

# Regular Solution Theory Model Used to Predict Supercritical CO<sub>2</sub> Extraction of p-chlorophenol Contaminant from Water Stream

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## Abstract

The objective of this paper is the assessments of the feasibility of the extraction process utilizing a near critical carbon dioxide solvent with p-chlorophenol contaminant solute, which would be speeded up if it were possible to predict mutual solubility data. The use of equations of state or empirical correlations for collating and predicting liquid-liquid and liquid-dense fluid equilibrium depend on critical constants properties which are not easy to obtain for complex heavy component contaminant solute and therefore, would be for the prediction of solubility related to vapor phase only. It is concluded that the estimation by using equation of state for some of the parameters required these calculations would be difficult if the solute was a complex substance about which little was known apart from its structural formula. An alternative procedure is to apply activity coefficient expressions of the regular solution theory to each phase. Calculations along these lines are described and the physical basis for applying these methods under the relevant conditions discussed. Regular solution theory approach in particular has been found to be that the interaction parameters for the prediction activity coefficients must be regarded as pressure dependent and therefore would be independent to temperature.

**Keywords:** p-chlorophenol; Carbon dioxide; Supercritical extraction; Regular solution theory; Phase equilibrium.

## 1. Introduction

Supercritical fluid extraction of p-chlorophenol contaminant is an unit operation in which supercritical fluid is a solvent such as CO<sub>2</sub> which is a substance above its critical temperature and pressure, is used to preferentially solubilize specific components from a mixture containing low vapor pressure compounds. In recent years, supercritical fluid extraction has attracted attention because of the increase extraction efficiency it some things provides over liquid-liquid extraction. The fluid density of supercritical fluid can be varied from gas-like to liquid-like with relatively small changes in pressure. Methods available for cleaning up water contaminated with over one percent organic include distillation incineration and liquid extraction. Distillation is energy

intensive for dilute aqueous solutions and incineration is both energy intensive and produce ashes and gaseous products of in complete technique has had limited use to concern over residual solvent present in the processed water. One alternative technique applicable to both contaminated water and contaminated soil is structural extraction by Groves et al. in 1989 [1]. The ability of supercritical fluid with and without entrainers to solubilize heavy molecular organic is well documented. However, limited data are available in the literature dealing with extraction of p-chlorophenol contaminants from water or soil. In 1986, Capriel et al. used supercritical method to extract bound pesticide residues from soil and plant samples, experimentally [2]. In 1987, Brady et al. extracted DDT and toxaphene from soil with carbon dioxide and mixtures of methanol/carbon dioxide and toluene/ carbon dioxide [3]. The fundamental thermodynamic parameters of interest for the extraction of contaminated p-chlorophenol from water or soil in the activity coefficients calculated from the regular solution theory based on the group interaction parameters of the solute and solvent in system under consideration CO<sub>2</sub>-p-chlorophenol in order to obtain the final results for the assessment feasibility of the extraction process utilizing a near critical CO<sub>2</sub> which is the mutual solubility. As a model system for the extraction of toxic contaminants from water stream, the supercritical extraction of p-chlorophenol using carbon dioxide as the primary solvent which is environmentally acceptable, inexpensive and readily available was studied.

## 2. Model

### 2.1 Regular solution theory

The regular solution theory adopted as a model for this system is based on the activity coefficients by applying the following equations:

$$RT \ln \gamma_i = \left( \frac{d(nG_{mixing}^{Excess})}{dn_i} \right)_{T,P,n_{j \neq i}} = \left( \frac{d(nH_{mixing}^{Excess})}{dn_i} \right)_{T,P,n_{j \neq i}} - T \left( \frac{d(nS_{mixing}^{Excess})}{dn_i} \right)_{T,P,n_{j \neq i}} \quad (1)$$

$$\ln \gamma_i = (\ln \gamma_i)^{Extract} + (\ln \gamma_i)^{Solute} \quad (2)$$

$$(\ln \gamma_i)^{Extract} = \frac{1}{R \times T} \times \left( \frac{d(nH_{mixing}^{Excess})}{dn_i} \right)_{T,P,n_{j \neq i}} \quad (3)$$

$$= \left( \frac{\phi_j^2 \times V_{mi}}{R \times T} \right) (d_i - \zeta_{ij} d_j)^2 + 2l_{ij} d_i d_j \zeta_{ij}$$

where

$$\zeta_{ij} = \left[ \left( \frac{V_{mj}}{V_{mi}} \right) \left( \frac{q_i}{q_j} \right) \right]^{\frac{1}{2}} \quad (4)$$

and

$$d_i = \left[ \frac{(U_{mi}^0 - U_{mi})}{V_{mi}} \right]^{\frac{1}{2}} \quad (5)$$

$d_i$  is the well known ‘‘solubility parameter’’ of component (i).  $U_{mi}$  and  $U_{mi}^0$  are the molar internal energy of the compressed fluid component (i) and the same fluid at the same temperature but a very low pressure. These parameters are calculated by the same equations but for component (j), as well. Eq. (3) may be compared with the expression given by the Vander Waals approach [4],

$$(\ln \gamma_i)^{Extract} = \left( \frac{\phi_j^{v2} \times V_{mi}}{R \times T} \right) \times \left( (d_i - d_j)^2 + 2l_{ij} d_i d_j \right) \quad (6)$$

It differs from this only in the term  $\zeta$  (which is usually close to unity) and in the replacement of the area function ( $\phi_j^v$ ) by the volume function,

$$\phi_j^v = \frac{(x_j \times V_{mj})}{(x_i \times V_{mi} + x_j \times V_{mj})} \quad (7)$$

where ( $V_{mi}$ ) is the molar volume of the pure liquid (i).

For a non-spherical molecule of type (i), 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 nearest neighbor molecules (following X-ray diffraction information for simple fluids  $Z$  is normally given a value of 10). ( $q_i$ ) is termed the area function for the molecule. For a linear molecule [5, 6],

$$q_i = r_i - \left( \frac{2 \times (r_i - 1)}{Z} \right) \quad (8)$$

( $r$ ) is the number of segments and it is calculated as a function of number of carbon atoms, for example ( $n$ ) for alkanes can be determined for the calculation, therefore,

$$r = 0.90 + 0.283(n - 1)$$

Also, there would be an arrangement for Eq. (3) as following,

$$\ln \gamma_i^{Extract} = \sum_{K=1}^N v_K^{(i)} (\ln \Gamma_K - \ln \Gamma_K^{(i)}) \quad (9)$$

$$\ln \Gamma_K = Q_K \left[ \frac{1 - \ln \left( \sum_m \theta_m \Psi_{mK} \right)}{\sum_{m=1}^N \frac{\theta_m \Psi_{mK}}{\sum_{n=1}^N \theta_n \Psi_{nm}}} \right] \quad (10)$$

where

$$\Psi_{mK} = \text{Exp} \left( - \frac{a_{mn}}{T} \right) \quad (11)$$

$Q_K$  is the area function for group  $k$  and  $\theta_m$  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.

$$(\ln \gamma_i)^{Solute} = \ln \left( \frac{\phi_i}{x_i} \right) + \left( \frac{Zq_i}{2} \right) \times \left[ \ln(\theta_i / \phi_i) + l_i - (\phi_i / x_i) \sum_{j=1}^M x_j l_j \right] \quad (12)$$

where  $M$ ,  $\theta_i$  and  $\phi_i$  are the number of components in the solution, the area fraction for component  $i$  in the solution and the segment fraction, respectively.

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

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^M x_i r_i}$$

Also there is another arrangement for Eq. (12),

$$(\ln \gamma_i)^{Solute} = \ln \left( \frac{\phi_i}{x_i} \right) - \left( \frac{Zq_i}{2} \right) \times \left[ \ln \left[ 1 + (2\phi_j / Zq_i) \left( (r_i / r_j) - 1 \right) \right] \right] \quad (13)$$

In the present work activity coefficient is calculated using Eqs. (2), (9) and (12).

In order to present details calculations of the mutual solubilities for the system CO<sub>2</sub> (i)/heavy component (p-chlorophenol) (j) it is necessary to define that  $x_i^E$  is the mole fraction of component (i) based on the extract phase (carbon dioxide) and  $x_i^S$  is the mole fraction of component (i) based on the solute phase (heavy component). Therefore  $x_i^E$  and  $x_i^S$  can be calculated from the activity coefficients data  $\gamma_i^E$  and  $\gamma_i^S$  for the phases and from the distribution factors  $k_i$  and  $k_j$  as:

$$\gamma_i^E x_i^E = \gamma_i^S x_i^S \quad (14)$$

$$k_i = \frac{x_i^E}{x_i^S} \quad (15)$$

The procedure is as follows:

- Guessing initial k-values for each component given by Eq. (15).
- Use these guessed k-values to obtain the approximate mole fraction of component (i) in each layer.

$$x_i^E = \frac{1 - k_j}{1 - \frac{k_j}{k_i}} \quad (16)$$

$$x_i^S = \frac{x_i^E}{k_i} \quad (17)$$

These values were then inserted at step b and the cycle was repeated until the mole fractions calculated in step b showed negligible change from one step to the next.

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

$$Q_i = -[x_i \ln(x_i \gamma_i) + x_j \ln(x_j \gamma_j)] = -\frac{G_m^{\text{mixing}}}{RT} \quad (18)$$

$$\left(\frac{\partial Q_i}{\partial x_i}\right)^E = \left(\frac{\partial Q_i}{\partial x_i}\right)^S = \frac{(Q_i^E - Q_i^S)}{(x_i^E - x_i^S)} \quad (19)$$

$$\frac{dQ_i}{dx_i} = -\ln \frac{\gamma_i x_i}{\gamma_j x_j} \quad (20)$$

$$\frac{d^2 Q_i}{dx_i^2} = -\frac{d\left(\ln \frac{\gamma_i x_i}{\gamma_j x_j}\right)}{dx_i} \quad (21)$$

( $G_m^{\text{mixing}}$ ) is the molar Gibbs function of mixing and from standard thermodynamic relationships, it follows that  $(\partial^2 Q_i / \partial x_i^2)$  should be negative at all points in a completely miscible system. If the system is partially miscible there will be 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 Eq. (19).

where  $(\partial^2 Q_i / \partial x_i^2)^E = \text{gradient}$ ,  $(\partial^2 Q_i / \partial x_i^2)^E$  taken at the mole fraction ( $x_i^E$ ) of component (i) in the solvent-rich phase and  $(\partial^2 Q_i / \partial x_i^2)^S = \text{gradient}$  taken at mole fraction ( $x_i^S$ ) of component (i) in the solute-rich phase.

If first good estimates of  $(x_i^E)^0$  and  $(x_i^S)^0$  for the mole fractions ( $x_i^E$ ) and ( $x_i^S$ ) were already available, the following routine was found to be satisfactory for locating  $(x_i^E)$  and  $(x_i^S)$  such that Eq. (19) was accurately obeyed. This procedure was repeated until no further adjustment was required. Eq. (19) was then satisfied and the mole fractions ( $x_i^E$ ) and ( $x_i^S$ ) specified the required calculated phase compositions.

### 3. Result and Discussion

Calculations reported above suggest that prediction equations of the thermodynamic model type are valuable for the calculations of mutual solubilities in compressed fluid solvents. However, when applied to compressed system or over an extensive pressure range, the parameters should be taken as pressure dependent. This approach leads to the prediction solubility of contaminate component about which very little is known apart from its structural formula by using grouping interaction parameters.

Using the liquid-liquid equilibrium data for the system carbon dioxide-phenol at various pressures and at  $T=25$  °C (extrapolated data at  $T=25$  °C from ref. [7]), together with the regular solution derived model in order to calculate effective values for the  $a_{\text{CO}_2/\text{Ach}}$  and  $a_{\text{Ach}/\text{CO}_2}$  interaction parameters as a function of pressure and also the systems carbon dioxide-p-chlorophenol at exist pressure (65 bar) and temperature (25 °C) [8], together with the regular solution derived model in order to calculate effective values for  $a_{\text{CO}_2/\text{Accl}}$  and  $a_{\text{Accl}/\text{CO}_2}$  interaction parameters as an average at exist pressure and temperature [8] and used these to predict data in the carbon dioxide-p-chlorophenol system at temperatures 40, 50 °C and at various pressures. The other parameters required in the regular solution model were evaluated using the standard methods described in [9] and extracted data of ref. [7] for p-chlorophenol. Furthermore the derived model based on the regular solution theory used in the present work is given in [10]. In order to examine the behavior of being the system CO<sub>2</sub>-p-chlorophenol at various pressures and temperature

miscible or immiscible, it is necessary to calculate the values of the activity coefficient ( $\gamma$ ), Gibbs function (G) and its derivatives ( $dG/dx$ ) and ( $d^2G/dx^2$ ).

Table 1: Experimental data for the system CO<sub>2</sub>-P-chlorophenol

Pressure/ $K_{p\text{-chlorophenol}}/x_{p\text{-chlorophenol}}^E/x_{p\text{-chlorophenol}}^S$ of p-chlorophenol at 40 °C and at 50 °C extracted from ref. [7]			
Pressure (MPa)	$K_{p\text{-chlorophenol}}$	$x_{p\text{-chlorophenol}}^E$	$x_{p\text{-chlorophenol}}^S$
40 °C			
9.65	1.94	0.003	$1.54639 \times 10^{-3}$
11.025	3.00	0.0033	$1.10000 \times 10^{-3}$
12.404	3.47	0.0035	$1.00860 \times 10^{-3}$
13.80	4.96	0.004	$8.06452 \times 10^{-4}$
15.16	5.24	0.0047	$8.96946 \times 10^{-4}$
16.54	5.38	0.0048	$8.92193 \times 10^{-4}$
50 °C			
9.65	0.44	0.00081	$1.8409 \times 10^{-3}$
11.025	0.68	0.0011	$1.6176 \times 10^{-3}$
12.404	1.32	0.0014	$1.0606 \times 10^{-3}$
13.80	2.00	0.0026	$1.3000 \times 10^{-3}$
15.16	2.4	0.0029	$1.2083 \times 10^{-3}$
16.54	2.75	0.0033	$1.2000 \times 10^{-3}$

Table 2: Using data in Table 1 at 25 °C together with the above regular solution equations model to obtain the results of the back-calculated effective values of interaction parameters (for  $a_{CO_2/ACH}$  and  $a_{ACH/CO_2}$ ) and used these to predict data in the CO<sub>2</sub>-phenol system in Tables 4 and 5, (interaction parameters as independent of temperature)

P (MPa)	$a_{CO_2/ACH}$	$a_{ACH/CO_2}$
9.65	94.0	-3928.4839
11.025	-64.0	-2687.5791
12.404	24.5	-1814.0198
13.80	29.6	-1808.8107
15.16	35.0	-1803.6016
16.54	90.0	-9985.2080

Table 3: Interaction parameters  $a_{CO_2/Achl}$  and  $a_{Achl/CO_2}$  extracted from ref. [8] at 65 bar and at 25 °C.

P (bar)	$a_{CO_2/Achl}$	$a_{Achl/CO_2}$
65	1.0	644.9838

Table 4: Comparison of the experimental data in Table 1 at 40 °C (extracted phase (E) based on CO<sub>2</sub> mole fraction) with values predicted by the standard regular solution equation model with parameter ( $a_{ij}$  and  $a_{ji}$ ) taken from Tables 2 and 3.

P (MPa)	$x_{CO_2}^S$ (exp.)	$x_{CO_2}^E$ (exp.)	$x_{CO_2}^E$ (model)	$\gamma_{CO_2}^S$ (model)	$\gamma_{CO_2}^E$ (model)
9.65	0.9984536	0.997	0.9998	0.0000	0.0296
11.025	0.9989000	0.9967	0.9998	0.0006	0.6939
12.404	0.9989914	0.9965	0.9998	0.0099	0.9954
13.80	0.9991935	0.9960	0.9998	0.0100	0.9955
15.16	0.9991031	0.9953	0.9998	0.0102	0.9956
16.54	0.9991078	0.9952	0.9998	0.0000	0.0000

Table 5: Comparison of the experimental data in Table 1 at 50 °C (extracted phase (E) based on CO<sub>2</sub> mole fraction) with values predicted by the standard regular solution equation model with parameter ( $a_{ij}$  and  $a_{ji}$ ) taken from Tables 2 and 3.

P (MPa)	$x_{CO_2}^S$ (exp.)	$x_{CO_2}^E$ (exp.)	$x_{CO_2}^E$ (model)	$\gamma_{CO_2}^S$ (model)	$\gamma_{CO_2}^E$ (model)
9.65	0.9981591	0.99919	0.9998	0.0000	0.0432
11.025	0.9983824	0.9989	0.9998	0.0007	0.7634
12.404	0.9989394	0.9986	0.9998	0.0117	0.9967
13.80	0.9987000	0.9974	0.9998	0.0119	0.9968
15.16	0.9987917	0.9971	0.9998	0.0122	0.9969
16.54	0.9988000	0.9967	0.9998	0.0000	0.0000

Parameter  $d^2Q_i/dx_i^2$  (molar Gibbs function second derivative) shows that it should be negative at all points in a completely miscible system. If the system is partially miscible these will be a region over which the parameter is positive. Figs 2, 4, 6, 8, 10, 12 and 14 show parameter ( $d^2Q_{CO_2}/dx_{CO_2}^2$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{CO_2}$ ) at constant pressures 9.65, 11.025, 12.404, 13.80, 15.16 and 16.54 MPa and at temperature 40 °C and at 50 °C. Interaction parameters obtained from Tables 2 and 3.

The temperature has no significant effect on miscibility at various pressures, therefore miscibility increases with increasing heavy component mole fractions. Tables 4 and 5 show two phases equilibrium data based on regular solution model, these data are compared with experimental data which extracted from Table 1. Figs 13 and 14 show supercritical vapor phase based on experimental and theoretical data at 40 °C and 50 °C respectively. Fig 15 shows distribution coefficient based on CO<sub>2</sub> against pressure at 40 °C and at 50 °C. Data extracted from regular solution theory model.

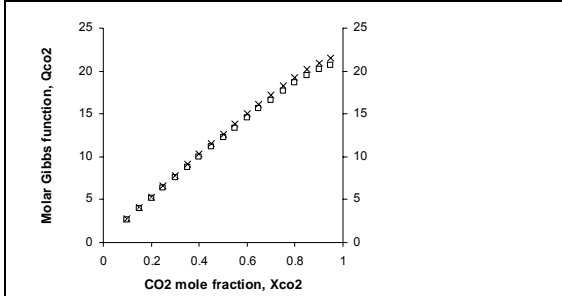


Fig 1: Molar Gibbs function for CO<sub>2</sub> ( $G_m^{\text{mixing}}$ ) against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 9.65 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

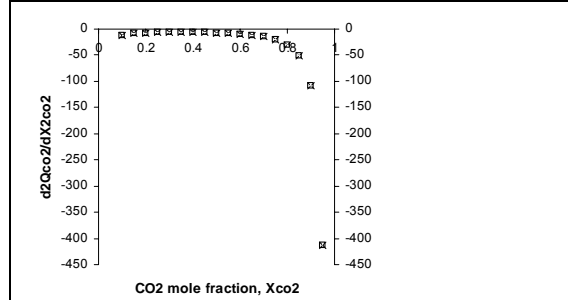


Fig 4: Parameter ( $d^2Q_{\text{CO}_2}/dx^2_{\text{CO}_2}$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 11.025 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

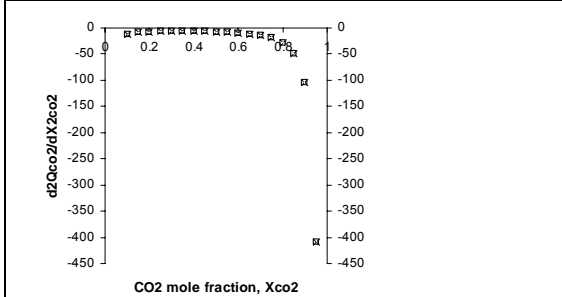


Fig 2: Parameter ( $d^2Q_{\text{CO}_2}/dx^2_{\text{CO}_2}$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 9.65 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

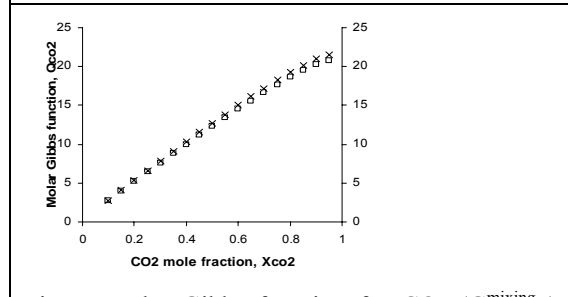


Fig 5: Molar Gibbs function for CO<sub>2</sub> ( $G_m^{\text{mixing}}$ ) against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 12.404 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

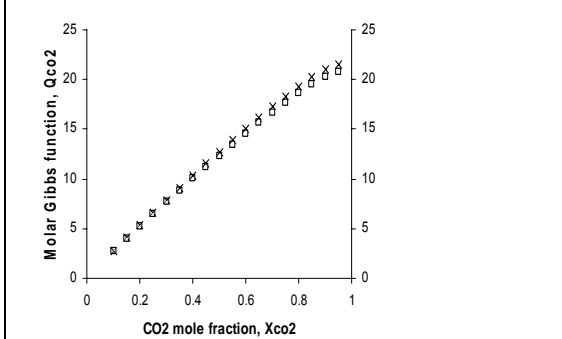


Fig 3: Molar Gibbs function for CO<sub>2</sub> ( $G_m^{\text{mixing}}$ ) against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 11.025 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

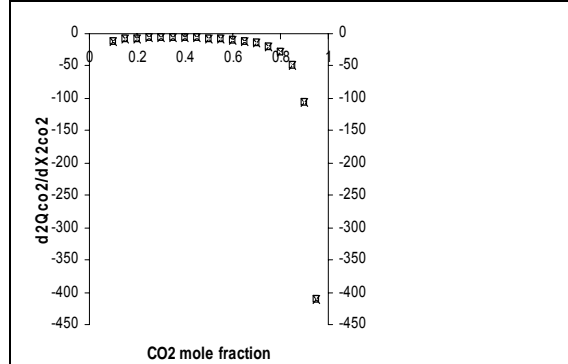


Fig 6: Parameter ( $d^2Q_{\text{CO}_2}/dx^2_{\text{CO}_2}$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 12.404 MPa and at temperature 40 °C and 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

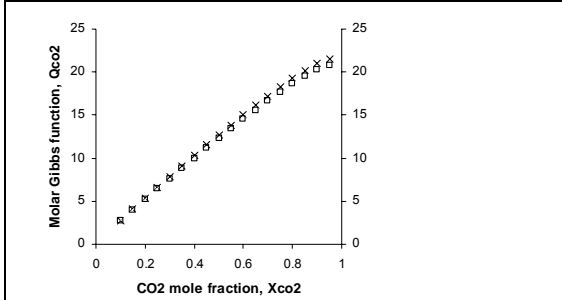


Fig 7: Molar Gibbs function for CO<sub>2</sub> ( $G^{\text{mixing}}_m$ ) against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 13.8 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

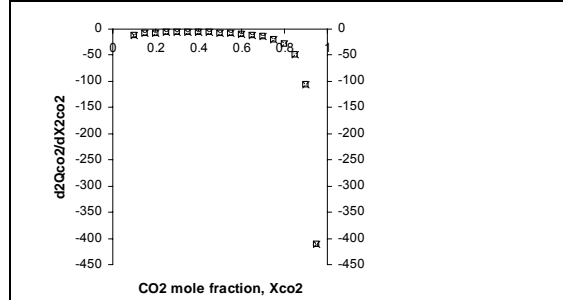


Fig 10: Parameter ( $d^2Q_{\text{CO}_2}/dx^2_{\text{CO}_2}$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 15.16 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

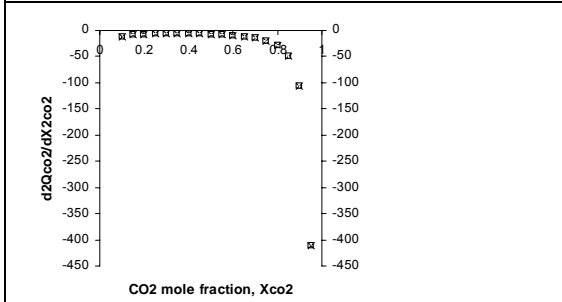


Fig 8: Parameter ( $d^2Q_{\text{CO}_2}/dx^2_{\text{CO}_2}$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 13.8 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

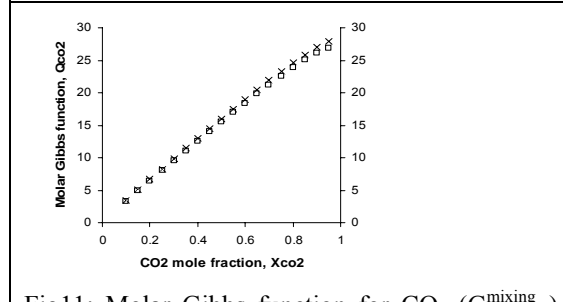


Fig 11: Molar Gibbs function for CO<sub>2</sub> ( $G^{\text{mixing}}_m$ ) against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 16.54 MPa at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

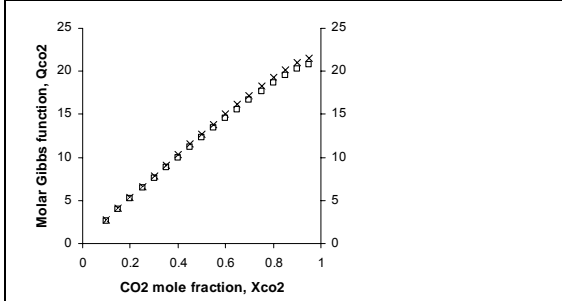


Fig 9: Molar Gibbs function for CO<sub>2</sub> ( $G^{\text{mixing}}_m$ ) against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 15.16 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

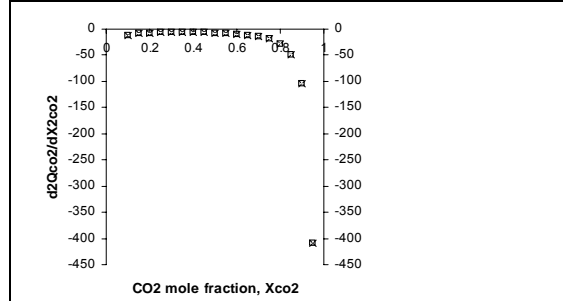


Fig 12: Parameter ( $d^2Q_{\text{CO}_2}/dx^2_{\text{CO}_2}$ ) for CO<sub>2</sub> against CO<sub>2</sub> mole fraction ( $x_{\text{CO}_2}$ ) at constant pressure 16.54 MPa and at temperature 40 °C and at 50 °C.  
 ×: t=40 °C.  
 □: t=50 °C.

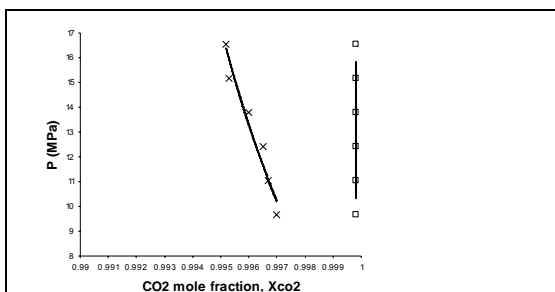


Fig 13: Supercritical vapor phase based on experimental and theoretical data at 40 °C.

×: Based on experimental data.

□: Based on theoretical data.

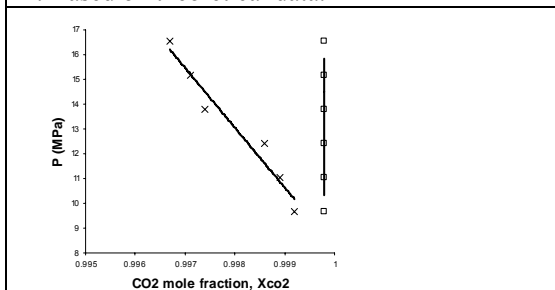


Fig 14: Supercritical vapor phase based on experimental and theoretical data at 50 °C.

×: Based on experimental data.

□: Based on theoretical data.

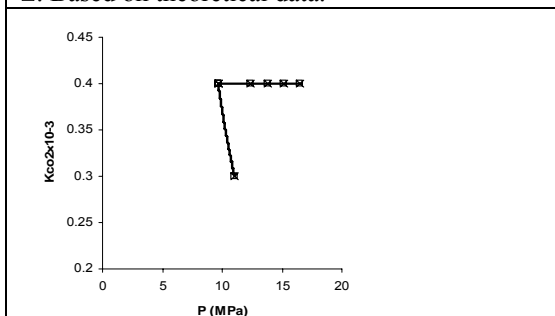


Fig 15: Distribution coefficient based on CO<sub>2</sub> against pressure at temperature 40 °C and at 50 °C. Data extracted from regular solution theory.

×: t=40 °C.

□: t=50 °C.

#### 4. Conclusion

The use of solubility parameters based on regular solution theory with category that the use of quasi-lattice treatments of various degree of complexity is a characteristic version of these treatments that account may be taken of the differing shapes of the molecules and in this case random mixing is assumed. The model used in present work is of this type. In this treatment, the interaction between the individual groups

constituting the molecules is considered based on this work. Table of group interaction parameters have been generated, together with parameters describe the size and shape of the molecules, it is possible to make predictions of liquid-liquid equilibrium from knowledge of the structural formula of the constituent molecular species. It is concluded that the theoretical data calculated from the regular solution theory in comparison with experimental data obtained from ref. [7] in good agreement. It is calculated that at pressure 9.65 MPa and at temperature 40 °C and at 50 °C extracted p-chlorophenol percentage is about 0.02% give good opportunity to has this material extracted using supercritical CO<sub>2</sub> method in order to scale up the system.

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