DETERMINATION OF THE HIGH PRESSURE VAPOUR-LIQUID PHASE EQUILIBRIUM FOR THE BINARY SYSTEM CARBON DIOXIDE – METHYL ACETATE

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Experimental data for the high pressure vapour-liquid equilibrium of the binary system of carbon dioxide and methyl acetate have been measured. Pressure-composition (P–x) isotherms were determined at 308 K and 318 K and an operation pressure up to 9 MPa. The data were modelled using the Peng-Robinson equation of state. Van der Waals one-fluid mixing rules were used for the temperature-dependent function a and for parameter b in the Peng-Robinson equation. Classical one parameter van der Waals model for the cross coefficient terms a_{ij} and b_{ij} were used, which both contain one adjustable binary interaction parameter k_{ij} and l_{ij} respectively. In a second modelling method the temperature dependence of k_{ij} and l_{ij} was determined. A comparison of the results with calculations obtained from PR equation showed a reasonable accordance of the data over a wide range of composition.

1. INTRODUCTION

Carbon dioxide is a convenient solvent for use in liquid and supercritical fluid processes. Carbon dioxide is non-toxic. The low critical temperature and its low prize predetermine its application in chemical reaction with extraction in the food and pharmaceutical industries. The design of such supercritical processes requires an intense knowledge of the encountered phase equilibrium. These phase equilibria are usually predicted on parameters from pure component and binary data alone. Recently, correlation and prediction of vapour-liquid phase equilibria under higher pressure has been reviewed by, e.g. Fornari et al. [1], Dohrn and Brunner [2], Christov and Dohrn [3]. Data on the system CO_2 – methyl acetate have not been published. Furthermore, the bibliographic database by Wichterle et al. [4] reveal that vapour-liquid equilibrium data for mixtures of carbon dioxide with esters at high pressure are rare. However, the design of esterification reactions requires the knowledge of phase equilibrium data over a wide range of temperature and pressure. Therefore methyl acetate was selected as a representative of esters in this work. The experimental results are correlated by using the Peng-Robinson equation of state [5]. For the system carbon dioxide – methyl acetate this correlation resulted in a reliable description of the experimental data.

2. EXPERIMENTAL

2.1. Reagents

Carbon Dioxide with purity of >99.94 volume% was purchased from Linde (Graz) and stored in a tank with a capacity of 3200 L. Methyl Acetate of p.a. quality and the solvent

Tetrahydrofuran (THF) of p.a. quality were supplied by Fluka (Buchs). Both chemicals were used without further purification.

2.2. Apparatus and procedure

Determination of high-pressure vapour-liquid phase equilibrium data was performed in a static apparatus, which was described previously by Gamse [6]. The dynamic circulation method for determination of equilibrium concentration was used. To verify the accuracy of the experimental set up (Fig. 1) and the reproducibility of phase equilibrium data, the test system carbon dioxide – methanol at 303 K was investigated. Comparison of the experimentally determined equilibrium concentration data with literature data at this temperature level showed a good correspondence on both, the liquid and the gaseous phase.

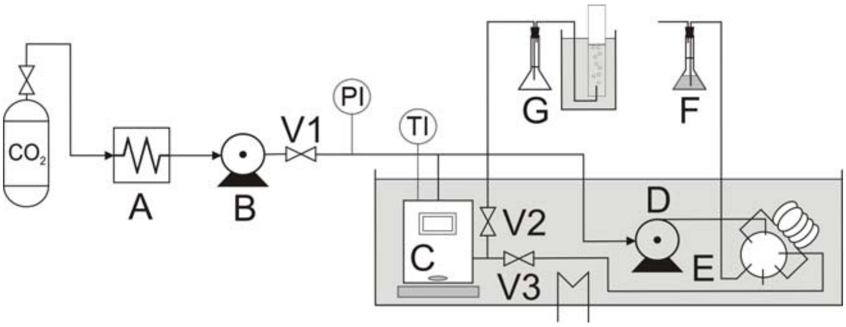

Figure 1: Schematic diagram of the experimental set up used for the solubility measurements: (A) cryostat, (B) membrane pump, (C) equilibrium cell, (D) gear pump, (E) HPLC sample valve, (F) gas phase sample flask, (G) liquid phase sample flask, V1 inlet valve, V2 outlet valve, V3 valve for cycle.

The equilibrium cell is designed for an operating pressure of 400 bar at maximum temperature of 373 K. Volume of the cell is 140 mL. Two inspection glasses are installed at front and back side of the cell over the whole height so that experiments can be watched continuously. The CO_2-rich phase is withdrawn at the top of the cell by a gear pump. It passes a 6-port-HPLC-valve with a sample loop of 200 μL and it is recycled at the bottom of the cell. The apparatus is placed in a temperature controlled water bath to prevent separation of substances due to temperature gradients. Pressure and temperature are measured with an accuracy of ± 0.1 K and ± 0.1 bar.

In each series of experiments a sample of 40 ml of methyl acetate was placed in the cylindrical equilibrium cell. After adjusting the desired conditions (temperatures of 308 K and 318 K and pressures up to 9 MPa) for each experiment, the liquid/supercritical carbon dioxide was pumped through the cell with a gear pump. Mixing of the liquid solution by strong turbulences was induced by circulating the gaseous phase and by stirring. During residence time of the gaseous phase in the cell, equilibrium concentration was established in the gas as well as in the condensed phase. The equilibrated gaseous phase was withdrawn from the cell through a HPLC sample valve and was expanded into a prepared solvent (Tetrahydrofuran). About 2-3 mL of THF is prepared in a calibrated 5 mL flask, which is placed in ice water in order to collect all of the sample. After expansion the sample loop (200 μL) is washed with THF and purged with compressed air. The final sample is 5 mL. The so prepared sample is analysed by gas chromatography.

The method of determining the gas phase concentration (dynamic circulation method) was preferred because of the higher accuracy since solutes can be accumulated.

Carbon dioxide composition of the liquid phase was determined by expanding a sample of liquid phase from the bottom of the equilibrium cell into a glass vial which was weighted before and after sampling. The CO_2 stripped from the sealed top of the glass vial into a volume-calibrated glass cylinder which was filled with acidified water of pH-value 0.5 to avoid loss of CO_2. From the volume of CO_2 gas collected in the glass cylinder and the weight of substance in the glass vial the amount of dissolved CO_2 in the liquid phase was calculated.

The density of pure carbon dioxide was derived from Bender equation [7].

2.3. Gas chromatographic method

All samples were analysed on a HP 6890N gas chromatograph with flame ionisation detector (GC-FID) using a capillary column (DBVRX, 30 m x 0.32 mm x 1.8 µm). The temperature of the column was kept constant for 1 minute at 80°C, increased by 3°C min^{-1} up to 130°C, then increased by 10°C min^{-1} up to 170°C and held constant for 2 minutes. For calibration the substances were dissolved in tetrahydrofuran.

3. RESULTS

High-pressure vapour-liquid equilibrium of carbon dioxide – methyl acetate was investigated at 308 K and 318 K. The experimental results are given in Table 1. The results are averaged from at least two experiments.

Table 1: Experimental VLE data for system CO_2 – methyl acetate

308.15 K			318.15 K		
P [bar]	x_{CO2} [mole/mole]	y_{CO2} [mole/mole]	P [bar]	x_{CO2} [mole/mole]	y_{CO2} [mole/mole]
10.6	0.2806	0.9849	7.4	0.1676	0.9832
12.1	0.3365	0.9843	10.1	0.2602	0.9837
12.2	0.3932	0.9854	12.4	0.2826	0.9850
15.4	0.4346	0.9866	15.4	0.3669	0.9850
16.3	0.4986	0.9875	17.4	0.3989	0.9868
17.8	0.5242	0.9881	18.8	0.4280	0.9874
19.5	0.5314	0.9895	20.1	0.4704	0.9865
20.8	0.5905	0.9887	21.8	0.4980	0.9880
24.2	0.6216	0.9896	22.3	0.5242	0.9884
27.2	0.6613	0.9919	25.3	0.5469	0.9891
29.3	0.6914	0.9895	27.1	0.5699	0.9874
31.3	0.7268	0.9906	29.8	0.6108	0.9896
35.0	0.7789	0.9913	30.9	0.6422	0.9889
40.5	0.7999	0.9928	33.6	0.6760	0.9886
44.9	0.8295	0.9941	38.2	0.7180	0.9896
50.0	0.8599	0.9951	43.2	0.7688	0.9900
55.6	0.8896	0.9961	50.4	0.8115	0.9914
61.8	0.9198	0.9969	58.2	0.8536	0.9913
68.6	0.9497	0.9978	67.6	0.8951	0.9928
			78.3	0.9377	0.9933
			88.4	0.9802	0.9920

The experimental results were correlated with the Peng-Robinson equation of state [5], shown in equations 1 through 5. The Peng-Robinson equation is widely used in modelling the solubility of compounds in supercritical fluids.

$$P = \frac{R \cdot T}{V - b} - \frac{a \cdot \alpha(T)}{V \cdot (V - b) + b \cdot (V - b)} \tag{1}$$

with

$$a = 0.45724 \cdot \frac{R^2 \cdot {T_c}^2}{P_c} \tag{2}$$

$$b = 0.0778 \cdot \frac{R \cdot T_c}{P_c} \tag{3}$$

$$\alpha(T) = \left[1 + m \cdot (1 - {T_r}^{1/2}) \right]^2 \tag{4}$$

$$m = 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2 \tag{5}$$

In equation 1 through 5 P and V represent the pressure and molar volume, R represents the ideal gas constant, while T_c and P_c consider the critical temperature and the critical pressure of the pure component. The parameters ω and T_r consider the acentric factor and reduced temperature.

Mixing rules must be introduced for the EOS parameters in order to use the Peng-Robinson EOS for the prediction of solubility data in supercritical fluids. The Parameters a and b are expressed according to van der Waal mixing rules:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i \cdot x_j \cdot a_{ij} \tag{6}$$

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i \cdot x_j \cdot b_{ij} \tag{7}$$

a_{ij} and b_{ij} consider the cross coefficients, which can be obtained from several combining rules. The classical one parameter van der Waals model for the cross coefficient term a_{ij} is calculated from equation 8.

$$a_{ij} = \sqrt{a_i \cdot a_j} \cdot (1 - k_{ij}) \tag{8}$$

The Peng-Robinson parameters a_i and a_j for pure component i and j are calculated with Eq. (2). Equation (8) considers one adjustable binary interaction parameter k_{ij}. A further adjustable binary interaction parameter l_{ij} is introduced in the cross coefficient term b_{ij} as shown in equation 9:

$$b_{ij} = 0.5 \cdot (b_i + b_j) \cdot (1 - l_{ij}) \tag{9}$$

with the Peng-Robinson parameters b_i and b_j for pure components i and j obtained from Eq. (3).

In the second method for correlation of the experimental data the influence of temperature on binary interaction parameters k_{ij} and l_{ij} is incorporated according to Eq. (10) and Eq. (11).

$$k_{ij} = k_{ij,0} + k_{ij,1} \cdot \left(\frac{298.15}{T} - 1 \right) \tag{10}$$

$$l_{ij} = l_{ij,0} + l_{ij,1} \cdot \left(\frac{298.15}{T} - 1 \right) \tag{11}$$

Table 2 shows the critical data T_c and P_c and the acentric factor ω of the pure components used for correlation of data with Peng-Robinson equation of state.

Table 2: Critical parameters T_c and P_c and acentric factor ω of pure components [8]

	Molecular weight MW [g/mol]	Critical temperature T_c [K]	Critical pressure P_c [bar]	Acentric factor ω [-]
Carbon Dioxide	44.01	304.1	73.8	0.225
Methyl Acetate	74.08	506.8	46.9	0.326

All calculations were done with the program OHGFOR developed by Prof. Evelyne Neau at the Laboratoire de Chimie Physique, Marseille. Values of binary interaction parameter k_{ij} and l_{ij} were optimized by minimising $\Delta P/\%$ values (Eq. 12) in the predicted bubble point pressure from experimentally obtained temperature, pressure, liquid and gas phase composition records. Optimized values for k_{ij} and l_{ij}, $\Delta P/\%$ and mean deviation $\Delta Y/\%$ between experimental and calculated vapour composition (Eq. 13) are shown in Table 3.

$$\Delta P / \% = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{\left| P_i^{\exp} - P_i^{calc} \right|}{P_i^{\exp}} \tag{12}$$

$$\Delta Y / \% = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{\left| Y_i^{\exp} - Y_i^{calc} \right|}{Y_i^{\exp}} \tag{13}$$

Table 3: Optimized k_{ij} and l_{ij} values, predicted bubble point pressures *ΔP/%* and mean deviations *ΔY/%*

Method 1 (independent of temperature)

	308.15 K	318.15 K
k_{ij}	-0,3588	
l_{ij}	-0,2318	
ΔP/%	3,85	3,75
ΔY/%	0,84	1,91

Method 2 (dependent of temperature)

	308.15 K	318.15 K
$k_{ij,0}$	-0,4913	
$k_{ij,1}$	-2,6187	
$l_{ij,0}$	-0,4012	
$l_{ij,1}$	-3,2690	
ΔP/%	3,00	3,75
ΔY/%	0,97	1,82

4. CONCLUSION

Pressure-composition (P–x) isotherms were determined at temperatures of 308 K and 318 K and an operation pressure up to 9 MPa. Three phases were not observed at any time during the experiments. Therefore the P-x isotherms were consistent with those expected for a type-I system [9] where the critical mixture curve passes a maximum. The experimental data obtained in this work were modelled with the Peng–Robinson equation of state. The one parameter van der Waals model for the cross coefficient terms a_{ij} and b_{ij} with the adjustable binary interaction parameters k_{ij} and l_{ij} was used. A comparison of the results with two different calculation methods obtained from Peng-Robinson equation showed a reasonable accordance of the data over a wide range of composition.

For the first method, optimized values of k_{ij} = -0.3588 and l_{ij} = -0.2318 for the interaction parameters were found. In the second method a temperature dependent term was introduced in both interaction parameters and resulted in an improvement in the value of the predicted bubble point pressure *ΔP/%* at 308 K, and in a decrease of the mean deviation *ΔY/%* at 318K. Optimized values for interaction parameters at 308 K were $k_{ij,308K}$ = -0.4063 and $l_{ij,308K}$ = -0.2951 and at 318 K $k_{ij,318K}$ = -0.3267 and $l_{ij,318K}$ = -0.1957 respectively.

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