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Binary Phase Diagram of Tetraethyl Orthosilicate and Carbon Dioxide

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Phase equilibrium data for the system tetraethyl orthosilicate (TEOS)−carbon dioxide (CO_2) are presented. The measurements were conducted in a variable volume phase monitoring cell at different temperatures (306.2, 313.2, 323.2, 333.2, and 343.2) K. The mole fraction of TEOS in the binary mixture was varied from 0.00 to 0.08. The data were fitted using the Peng−Robinson equation of state. The model accounts for literature data on phase behavior over the entire composition range.

Introduction

In the area of materials synthesis and modification, the use of supercritical carbon dioxide as a solvent is gaining momentum.[1–3] Knowledge on the phase behavior of material precursors in supercritical carbon dioxide is essential in this context.[4] Tetraethyl orthosilicate is a common precursor for the synthesis of porous silica materials. Previously, Spuhl et al.[4] investigated the binary system TEOS−CO_2 with high TEOS mole fractions ranging from 0.10 to 1. In the current study, we complement these investigations and investigate the low range of TEOS molar fractions. The data were fitted using the Peng−Robinson equation of state.[5]

Experimental Section

Phase behavior was studied in a phase monitor (NWA, Lorrach, Germany). This equipment consists of a pressure chamber with variable volume (35 mL to 66 mL) equipped with heating coils, one inlet for CO_2, one inlet for chemicals, and one outlet. Two sapphire windows allow observation of the system. The pressure in the system is measured with a pressure gauge (Leo 2, Keller, The Netherlands) for which the precision is specified at 0.1 % full scale with a maximum pressure of 70.0 MPa. The temperature is monitored precisely to 0.1 K. Stirring was performed using an external stirrer. The proper working of the experimental setup was evaluated in a preliminary test with pure CO_2. The phase transition was observed at the expected temperature and pressure according to ref 6, viz. 304.1 K and 7.38 MPa. CO_2 was injected into the system by the use of ISCO 260D pumps that were fed with bottled CO_2 (Air Liquide SA, France, purity ≥ 99.9 %). The pump was kept isothermal and was operated in constant pressure mode so that the number of moles of CO_2 injected into the system could be calculated from the volume of CO_2 delivered by the pump by using pressure−density tables.[6] Pumped volume readout was in milliliters with two decimal digits. The specified displacement resolution of the pump was 16.6 nL. A 0.06 $mL \cdot min^{-1}$ background CO_2 flow out of the pump is typical in this setup but is negligible with respect to the volumes pumped, viz. at least 17 mL in a time of 20 s at the maximum. We introduced TEOS (Merck, Germany, purity ≥ 99 %) to the system using a syringe at atmosphere pressure. The amount of TEOS injected was determined by weighing the syringe before and after injection. The precision of the balance was 0.1 mg. The amount of introduced TEOS varied from 0.23 g to 9.40 g. To determine the phase transition, the pressure and temperature were built up until a monophasic system was achieved. At this point, the volume was slowly expanded toward phase separation, assuring that the equilibrium state was established at all times. Phase transitions were observed visually through the monitor window and by the change in the pressure−volume relation upon phase transition.

Results and Discussion

Bubble, dew, and critical point data for the TEOS−CO_2 system were collected at different temperatures and compositions up to a TEOS mole fraction of 0.08. Under these conditions, no three-phase systems were encountered. Both components could be dissolved in the applied temperature and pressure domain. The experimental pressure−composition ($P-x$) isotherms at T = 306.2 K, 313.2 K, 323.2 K, 333.2 K, and 343.2 K are reported in Table 1 and Figure 1. Several phase transitions were realized three times. The pressure variation between the determinations was 0.02 MPa at the maximum. Mean values are tabulated in Table 1. Literature data for higher molar TEOS fractions determined by Spuhl et al.[4] (0.1 to 1 TEOS mole fraction) are included in Figure 1.

The experimental phase behavior data obtained in this work were fitted using the Peng−Robinson equation of state (eq 1) in combination with quadratic mixing rules (eqs 2 and 3). The parameters k_{ij} and l_{ij} are binary interaction parameters that can be determined by fitting experimental pressure−composition data. The parameters a_i, a_j, b_i, and b_j are pure component parameters determined by Peng−Robinson.

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$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m^2 + 2bV_m - b^2} \tag{1}$$

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \text{ with } k_{ij} = k_{ji} \tag{2}$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \frac{b_i + b_j}{2}(1 - l_{ij}) \text{ with } l_{ij} = l_{ji} \tag{3}$$

The critical temperature (T_c), pressure (P_c), and acentric factor (ω) of the pure components are reported in Table 2. Parameters of CO_2 are available in the literature.[7] The critical parameters of TEOS were calculated using Lydersen's[8] and Fedor's[9] group contribution theories.

PRMIX[10] was used to fit the experimental data with the Peng−Robinson equation of state. Accurate values of the binary parameters for this system were found to be $k_{ij} = 0.03$ and $l_{ij} = 0.00$ by applying the objection function (eq 4) and by minimizing the root-mean-square deviation (eq 5) in the fitting of the experimental data at 313.2 K. PRMIX allows the calculation of bubble point pressure data for a binary mixture with a given composition using the Peng−Robinson equation of state with input of the critical parameters of both components and the binary interaction parameters. This modeled phase diagram is shown in Figure 1. The model corresponds well with both the data from the present work and the data reported by Spuhl et al.[4] with a mean relative deviation of only 1.3 %.

$$\text{OBF} = \sum_{i}^{N} \left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}} \right) \tag{4}$$

$$\text{RMSD (\%)} = \sqrt{\frac{\text{OBF}}{N}} \cdot 100 \tag{5}$$

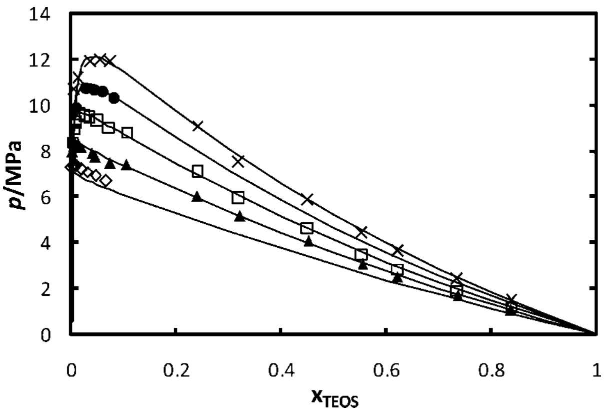

Figure 1. Phase diagram of the tetraethyl orthosilicate−carbon dioxide binary mixture at different temperatures (◇, 306.2 K; ▲, 313.2 K; □, 323.2 K; ●, 333.2 K; ×, 343.2 K) and the model (solid lines) obtained with the Peng−Robinson equation of state with $k_{ij} = 0.03$. Experimental data at low TEOS mole fractions (0 to 0.08) were gathered in this work. The experimental data shown for higher TEOS mole fractions (0.1 to 1) are from Spuhl et al.[4]

Table 1. Experimental Pressure (P_{exptl})−Composition Data and the Corresponding Calculated Pressures (P_{calcd}) and Deviations (dev) for Tetraethyl Orthosilicate (1) + Carbon Dioxide (2) from 306.2 K to 343.2 K[a]

x_1	P_{exptl} / MPa	P_{calcd} / MPa	dev / MPa	type of transition
		T = 306.2 K		
0.0020	7.28			DP
0.0031	7.38	7.31	0.08	CP
0.0067	7.40	7.46	−0.06	BP
0.0071	7.38	7.42	−0.04	BP
0.0087	7.34	7.43	−0.09	BP
0.0203	7.18	7.24	−0.06	BP
0.0303	7.08	7.12	−0.04	BP
0.0462	6.90	6.94	−0.04	BP
0.0662	6.68	6.75	−0.06	BP
		T = 313.2 K		
0.0021	7.92			DP
0.0051	8.20			CP
0.0071	8.34	8.42	−0.07	BP
0.0147	8.24	8.34	−0.10	BP
0.0195	8.12	8.28	−0.15	BP
0.0384	7.86	8.03	−0.17	BP
0.0472	7.74	7.92	−0.18	BP
0.0738	7.46	7.62	−0.16	BP
		T = 323.2 K		
0.0026	8.38			DP
0.0053	8.94			DP
0.0089	9.22	9.50	0.18	CP
0.0108	9.32	9.59	−0.27	BP
0.0166	9.54	9.67	−0.13	BP
0.0249	9.48	9.65	−0.17	BP
0.0342	9.44	9.56	−0.11	BP
0.0504	9.26	9.34	−0.08	BP
0.0722	9.02	9.07	−0.05	BP
		T = 333.2 K		
0.0097	9.90			DP
0.0267	10.72	10.90	−0.18	CP
0.0423	10.68	10.87	−0.19	BP
0.0581	10.58	10.70	−0.12	BP
0.0819	10.32	10.37	−0.05	BP
		T = 343.2 K		
0.0083	10.64			DP
0.0120	11.12			DP
0.0396	11.84	12.08	−0.24	CP
0.0582	11.92	12.01	−0.09	BP
0.0772	11.84	11.78	0.06	BP

[a] Types of transition: DP, dew point; CP, critical point; BP, boiling point.

Table 2. Molecular Weight (MW), Critical Temperature (T_c), Critical Pressure (P_c), and Acentric Factor (ω) of Tetraethyl Orthosilicate (Calculated[8,9]) and Carbon Dioxide[7]

	CO_2	TEOS
MW/g·mol^{-1}	44.01	208.33
T_c/K	304.3	574.8
P_c/MPa	7.38	1.98
ω	0.225	0.792

Conclusions

This research led to the completion of the phase equilibrium diagram for the binary system TEOS−CO_2. The acquired experimental phase behavior data cover compositions of low TEOS loadings at different temperatures (306.2 K, 313.2 K, 323.2 K, 333.2 K, 343.2 K). Three phases were not observed in any of the investigated composition−temperature conditions. The data were fitted using the Peng−Robinson equation by which the phase behavior of the TEOS−CO_2 system could be modeled using one binary interaction mixture parameter.

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