



Vapour-Liquid Phase Equilibrium for CO₂ + 2-Pentanol at Elevated Pressure

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Vapour-liquid phase equilibrium data for CO₂ + 2-pentanol were measured at temperatures of 313.4, 333.5, 343.5 and 353.4 K in the pressure range of 4.88 to 13.51 MPa. The measurements were carried out in a variable-volume visual high-pressure cell. The experimental data were well correlated with Peng-Robinson equation of state (PR-EOS) together with van der Waals-2 mixing rule. Henry's constants and partial molar volumes of CO₂ at infinite dilution were estimated with Krichevsky-Kasarnovsky equation.

Key Words: Carbon dioxide, 2-Pentanol, Phase equilibrium, Henry's constant.

INTRODUCTION

Supercritical CO₂ has widely been used in chemical engineering separation and chemical reactions for its non-toxicity, moderate critical conditions, low cost and small impact on the earth's environment^{1,2}. The high-pressure phase equilibrium properties of the systems are required for the design and operation of separation equipments in many chemical processes and separation operations. Furthermore, the thermodynamic model established with the vapour-liquid equilibrium data can be used to predict phase behavioural patterns of the systems at different temperatures and pressures^{3,4}.

The mixtures of supercritical CO₂ and alcohols have received much attention for the mixtures are often encountered in the petroleum, oil and natural gas^{5,6}. However, there were fewer phase equilibrium reports on 2-pentanol in CO₂. Silver-Oliver *et al.*⁷ published a paper concerning to vapour-liquid equilibria and critical points for CO₂ + 2-pentanol systems at temperatures of 332.10, 343.61, 397.56 and 432.10 K. In previous work, we reported phase equilibrium data for *iso*-butanol, *tert*-butanol and 2-butanol in carbon dioxide⁸⁻¹⁰. Therefore, in the present work phase equilibrium for the binary system of CO₂ + 2-pentanol is studied. New vapour-liquid equilibrium data for CO₂ + 2-pentanol at temperatures from 313.4 to 343.5 K in the pressure range of 4.88 to 13.51 MPa were measured in a variable-volume visual cell and high pressure phase equilibrium models for CO₂ + 2-pentanol binary system were obtained with Peng-Robinson equation of state (PR-EOS) coupled with van der Waals-2 mixing rules. Moreover, the vapour-liquid equilibrium data of every isotherm were used to calculate Henry's constant ($H_{1,2}^{(p_2^s)}$) and partial molar volumes

of CO₂ at infinite dilution (\bar{V}_1^∞) with Krichevsky-Kasarnovsky equation.

EXPERIMENTAL

Carbon dioxide with purity of 99.99 % was purchased from Nanyang Tianguan Co. Ltd. and 2-pentanol with purity of more than 99.9 % by mass was provided by Shanghai Chemical Reagent plant. The purity of materials was checked with GC102M gas chromatography. They were used directly without further purification.

The experimental apparatus used in the work is a variable-volume visual cell, which is similar to that in the literature¹¹ and a schematic diagram of the variable-volume visual cell is shown in Fig. 1. The cell was produced by Jiangsu Nantong Hai'an Petroleum Research Instrument Plant. It has one quartz visual window and its internal volume can be adjusted from 25 mL to 100 mL by moving an internal movable piston. Its inner diameter is 22.12 mm. The maximum operating temperature and pressure of the apparatus are 423 K and 20 MPa with an accuracy of ± 0.1 K and ± 0.01 MPa, respectively. The equilibrium pressure in the cell is measured by a CYB-20S differential pressure gauge; cell temperature is controlled by a ZCY-15 B digit constant temperature encircling liquid bath controller and measured by a XMZ intelligent temperature regulation indicator. The motion distance of the piston is measured with a NS-YB05C-A-I-0-0-1 displacement meter. The stainless steel piston is sealed with double O-rings against the pressure of the equilibrium cell. A magnetic stirrer, which is driven by a pneumatic drive pump is used for mixing the fluid in the cell. The reliability of measurement was tested by

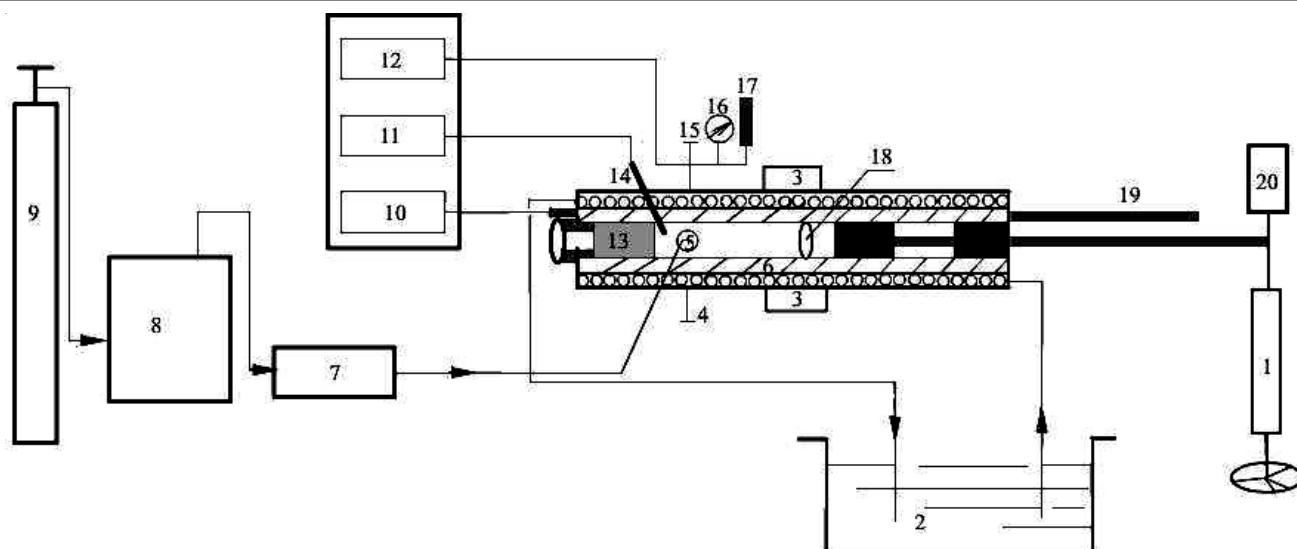


Fig. 1. A schematic diagram of the variable-volume visual cell; 1. Handpump; 2. Digit constant temperature liquid bath; 3. Magnet; 4. Liquid phase sampling valve; 5. Intake valve; 6. Variable-volume cell; 7. High pressure pump; 8. Refrigerator; 9. CO₂ cylinder; 10. Displacement indicator; 11. Temperature indicator; 12. Pressure indicator; 13. Quartz visual window; 14. Thermocouple; 15. Vapour phase sampling valve; 16. Pressue gauge; 17. Safety valve; 18. Magneton; 19. Displacement meter; 20. Water cup

comparison with the published accurate data of a CO₂ + ethanol system¹².

Before each experiment, the entire internal loop of the equilibrium cell was rinsed several times with carbon dioxide to remove traces of air. Then, the equilibrium cell was evacuated with a vacuum pump. A known amount of 2-pentanol was sucked in the equilibrium cell. It was slightly pressurized to the experimental pressure with carbon dioxide by hand-pump and was heated to the experimental temperature with isothermal liquid. Once the pressure and temperature were adjusted to designated values, the mixture in the cell was stirred for a few hours to equilibrium state. Then, the stirrer was switched off. About 1.5 h later, the coexisting phases were separated completely. Phase interface could be observed from the visual window. Samples of the vapour and liquid phase were collected with small steel vessel from their own sampling valve by pushing hand pump slowly, respectively. The samples were weighed up with a FA1104 electronic balance with an accuracy of ± 0.0001 g.

Analytical method: The small steel vessel after sampling was placed in an ice-water bath and connected with a desorption tank by capillaries and a needle-type valve. The volume of the desorption tank was calibrated in advance. After the desorption tank was evacuated, carbon dioxide was desorbed to desorption tank very slowly until pressure of the tank didn't change. The amount of CO₂ in each phase was determined by measuring the corresponding pressure variation in the desorption tank. The mass of 2-pentanol was equal to the sample mass minus CO₂ mass. The content of water in 2-pentanol was detected with GC102 M gas chromatography and the O-rings were replaced when the content of water was over 0.5 %. The molar fractions in two phases were calculated.

The above measurements at every equilibrium were repeated at least five times and the vapour and liquid phase compositions were found reproducible with a molar fraction of ± 0.0010 and ± 0.0008 .

RESULTS AND DISCUSSION

To test the reliability of the apparatus, the vapour-liquid equilibrium data for CO₂ + 2-pentanol was measured at 333.4 K. The data were compared with the high accuracy data at 333.4 K by Joung *et al.*¹². The comparison is shown in Fig. 2. The results (Fig. 2) show that both the measured and the literature data for CO₂ + 2-propanol agree well. Based on the comparison it is concluded that the experimental apparatus used in the present study is reliable and can generate accurate vapour-liquid data.

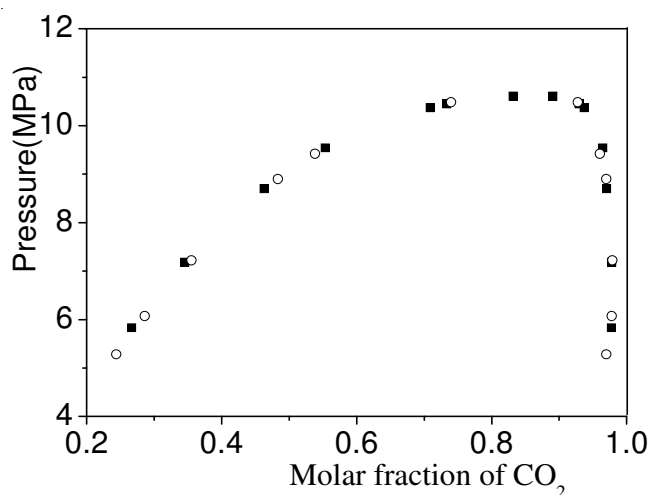


Fig. 2. Phase behaviour of CO₂ + ethanol at 333.4 K; □ Data obtained in the work; ■ Data reported by Joung *et al.*¹²

Vapour-liquid equilibrium data for CO₂ + 2-pentanol binary system at 313.4, 333.4, 343.5 and 353.5 K were measured. The results are listed in Table-1, where x_1 and y_1 are molar fraction of CO₂ in the liquid phase and vapour phase, respectively.

TABLE-1
VAPOUR-LIQUID PHASE EQUILIBRIUM
DATA FOR CO₂ + 2-PENTANOL

p (Mpa)	x _{1,exp}	y _{1,exp}	p (Mpa)	x _{1,exp}	y _{1,exp}
T = 313.4 K					
4.88	0.3344	0.9977	8.14	0.8176	0.9925
5.77	0.4261	0.9962	8.41	0.8897	0.9819
6.77	0.5312	0.9947	8.59	0.9349	0.9689
7.46	0.6470	0.9938			
T = 333.4 K					
5.16	0.3126	0.9862	9.58	0.7379	0.9839
6.14	0.3828	0.9947	9.99	0.8122	0.9706
7.10	0.4895	0.9964	10.32	0.8760	0.9564
8.52	0.6171	0.9839			
T=343.4 K					
4.91	0.2652	0.9901	9.79	0.6319	0.9903
5.78	0.3017	0.9918	10.67	0.7105	0.9708
6.46	0.356	0.9947	11.68	0.8156	0.9443
7.79	0.434	0.9966	11.96	0.8911	0.9195
8.78	0.5212	0.9961			
T=353.4 K					
7.79	0.3904	0.9927	11.74	0.6569	0.9678
8.77	0.4562	0.9951	12.53	0.7411	0.9544
9.85	0.5247	0.9882	13.12	0.8079	0.9289
10.92	0.5892	0.9799	13.28	0.8603	0.9005

Fig. 3 shows the P-x(y) diagram for CO₂ + 2-pentanol at four temperatures. Meanwhile, the reported values in literature⁷ are also drawn in Fig. 3. As can be seen from Fig. 3, the experimental data in the work are in good agreement with those reported by Silver-Oliver *et al.*⁷. The experimental results also show that the solubility of CO₂ in 2-pentanol increases with the increasing pressure.

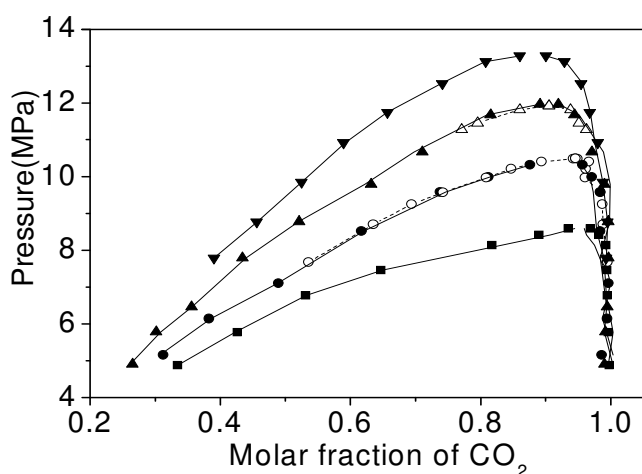


Fig. 3. P-x(y) diagram for CO₂ + 2-pentanol system at different temperatures; This work: ■ 313.4 K, ● 333.4 K, ▲ 343.5 K, ▼ 353.5 K; Ref.⁷: ○ 332.10 K, □ 343.61 K; -calculated value

Data correlation with equation of state (EOS)-based model: In this work, the Peng-Robinson equation of state (PR-EOS)¹³ together with Panagiotopoulous-Reid¹⁴, Stryjek-Vera mixing rules¹⁵, van der Waals-1¹⁶ and van der Waals-2¹⁷ mixing rules were chosen for description of the phase behaviour of the binary system, respectively. Having tried many, van der Waals-2 mixing rule was found to be the most accurate for the description of the phase behaviour of the binary system. Hence, this one was dealt.

The simplex optimization was done with matlab 7.0 software according to the PR-EOS together with Van der Waals-2 mixing rule. The critical properties and acentric factor for the pure component used in the work come from literature¹⁸.

The optimized binary interaction parameters k_{ij} , n_{ij} and derivation analyses from PR-EOS are summarized in Table-2. Using these binary interaction parameters, the calculated results at four different experimental temperatures were obtained and also drawn in Fig. 3 in order to direct comparison with experimental data. Results in Fig. 3 also show the calculated results agree well with the experimental data. Therefore, PR-EOS coupled with Van der Waals-2 mixing rule can be applied to better description of the phase behaviour for CO₂ + 2-pentanol binary system at high pressures and near-critical areas.

TABLE-2
BINARY INTERACTION PARAMETERS FOR
CO₂+2 PENTANOL BASED ON PR-EOS

T (K)	P (MPa)	k ₁₂	n ₁₂	^a AARDx (%)	^b AARDy (%)
313.4	4.88-8.59	0.1002	-0.0444	0.8825	0.8714
333.4	5.16-10.35	0.0571	-0.0716	0.6941	0.6956
343.5	4.90-12.38	0.0862	-0.0463	1.0498	1.0518
353.5	7.79-13.51	0.0813	-0.0582	0.1456	0.1455

$$^a \text{AARDx} = \frac{1}{N} \sum_{i=1}^M \left| \frac{x_{1,\text{exp}} - x_{1,\text{cal}}}{x_{1,\text{exp}}} \right| \times 100\% ;$$

$$^b \text{AARDy} = \frac{1}{N} \sum_{i=1}^M \left| \frac{y_{1,\text{exp}} - y_{1,\text{cal}}}{y_{1,\text{exp}}} \right| \times 100\%$$

Data correlation with Krichevsky-Kasarnovsky equation-based model: Krichevsky-Kasarnovsky (KK) equation¹⁹ was used to represent the dependence of solubility of CO₂ in liquid phase on pressure. The KK model is given by eqn. (1).

$$\ln\left(\frac{f_1^l}{x_1}\right) = \ln H_{1,2}^{(p_2^s)} + \frac{\bar{V}_1^\infty}{RT} (P - P_2^s) \quad (1)$$

where, subscript 1 and 2 represent CO₂ and 2-pentanol, respectively, ($H_{1,2}^{(p_2^s)}$) Henry's constant at the saturated vapour pressure of 2-pentanol (P_2^s), \bar{V}_1^∞ partial molar volume of CO₂ at infinite dilution and f_1^l fugacity of CO₂ in liquid phase.

By linear fitting $\ln(f_1^l/x_1)$ as a function of $(P - P_2^s)/(RT)$, $H_{1,2}^{(p_2^s)}$ and \bar{V}_1^∞ can be obtained. The Krichevsky-Kasarnovsky equation regression results and deviation analyses are summarized in Table-3. The results in Table-3 show that Henry's constants for CO₂ + 2-pentanol binary system and partial molar volumes of CO₂ at infinite dilution only depend on the temperature. As also can be shown in Table-3, Henry's constants

TABLE-3
CALCULATED EFFECTS OF KRICHEVSKY-
KASARNOVSKY EQUATION

T (K)	H _{1,2} ^(p₂^s) (MPa)	\bar{V}_1^∞ (cm ³ mol ⁻¹)	r ^a	AARD (%)
313.4	21.6102	-414.2812	-0.9867*	0.2169
333.4	24.2447	-309.2681	-0.9973*	0.0651
343.5	25.3389	-250.1920	-0.9886*	0.1149
353.5	29.3106	-235.1234	-0.9846*	0.0903

^aCorrelative coefficient

increase with increasing temperature and the magnitudes of partial molar volumes of CO₂ at infinite dilution, which are negative values decrease with temperature.

Conclusion

The vapour-liquid equilibrium data for CO₂ + 2-pentanol binary system were measured in a variable-volume view cell at temperatures from 313.4 to 353.5 K and at pressure range of 4.88 to 13.51 MPa. Peng-Robinson equation of state and van der Waals-2 mixing rule were used to correlate the experimental data. Satisfactory regression results were got. Henry's constants and partial molar volumes of CO₂ at infinite dilution were estimated with Krichevsky-Kasarnovsky equation. The phase equilibrium data, predicted models obtained and partial molar volume properties are expected to be a useful tool for the process design and recovery of 2-pentanol with supercritical CO₂ technique.

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