (23)$$

Q_k is the area function for group k, and θ_m is the area fraction of group m. $\ln\Gamma_k{}^{(i)}$ is defined similarly except that the group area fractions refer to the pure liquid *i* and not to the mixture:

$$(\ln\gamma_i)^{Solute} = \ln\left(\frac{\phi_i}{x_i}\right)+\left(\frac{Zq_i}{2}\right)\times\ln(\theta_i/\phi_i)+l_i-(\phi_i/x_i)\sum_{j=1}^{M}x_jl_j \quad (24)$$

where M, θ_i and ϕ_i are the number of components in the solution, the area fraction for component *i* in the solution and the segment fraction, respectively. ϕ_i and l_i are given as:

$$l_i = (Z/2)(r_i-q_i)-(r_i-1) \quad (25)$$

$$\phi_i = \frac{x_ir_i}{\sum\limits_{i=1}^{M}x_ir_i} \quad (26)$$

Eq. (24) can also be arranged as follows:

$$\left(\ln\gamma_i\right)^{Solute} = \ln\left(\frac{\phi_i}{x_i}\right)-\left(\frac{Zq_i}{2}\right)$$
$$\times\ln\left[1+\left(2\phi_j/Zq_i\right)\left(\left(r_i/r_j\right)-1\right)\right] \quad (27)$$

In the present work an activity coefficient is calculated using Eqs. (13), (21) and (27).

In order to present the calculations of the mutual solubilities for the system CO_2 (*i*) - heavy component (ethanol/octane mixture) (*j*), it is necessary to define that x_i^E is the mole fraction of component *i* based on the extracted phase (carbon dioxide) and x_i^S is the mole fraction of component *i* based on the solute phase. Therefore, x_i^E and x_i^S can be calculated from the activity coefficients data, γ_i^E and γ_i^S for the phases, and from the distribution factors k_i and k_j as:

$$\gamma_i^Ex_i^E = \gamma_i^Sx_i^S \quad (28)$$

$$k_i = \frac{x_i^E}{x_i^S} \quad (29)$$

The calculation procedure is as follows:

1. Guess initial k values for each component given by Eq. (29).
2. Use the guessed k values to obtain the approximate mole fraction of component *i* in each layer.

$$x_i^E = \frac{1-k_j}{1-\frac{k_j}{k_i}} \quad (30)$$

$$x_i^S = \frac{x_i^E}{k_i} \quad (31)$$

3. Use these first approximation values for mole fractions. The activity coefficients for component *i* and *j* in each phase are calculated under the given conditions using regular solution theory.

4. The activity coefficients thus obtained are used to obtain better estimates for k_i and k_j using:

$$k_i = \frac{\gamma_i^E}{\gamma_i^S} \tag{32}$$

$$k_j = \frac{\gamma_j^E}{\gamma_j^S} \tag{33}$$

These values are then used in step 2 and the calculations are repeated until the mole fractions calculated in step 2 show negligible changes from one iteration cycle to the next.

An alternative approach is used in the regular solution theory calculations to establish analytic expressions for a function Q and its derivatives with respect to mole fraction:

$$Q_i = -\left[x_i \ln\left(x_i\gamma_i\right) + x_j \ln\left(x_j\gamma_j\right)\right] = -\frac{G_m^{mixing}}{RT} \tag{34}$$

where (G_m^{mixing}) is the molar Gibbs function of mixing. Also:

$$\left(\frac{\partial Q_i}{\partial x_i}\right)^E = \left(\frac{\partial Q_i}{\partial x_i}\right)^S = \frac{\left(Q_i^E - Q_i^S\right)}{\left(x_i^E - x_i^S\right)} \tag{35}$$

$$\frac{dQ_i}{dx_i} = -\ln\frac{\gamma_i x_i}{\gamma_j x_j} \tag{36}$$

$$\frac{d^2Q_i}{dx_i^2} = -\frac{d\left(\ln\frac{\gamma_i x_i}{\gamma_j x_j}\right)}{dx_i} \tag{37}$$

where $(\partial^2 Q_i / \partial x_i^2)^E$ is taken at the mole fraction (x_i^E) of component *i* in the solvent-rich phase and $(\partial^2 Q_i / \partial x_i^2)^S$ is taken at the mole fraction (x_i^S) of component *i* in the solute-rich phase . $(\partial^2 Q_i / \partial x_i^2)$ should be negative at all points in a completely miscible system. If the system is partially miscible there is a region over which $(\partial^2 Q_i / \partial x_i^2)$ is positive. In the latter case, the points on the Q_i versus x curve corresponding to the equilibrium phase extract (E) and solute (S) have a common tangent to the expression given in Eq. (35).

If initial good estimations of $(x_i^E)^0$ and $(x_i^S)^0$ for the mole fractions (x_i^E) and (x_i^S) are already available, the described routine is found to be satisfactory for locating (x_i^E) and (x_i^S) such that Eq. (35) is accurately obeyed. This procedure is repeated until no further adjustment is required. Eq. (35) is then satisfied and the mole fractions (x_i^E) and (x_i^S) specify the required calculated phase compositions.

4. Results and Discussion

Table 1 shows two phase equilibrium data obtained experimentally when the distribution factor (k_i=y_i/x_i) was applied. Ethanol was slightly separated, particularly at low pressures (such as 36.9 bar) whereas octane was enriched in the liquid phase during this process, which may have been caused by the ethanol natural volatility. On the other hand, two-phase equilibrium study based on the solvent (CO_2) showed that the liquid phase was enriched from heavy components (ethanol + octane) because the distribution factor was always less than one.

Table 1. Compositions of the Vapor and Liquid Equilibrium Phases.

P (bar)	$(x^E)^{Ethanol}$	$(x^S)^{Ethanol}$	Y	X
102.75	0.8118	0.8048	0.9688	0.8850
100.75	0.8121	0.8048	0.9692	0.8625
98.25	0.8124	0.8052	0.9686	0.8508
95.00	0.8128	0.8052	0.9692	0.8150
91.50	0.8133	0.8048	0.9693	0.7851
83.00	0.8144	0.8050	0.9698	0.7115
78.50	0.8149	0.8048	0.9694	0.6851
74.00	0.8156	0.8052	0.9693	0.6351
67.50	0.8164	0.8049	0.9695	0.5951
59.00	0.8176	0.8048	0.9684	0.5211
36.90	0.8260	0.8051	0.9642	0.3250

In terms of uncertainties, Eqs. (9), (10) and (11) were examined. The results show that the calculated mole and weight fractions are affected by errors in the pressure rise, in the absolute temperature of the expansion system and in the mass of heavy component collected. The error function ε (x_w) arising from errors of ε (ΔP) in ΔP, ε (T) in T and ε (m) in m can be obtained by differentiation as given in (Scarborough, 1966).

The experimental compositions in the vapor phase (interpolated from the current research data) and the errors in the weight ε (x_w) and mole ε (x_M) fractions of CO_2 – ethanol/octane system at 75ºC are presented in Table 2.

Table 2. Uncertainties in the Vapor Phase Weight and Mole Fraction.

P (bar)	x_M $\times 10^2$	x_w $\times 10^2$	ε (x_M) $\times 10^4$	ε (x_w) $\times 10^4$	ε(x_M)/x_M $\times 10^2$
30	2.129	3.880	1.75	3.19	0.82
40	2.464	4.494	1.86	3.38	0.76
75	2.697	4.916	1.29	2.35	0.48
100	2.884	5.270	0.98	1.78	0.34

Furthermore, a maximum error of 0.82% was observed at a pressure of 30 bar while a minimum error of 0.34% was obtained at a pressure of 100 bar. The errors in the individual weight and mole fractions in the ethanol and octane are expected to be larger than that arising from the chromatographic analysis of the condensate.

In the liquid phase composition the absolute errors in the weight and mole fractions of CO_2 in the CO_2 – ethanol/octane system at 75ºC are shown in Table 3. These are equal to the absolute errors ε (x_w) and ε (x_M) in the overall weight and mole fractions of the heavy component.

A maximum error of 0.269% was observed at a pressure of 100 bar while a minimum error of 0.238% was obtained at a pressure of 30 bar. Similar to the previous case, the errors in the individual weight and mole fractions in the ethanol and octane are expected to be larger than that arising from the chromatographic analysis of the condensate.

Table 3. Uncertainties in the Liquid Phase Weight and Mole Fraction.

P (bar)	x_M $\times 10^2$	x_w $\times 10^2$	ε (x_M) $\times 10^4$	ε (x_w) $\times 10^4$	ε (x_M)/x_M $\times 10^2$
30	0.640	0.764	1.52	1.190	0.238
40	0.407	0.555	0.974	0.997	0.239
75	0.097	0.164	0.236	0.369	0.243
100	0.022	0.039	0.058	0.103	0.269

In terms of thermodynamic modeling, liquid-liquid equilibrium data for the system of carbon dioxide + hexadecane substances at various pressures and 25ºC were used (Francis, 1954; Schneider et al., 1967) together with the regular solution derived model to determine the effective values for $a_{CO2/CH3\ or\ CH2\ or\ CH}$ and $a_{CH3/CO2}$ interaction parameters as a function of pressure. For the particular case, effective values for the interaction parameters $a_{CO2/OH}$ and $a_{OH/CO2}$ as a function of pressure are calculated using the liquid-liquid equilibrium data for the system CO_2 + heptylalcohol at the existing pressure (65 bar) and 25 ºC. Average values of the interaction parameters are obtained as $a_{CO2/OH} = 855.51$ and $a_{OH/CO2} = 3000$ for CO_2/OH and OH/CO_2 with varying pressure.

This method was supported by King et al. (1984), Davarnejad et al. (2007), Davarnejad et al. (2008a) and Kassim et al. (2007). The data is used to predict mutual miscibility of carbon dioxide-ethanol/octane system at 75 ºC and at various pressures. Interaction parameters and two phase equilibrium data calculated based on the regular solution model at various pressures and at 75ºC are shown in Table 4.

Table 4. Interaction Parameters based on Experimental Data Extracted from References (Francis, 1954) and (Schneider et al., 1967) at 25ºC and Two Phase Equilibrium Data based on Solvent for the Current System.

P (bar)	$a_{CH3/CO2}$	$a_{CO2/CH3}$	$(x^{E}_{CO2})^{RST}$	$(x^{S}_{CO2})^{RST}$
102.75	641.2959	89.7605	0.9750	0.6268
100.75	640.3018	90.0105	0.9751	0.6270
98.25	637.4674	90.3275	0.9753	0.6273
95.00	634.4533	90.7471	0.9755	0.6277
91.50	630.8486	91.2084	0.9560	0.8260
83.00	630.1543	92.3692	0.9583	0.8216
78.50	629.5920	93.6619	0.9595	0.8193
74.00	624.7362	93.6619	0.9606	0.8169
67.50	618.0068	94.6356	0.9621	0.8137
59.00	608.0218	95.9599	0.9640	0.8098
36.90	610.8429	99.6736	0.9685	0.8002

Two phase equilibrium data based on experiments and theory are shown in Figure 2. Experimental and theoretical values of the vapor phase (extracted phase) data show good agreement, however, liquid phase data show some discrepancies. It appears that the differences between experimental and theoretical data for the liquid phase is partly due to experimental uncertainty and values of the interaction parameters calculated from a set of data obtained from literature.

Figure 3 shows CO_2 activity coefficient (γ_{CO2}) against CO_2 mole fraction (x_{CO2}) at 75ºC and 100 bar. Activity coefficients for other pressures are shown in Table 5. Figure 4 shows the molar Gibbs function of CO_2 (G^{mixing}_{m}) against CO_2 mole fraction (x_{CO2}) at 75ºC and 100 bar. The figure shows a parabolic profile with a maximum at $x_{CO2}=0.35$.

Figure 5 shows the variation of the gradient of the molar Gibbs function of CO_2 (dG^{mixing}_{m}/dx) with CO_2 mole fraction (x_{CO2}) at 75ºC and 100 bar. It shows that the first derivative of the G^{mixing}_{m} curve has a logarithmic profile. It decreases continuously as the CO_2 mole fraction increases to 1. Of course, the derivative is null at $x_{CO2}=0.35$.

Figure 6 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 75 ºC and 100 bar. The figure shows that the system is partially miscible at $x_{CO2} = 0.9$ and the sign of the second derivative of Q_{CO2} changes at $x_{CO2} = 0.9$. The solubility parameter data for other pressures are shown in Table 6. The solubility parameter is negative for a completely miscible system. If the system were partially miscible, this parameter would be positive. Hence, the results based on regular solution model predict that the system under study is completely miscible for the whole range of CO_2 mole fractions. The exceptions are the points $x_{CO2} = 0.9$ for the whole pressure range and $x_{CO2} = 0.95$ at 36.9 bar (the lowest pressure) at which the system is partially miscible.

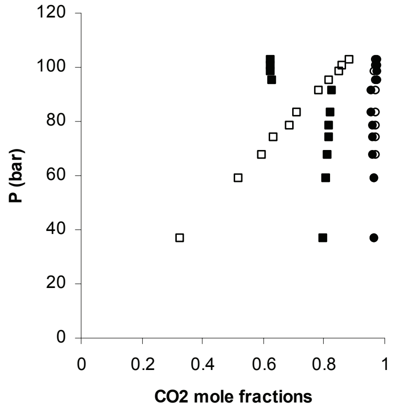

Figure 2. Two Phase Equilibrium Data based on Experiment and Regular Solution Theory. (□: Liquid phase based on Exp., ○: Vapor phase based on Exp., ■: Liquid phase based on RST, ●: Vapor phase based on RST).

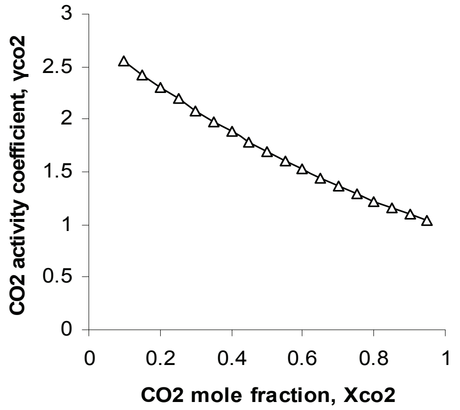

Figure 3. CO_2 Activity Coefficient (γ_{CO2}) vs CO_2 Mole Fraction (x_{CO2}) at 75 ºC and 100 bar.

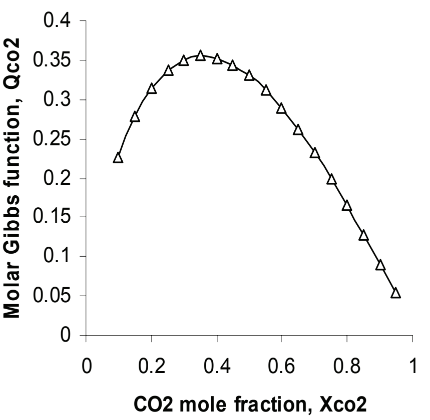

Figure 4. Molar Gibbs Function for CO_2 (G^{mixing}_{m}) vs CO_2 Mole Fraction (x_{CO2}) at 75 ºC and 100 bar.

Table 5. CO_2 Activity Coefficient (γ_{CO2}) vs CO_2 Mole Fraction (x_{CO2}) at 75 ºC and Various Pressures.

x_{co2}	$\gamma_{co2,\ 102.75\ bar}$	$\gamma_{co2,\ 98.25\ bar}$	$\gamma_{co2,\ 95\ bar}$	$\gamma_{co2,\ 91.5\ bar}$	$\gamma_{co2,\ 78.5\ bar}$	$\gamma_{co2,\ 74\ bar}$	$\gamma_{co2,\ 67.5\ bar}$	$\gamma_{co2,\ 36.90\ bar}$
0.1	2.5605	2.5535	2.5483	2.5425	2.5195	2.5109	2.4980	2.4293
0.15	2.4333	2.4276	2.4234	2.4186	2.3998	2.3927	2.3822	2.3252
0.20	2.3120	2.3075	2.3041	2.3003	2.2852	2.2795	2.2709	2.2244
0.25	2.1965	2.1930	2.1903	2.1874	2.1754	2.1709	2.1641	2.1268
0.30	2.0865	2.0838	2.0817	2.0795	2.0703	2.0668	2.0615	2.0322
0.35	1.9815	1.9796	1.9781	1.9764	1.9695	1.9669	1.9630	1.9406
0.40	1.8815	1.8801	1.8791	1.8779	1.8730	1.8712	1.8683	1.8520
0.45	1.7860	1.7851	1.7844	1.7837	1.7805	1.7793	1.7773	1.7660
0.50	1.6948	1.6944	1.6940	1.6936	1.6918	1.6910	1.6899	1.6828
0.55	1.6077	1.6076	1.6075	1.6073	1.6066	1.6063	1.6058	1.6021
0.60	1.5244	1.5245	1.5246	1.5247	1.5248	1.5248	1.5248	1.5238
0.65	1.4447	1.4450	1.4452	1.4454	1.4461	1.4463	1.4467	1.4477
0.70	1.3682	1.3686	1.3689	1.3692	1.3703	1.3707	1.3713	1.3737
0.75	1.2948	1.2953	1.2956	1.2959	1.2973	1.2977	1.2984	1.3016
0.80	1.2243	1.2247	1.2250	1.2254	1.2267	1.2272	1.2279	1.2313
0.85	1.1565	1.1569	1.1571	1.1574	1.1586	1.1590	1.1596	1.1627
0.90	1.0921	1.0924	1.0925	1.0928	1.0936	1.0939	1.0943	1.0965
0.95	1.0341	1.0342	1.0343	1.0344	1.0347	1.0348	1.0350	1.0360

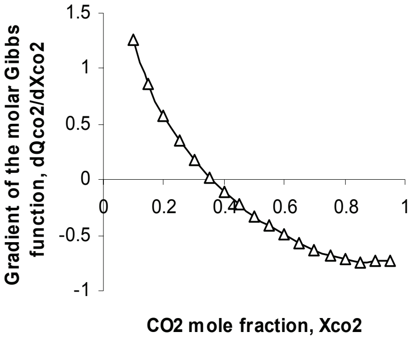

Figure 5. Gradient of the Molar Gibbs Function for CO_2 (dG^{mixing}_m/dx_{CO2}) vs CO_2 Mole Fraction (x_{CO2}) at 75 ºC and 100 bar.

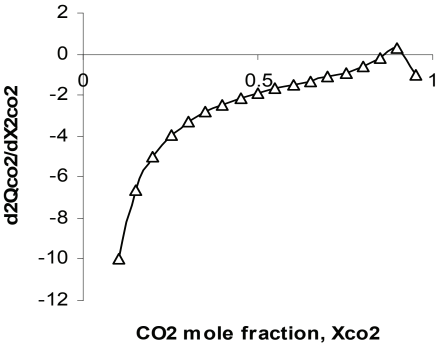

Figure 6. Solubility Parameter for CO_2 (d^2Q_{CO2}/dx^2_{CO2}) vs CO_2 Mole Fraction (x_{CO2}) at 75 ºC and 100 bar.

Table 6. Solubility Parameter, d^2Q_{CO2}/dx^2_{CO2}, for CO_2 vs CO_2 Mole Fraction (x_{CO2}) at 75 ºC and Various Pressures.

x_{co2}	dQ^2_{co2}/dx^2_{co2}, 102.75 bar	dQ^2_{co2}/dx^2_{co2}, 98.25 bar	dQ^2_{co2}/dx^2_{co2}, 95 bar	dQ^2_{co2}/dx^2_{co2}, 91.5 bar	dQ^2_{co2}/dx^2_{co2}, 78.5 bar	dQ^2_{co2}/dx^2_{co2}, 74 bar	dQ^2_{co2}/dx^2_{co2}, 67.5 bar	dQ^2_{co2}/dx^2_{co2}, 36.90 bar
0.10	-9.9797	-9.9888	-9.9955	-10.0030	-10.0324	-10.0432	-10.0593	-10.1435
0.15	-6.6424	-6.6514	-6.6581	-6.6655	-6.6949	-6.7056	-6.7218	-6.8064
0.20	-4.9708	-4.9797	-4.9864	-4.9938	-5.0230	-5.0338	-5.0499	-5.1349
0.25	-3.9647	-3.9736	-3.9802	-3.9875	-4.0166	-4.0274	-4.0435	-4.1286
0.30	-3.2904	-3.2992	-3.3058	-3.3131	-3.3419	-3.3526	-3.3686	-3.4538
0.35	-2.8046	-2.8133	-2.8198	-2.8270	-2.8555	-2.8661	-2.8820	-2.9670
0.40	-2.4351	-2.4436	-2.4500	-2.4571	-2.4852	-2.4957	-2.5114	-2.5958
0.45	-2.1412	-2.1495	-2.1557	-2.1626	-2.1902	-2.2005	-2.2159	-2.2994
0.50	-1.8975	-1.9055	-1.9115	-1.9182	-1.9450	-1.9549	-1.9700	-2.0519
0.55	-1.6866	-1.6942	-1.6999	-1.7063	-1.7318	-1.7414	-1.7559	-1.8351
0.60	-1.4945	-1.5015	-1.5068	-1.5127	-1.5366	-1.5455	-1.5591	-1.6344
0.65	-1.3083	-1.3145	-1.3192	-1.3244	-1.3456	-1.3537	-1.3660	-1.4348
0.70	-1.1129	-1.1178	-1.1215	-1.1257	-1.1429	-1.1495	-1.1597	-1.2181
0.75	-0.8872	-0.8900	-0.8921	-0.8946	-0.9053	-0.9096	-0.9163	-0.9574
0.80	-0.5987	-0.5979	-0.5974	-0.5969	-0.5963	-0.5964	-0.5971	-0.6075
0.85	-0.2023	-0.1947	-0.1892	-0.1832	-0.1612	-0.1536	-0.1427	-0.0944
0.90	0.2696	0.2915	0.3077	0.3253	0.3927	0.4168	0.4521	0.6265
0.95	-0.9754	-0.9173	-0.8744	-0.8274	-0.6450	-0.5791	-0.4815	0.0161

5. Conclusions

The regular solution theory as a general model can be applied for different systems at various conditions. The difference between the regular solution model and other models (such as equations of state) is that the latter requires specific constants which may not be available in the literature for phase equilibrium data. However, for the regular solution model, the data obtained are totally related to group interaction parameters and independent of temperature. It is possible to predict the liquid-liquid and vapor-liquid equilibrium from knowledge of structural formula of the constituent molecular species. The system miscibility can also be obtained by applying the solubility parameter which is calculated from the regular solution equations. In this study, the interaction between the individual groups constituting the molecules is considered and group interaction parameters are generated together with the parameters that describe the size and shape of the molecules. The regular solution equations are also applied to obtain the mutual feasibility of CO_2 – ethanol/octane system at 75°C and varying pressures. The experimental results show that a considerable separation is not achieved at the ethanol-octane ratio investigated in this work. This is consistent with the previous studies in the literature.

Acknowledgments

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Nomenclature

a_{mn}	Interaction parameter between groups *m* and *n* [K].
$a_{CH3/CO2}$	Interaction parameter between groups CH_3 and CO_2 [K].
$a_{CO2/CH3}$	Interaction parameter between groups CO_2 and CH_3 [K].
$a_{OH/CO2}$	Interaction parameter between groups OH and CO_2 [K].
$a_{CO2/OH}$	Interaction parameter between groups CO_2 and OH [K].
B_v	Second virial coefficient [cm^3. $mole^{-1}$].
d_i	Solubility parameter of component *i*.
E (superscript)	Extracted phase or vapor phase.
Exp.	Experimental data.
G_m^{mixing}	Molar Gibbs function of mixing [$bar.cm^3.mole^{-1}$].
$G^{Excess}{}_{mixing}$	Excess Gibbs free energy of mixing [$bar.cm^3$].
$H^{Excess}{}_{mixing}$	Excess Enthalpy of mixing [$bar.cm^3$].
i (in RST)	Solvent (carbon dioxide).
j (in RST)	Solute (heavy component).
k	Group of component *i*.
k_i, k_j	k-value (distribution factor) for components *i* and *j*.
m, n	Group in the mixture
m (in the precision calculations)	Weight of extracted heavy components [g].
M (in the precision calculations)	Molecular weight of the heavy components [g. $mole^{-1}$].
M_A	Molecular weight of ethanol [46.07 g. $mole^{-1}$].
M_B	Molecular weight of octane [114.23 g. $mole^{-1}$].
n_G	Number of molecules of CO_2 entering the expansion system.
$(ny)^G$	Number of moles of carbon dioxide in the vapor sample bomb.
$(ny)^G$	Number of moles of heavy component in the vapor sample bomb.
$(ny)^L$	Number of moles of carbon dioxide in the liquid sample bomb.
$(nx)^L$	Number of moles of heavy component in the liquid sample bomb.
$(nx_1)^L$	Number of moles of ethanol in the liquid phase on a carbon dioxide free basis.
$(nx_1)^G$	Number of moles of ethanol in the vapor phase on a carbon dioxide free basis.
$(nx_2)^L$	Number of moles of octane in the liquid phase on a carbon dioxide free basis.
$(nx_2)^G$	Number of moles of octane in the vapor phase on a carbon dioxide free basis.
P	System pressure [bar].
P_1	Expansion vessel pressure before expansion [bar].
P_2	Expansion vessel pressure after expansion [bar].
q_i	Area function for the molecule.
Q_k	Area function for group k.
Q_i	$- G_m^{mixing}/RT$.
R	Number of segments.
$\overline{R}$	Ratio, $(nx_1)^L/(nx_2)^L$.
$\overline{R}_1$	Ratio, $(nx_1)^G/(nx_2)^G$.
RST	Regular solution theory model data.
S (superscript)	Solute phase or liquid phase or raffinate phase.
$S^{Excess}{}_{mixing}$	Excess Entropy of mixing [$bar.cm^3$].
T	System temperature [K].
U_{mi}	Molar internal energy of the compressed fluid component *i* [$bar.cm^3.mole^{-1}$].
$U^0{}_{mi}$	Molar internal energy of the compressed fluid component *i* at a very low pressure [$bar.cm^3.mole^{-1}$].
V	System volume [cm^3] .
V_{mi}	Molar volume of the pure liquid of *i* [$cm^3.mole^{-1}$].
X	Mole fraction of carbon dioxide in the liquid phase.
X_1	Mole fractions of ethanol in the liquid phase on a carbon dioxide free basis.
X_w	Overall weight fraction of the heavy components.
X_M	Overall mole fraction of heavy components.
$(x^E)^{Ethanol}$	Ethanol mole fraction in the extracted phase on CO_2 free basis.
$(x^S)^{Ethanol}$	Ethanol mole fraction in the liquid phase on CO_2 free basis.

x_A	Mole fraction of ethanol in the liquid sample bomb (or in the vapor sample bomb).
x_B	Mole fraction of octane in the liquid sample bomb (or in the vapor sample bomb).
$x_i^{\,E}$	Component *i* mole fraction in extracted phase.
$x_i^{\,S}$	Component *i* mole fraction in liquid phase.
Y	Mole fraction of carbon dioxide in the vapor phase.
Y_1	Mole fractions of ethanol in the vapor phase on a carbon dioxide free basis.
Z	Interactions with nearest neighbor molecules ~ 10.

Greek letters

γ_i	Component *i* activity coefficient.
$\varphi_i^{\,v}$	Volume fraction of component *j*.
Γ_k, $\Gamma_k^{(i)}$	Residual activity coefficient for group *k*.
θ_i, θ_m, θ_n	Area fraction of group *i* or *m* or *n*.
ψ_{mk}, ψ_{km}, ψnm	Group interaction parameters.
ϕ_i	Segment fraction.
$\upsilon_k^{(i)}$	Number of groups of type *k* in the molecule *i*.
ξ_i	Non-ideality factor of the vapor phase.
ε (x_w)	Absolute errors in the overall weight fraction of the heavy component.
ε (x_M)	Absolute errors in the overall mole fraction of the heavy component.
ΔP	Pressure increment before and after expansion process [bar].

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