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High pressure vapor–liquid equilibrium measurements of carbon dioxide with naphthalene and benzoic acid

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Abstract

High pressure vapor–liquid equilibrium data for binary systems of carbon dioxide with naphthalene and benzoic acid were measured at three different temperatures for each system. Experimental temperatures and pressures ranged from 373 to 458 K and 0 to 22 MPa, respectively. Dew points were also measured for naphthalene in the CO_2 rich region. The data measured provides valuable solubility information and is used to derive gas–solvent group interaction parameters for the predictive Soave–Redlich–Kwong equation of state.

Keywords: High pressure vapor–liquid equilibrium; Dew points; Carbon dioxide; Naphthalene; Benzoic acid

1. Introduction

High pressure vapor–liquid equilibrium (VLE) data were measured for CO_2 + naphthalene at 372.45, 403.85 and 430.65 K and for CO_2 + benzoic acid at 403.28, 432.62 and 458.37 K. Several sets of VLE data exist for the CO_2 + naphthalene system in open literatures [1–35]. The data, however, are predominately in the temperature range from 308 to 328 K. A few data sets for CO_2 + benzoic acid are available in literatures [36–41] in the temperature range from 308 to 343 K. In order to increase the range of applicability, in terms of temperature, of the predictive Soave–Redlich–Kwong equation of state (EOS), measurements were undertaken at the elevated temperatures.

The correlation and prediction of VLE is possible with cubic equations of state which have mixing rules that incorporate excess Gibbs energy models [42–46]. Furthermore, group contribution approaches such as UNIFAC can be used so that the applicability of methods, such as the predictive Soave–Redlich–Kwong (PSRK) group contribution EOS [47], are not restricted to systems for which experimental data are available. Data measured in this work are useful as they make the creating and refining of VLE predictive methods (as mentioned above) possible.

2. Experimental

2.1. Materials

Carbon dioxide was purchased from Messer–Griesheim with a purity of 99.999 mol%, and naphthalene (>98% GC) and benzoic acid (>99.5% GC) from Fluka. All chemicals were used without further purification. Naphthalene and benzoic acid are solids at room temperature but liquids at the temperatures for which data were measured.

2.2. Equipment and procedure

A static magnetically stirred pressure cell [48] constructed from titanium and thermally regulated with a stability of ±0.1 K in a temperature controlled air-bath was used to undertake the measurements. The experimental procedure for the measurement of vapor–liquid equilibria for supercritical systems has been previously described [49].

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The principle of synthetic measurement is to measure pressure as a function of overall composition (z_i). The cell was charged with a known quantity of the less volatile, solid compound and CO_2 was added in known quantities using a displacement pump. It is imperative that the quantities of the various chemicals be known precisely. The amount of the solid compound added to the cell was measured with an accuracy of ±1 mg using a mass balance and between 40 and 55 g. The displacement pump used for the addition of the CO_2 was maintained at a controlled temperature and pressure. The volume of material in the pump was recorded prior to the addition of CO_2 to the equilibrium cell as well as the temperature and pressure of the pump. Afterwards, the pump was left to equilibrate (at a controlled temperature and pressure) and the change in volume was recorded as well as the exact temperature and pressure of the pump. Thus, the number of moles of CO_2 added to the cell can be calculated with an estimated accuracy of $\pm 10^{-4}$ mol (<0.02% of the maximum CO_2 feed):

$$\begin{aligned}\Delta n_{CO_2} = {} & n_{CO_2}(T_{pump}, P_{pump}, V_{pump})_{before} \\ & - n_{CO_2}(T_{pump}, P_{pump}, V_{pump})_{after} \qquad (1)\end{aligned}$$

The pressure in the cell was recorded with an accuracy of $\pm 10^{-3}$ MPa, once equilibrium was attained. The temperature was measured with an accuracy of $\pm 10^{-2}$ K with two Pt100 probes in holes, one in the bottom and one in top part of the pressure vessel. In this manner precise isothermal z_i–P–T data were obtained. The total volume of the equilibrium cell was determined to be 112.82 cm^3 by filling the complete volume initially under vacuum with pure compressed water.

To measure dew points, a small, known amount (3–4 g) of the solid chemical (napthalene) was added to the cell. The cell was heated to the equilibrium temperature. CO_2 was then added to the cell until the mixture became a homogeneous gas. The amount of CO_2 added to the cell was calculated as explained above and thus the gas composition (y_i) was known. The cell was allowed to reach equilibrium temperature and then the homogeneous gas was slowly vented to atmosphere thus lowering the pressure in the cell but keeping the composition constant. The pressure was lowered until the first drops of liquid were seen on the view glass. The pressure was recorded as the dew point pressure corresponding to the vapor composition y_i.

2.3. Treatment of the raw data

The z_i–T–P data were converted to x_i–T–P data by solving the following two equations in an iterative algorithm:

$$n_i^{T} = n_i^{L} + n_i^{V} \qquad (2)$$

$$V^{T} = V^{L} + V^{V} \qquad (3)$$

V and n refer to volume and number of moles, respectively. Superscripts T, L, and V refer to total, liquid and vapor phases, respectively. Subscript i refers to component i. The total number of moles (n_i^{T}) of both components and the total cell volume (V^{T}) are known. Fischer and Wilken [49] give detailed explanations of two methods used to solve the above two equations. Their latter method (GLE FLASH) is used in this work. The method uses a combination of a suitable EOS and mixing rule (e.g. G^E mixing rule) to solve the above equations while the additional isofugacity criterion:

$$f_i^{L} = f_i^{V} \qquad (4)$$

is satisfied. From this procedure calculated values of composition for the vapor phase are also obtained. The Soave EOS with Huron–Vidal [42] mixing rules incorporating the NRTL activity coefficient model was used in this study. Table 1 lists the critical property data and the Mathias–Copeman constants used in the correlation routine. The accuracy of the finally obtained x_i–T–P data depends on the vapor volume in the cell and the relative volatilities of the compounds. Such effects were considered when planning the experiments with a final vapor phase volume of less than 30% of the total volume. This value must generally be lower when the gas solubility is smaller. Since the data were generated from at least two experiments with different initial loadings of the solid compounds, the consistency of the data from the different runs gives also an estimate of the accuracy of the liquid mole fraction: ±0.5% of the absolute liquid mole fraction. This indication comprises also the possible impact of the models on the results.

Table 1
Critical property data and Mathius–Copeman constants for the components (Dortmund Data Bank, DDBST)

Component	T_C (K)	P_C (MPa)	C_1	C_2	C_3
Carbon dioxide	304.20	7.3765	0.8250	0.1676	−1.7039
Naphthalene	748.40	4.0530	0.9652	−0.3538	0.7823
Benzoic acid	752.00	4.5596	1.4130	0	0

3. Results

The P–x data for $CO_2(1)$ + naphthalene(2) are presented in Table 2, the dew points in Table 3 and the P–x–($y_{calculated}$) data

Table 2
P–x data for the system $CO_2(1)$ + naphthalene(2)

T = 372.45 K		T = 403.85 K		T = 430.65 K	
x_1	P (MPa)	x_1	P (MPa)	x_1	P (MPa)
0.000	0.00	0.000	0.01	0.000	0.02
0.003	0.10	0.004	0.16	0.002	0.11
0.032	0.98	0.024	0.83	0.021	0.85
0.106	3.29	0.079	2.77	0.070	2.78
0.133	4.12	0.136	4.82	0.123	4.86
0.191	5.90	0.195	6.91	0.173	6.86
0.261	8.01	0.246	8.79	0.231	9.19
0.325	9.98	0.304	10.91	0.275	10.94
0.393	12.01	0.358	12.96	0.322	12.82
0.458	13.99	0.412	14.99	0.370	14.73
0.521	15.87	0.466	17.04	0.416	16.53
0.580	17.61	0.523	19.17	0.470	18.66
0.644	19.41	0.569	20.88	0.518	20.56