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Measurement and Modeling of the High-Pressure Phase Behavior of the Binary System Carbon Dioxide + 1,2-Epoxycyclohexane

Marcus A. van Schilt,[†] Rob M. Wering,[†] Maartje F. Kemmere,[*,†] Theo W. de Loos,[‡] and Jos T. F. Keurentjes[†]

Process Development Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and Physical Chemistry and Molecular Thermodynamics, Department of Chemical Technology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Experimental bubble point isopleths for the binary system carbon dioxide + 1,2-epoxycyclohexane have been determined for mole fractions from (10 to 50) % CO_2 and temperatures from (354 to 424) K. Vapor pressures and liquid densities of pure 1,2-epoxycyclohexane have been measured from (361 to 474) K and from (278 to 363) K, respectively. Using the Peng−Robinson equation of state and van der Waals one-fluid mixing rules, a good description of the phase behavior of both the vapor pressure and the bubble point data has been obtained. The binary interaction parameter k_{ij} has been found to be temperature-dependent.

Introduction

The tendency toward environmentally more benign processes has placed significant emphasis on the use of (supercritical) carbon dioxide (CO_2) as it is considered to be a “green” alternative to most traditional solvents.[1−5] Additionally, the use of CO_2 as an alternative building block for the synthesis of a wide range of materials is an interesting development in terms of CO_2 sequestration.[6,7] One example in this area is the copolymerization of CO_2 and oxiranes to polycarbonates.[8−10]

In our work, we focus on the synthesis of poly(cyclohexene carbonate) from CO_2 and 1,2-epoxycyclohexane. The development of such a process would provide a solvent-free alternative to polycarbonate synthesis. CO_2 contributes 31 % by mass to this polymer and thus provides an environmentally benign alternative to phosgene for the introduction of the carbonate functionality in polycarbonates.

For the successful development of such a process, phase behavior plays a significant role. In this paper attention is focused on the phase behavior of the reactants in this process (i.e., the binary system 1,2-epoxycyclohexane + CO_2) at pressures, temperatures, and compositions typical for this copolymerization. We present in this paper experimental bubble points of the binary system 1,2-epoxycyclohexane + CO_2, which extend and, in our opinion, improve currently available data.[11] The data have been determined visually in isoplethic series using a Cailletet apparatus.[12] Additionally, experimentally determined vapor pressures and liquid densities are reported for 1,2-epoxycyclohexane. The experimental data are modeled using the Peng−Robinson (PR) equation of state and van der Waals one-fluid mixing rules.[13] The group contribution method as proposed by Joback and Reid[14] and the bond contribution method as proposed by Marrero-Morejon and Pardillo-Fontdevila[15] are used to estimate the critical temperature and pressure of 1,2-epoxycyclohexane. The acentric factor of 1,2-epoxycyclohexane is subsequently estimated from the critical point and experimental vapor pressure curve. A temperature-dependent interaction parameter k_{ij} is fitted to correlate the experimental binary data. Finally, the performance of the various sets of model parameters are assessed for the description of the phase behavior of this system by comparison with experimental pure component and mixture data.

Experimental Section

Experimental Method. Vapor pressures of 1,2-epoxycyclohexane were experimentally determined from (294 to 474) K using a tensiometer equipped with a Baratron differential pressure gauge for vapor pressure measurements up to 100 kPa and a Cailletet setup for higher pressures. The tensiometer consisted of a dual static cell in which the pressure in the primary cell was measured relative to the pressure in the secondary cell. For these measurements, a high vacuum was applied to the secondary cell. Both cells were completely submerged in a thermostated bath, and the temperature was measured using a platinum resistance thermometer with an uncertainty of 0.03 K. The pressure difference between the two cells was measured using the Baratron with an uncertainty of 0.75 kPa. In the Cailletet setup, vapor pressures above 150 kPa were measured by visual determination of the bubble point. A glass tube was filled with 1,2-epoxycyclohexane and sealed with mercury, which acted as a pressure intermediate between the sample and a hydraulic pressure system. The hydraulic pressure system was equipped with a dead weight gauge, which allowed for pressure measurement with an uncertainty of 5 kPa.

Liquid densities were determined at atmospheric pressure from (273 to 363) K using a 10 cm^3 glass picnometer. To compensate for expansion of the picnometer, the exact volume was first determined gravimetrically with distilled and degassed water in combination with an experimental

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[*] Corresponding author. Telephone: +31 40 247 2241. Fax: +31 40 244 6104. E-mail: M.F.Kemmere@tue.nl.

[†] Eindhoven University of Technology.

[‡] Delft University of Technology.

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density temperature correlation.[16] Considering the accuracies of all steps involved, the overall uncertainty of density and temperature is estimated to be 0.5 kg·m^{-3} and 0.3 K, respectively.

Bubble points of the binary mixtures were measured from (353 to 423) K and mole fractions of CO_2 from (10 to 50) % according to the synthetic method. For this purpose a sample was prepared in a glass capillary tube, the so-called Cailletet tube, and sealed with mercury. The tube was then placed in a temperature-controlled environment. The mixtures were pressurized hydraulically, where the mercury acted as a pressure intermediate between the samples and the hydraulic pressure generating system. The dead weight gauge allowed for an uncertainty of the pressure measurement of 5 kPa. Temperature was measured using a platinum resistance thermometer with an uncertainty of 0.03 K. The composition of the samples was controlled within 0.1 % (mole fraction CO_2).

First, the Cailletet tube was filled with the less volatile components (i.e., dry 1,2-epoxycyclohexane) using a micrometer syringe. The amount of 1,2-epoxycyclohexane was gravimetrically determined with an uncertainty of 0.02 mg (0.05 %). Then the tube was connected to a low-pressure gas rack, where the contents were frozen with liquid nitrogen and gases were removed using high vacuum. After melting the 1,2-epoxycyclohexane, the liquid was degassed and frozen again. This sequence was repeated at least three times. Subsequently, a known amount of CO_2 (uncertainty 1 μmol) was introduced in the tube from a glass reservoir with a calibrated volume of 57.84 cm^3. The exact amount of CO_2 was determined from the temperature (uncertainty 0.05 K), pressure (uncertainty 5 Pa), and volume (uncertainty 0.005 cm^3) using the virial equation of state. As pressures were typically below 40 kPa, the influence of the third and higher order virial coefficients was neglected. After filling the Cailletet tube, the contents were frozen and sealed with mercury. Under these conditions, the tube was transferred to the Cailletet setup. As a result, the overall uncertainty of the sample composition is below 0.1 %. A more detailed description of the Cailletet setup and sample preparation is given in ref 12.

Materials. 1,2-Epoxycyclohexane (minimum 98 % purity, GC) was obtained from Aldrich. To remove trace elements of water, 1,2-epoxycyclohexane was refluxed overnight with calcium hydride and distilled, both under argon atmosphere. Prior to sample synthesis, gas was removed by at least three cycles of freezing with liquid nitrogen, applying vacuum, and heating to room temperature. CO_2 grade 4.5 (minimum purity 99.995 %) from Messer-Griesheim was used as received.

Results

Experimental Results. The results of the vapor pressure measurements of 1,2-epoxycyclohexane are presented in Table 1. As at low vapor pressures the experimental uncertainty becomes large relative to the vapor pressure, no measurements have been performed below 24 kPa. The data were fitted to the Antoine equation[17] with a 0.3 % average relative deviation:

$$\log P_{\mathrm{sat}}/\mathrm{MPa} = 3.0824 - 1385.2/(T/\mathrm{K} - 64.912) \quad (1)$$

Interpolation of these data with the Antoine equation provides a boiling point of 404.69 K at 101.325 kPa. This value matches those reported in the literature.[18–20] This vapor pressure correlation is further used for estimation of the critical temperature and acentric factor of 1,2-epoxycyclohexane.

Table 1. Vapor Pressure (P_{sat}) of 1,2-Epoxycyclohexane as a Function of Temperature (T)^a

T/K	P_{sat}/kPa	T/K	P_{sat}/kPa
360.91	25.5	423.87	167.0
361.13	25.8	443.95	268.0
382.47	52.4	453.99	333.0
383.09	53.6	463.99	409.0
404.87	101.3	474.03	497.0
405.48	103.8		

^{a} Determined with tensiometer and Cailletet setup.

Table 2. Liquid Density (ρ) of 1,2-Epoxycyclohexane Determined with a Picnometer at Atmospheric Pressure and Various Temperatures (T)

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
277.7	988.4	313.2	955.0	353.2	915.7
289.0	978.0	323.2	944.8	363.2	903.9
293.2	972.2	333.2	935.4		
303.2	963.8	343.2	925.5		

Table 3. Experimentally Determined Bubble Point Pressure (P) of 1,2-Epoxycyclohexane + CO_2 Isopleths at Various Temperatures (T) and Mole Fraction CO_2 ($x(CO_2)$)

$x(CO_2)$	T/K	P/MPa	T/K	P/MPa
0.101	353.92	1.535	393.90	2.220
	363.90	1.700	403.90	2.400
	373.89	1.870	413.92	2.580
	383.90	2.045	423.92	2.755
0.201	353.77	3.115	393.91	4.450
	363.74	3.450	403.90	4.775
	373.89	3.785	413.91	5.095
	383.87	4.115	423.95	5.415
0.300	353.73	4.670	393.98	6.695
	363.74	5.175	403.92	7.175
	373.81	5.685	413.90	7.640
	383.73	6.190	423.98	8.095
0.401	353.85	6.289	394.06	9.014
	363.88	6.979	403.97	9.654
	373.91	7.669	414.01	10.269
	383.94	8.349	423.98	10.849
0.499	353.75	7.942	393.83	11.392
	363.73	8.827	403.81	12.177
	373.78	9.702	413.83	12.917
	383.81	10.562	423.82	13.647

The results of the liquid density measurements of 1,2-epoxycyclohexane are presented in Table 2. Interpolation of these data results in a density of 974 kg·m^{-3} at 293.15 K. A modification of the Rackett equation by Daubert [21] describes the experimental data with a 0.06 % average relative deviation. The value of the density deviates (2 to 7) kg·m^{-3} from reported values.[18–20]

The results of the isoplethic bubble point determinations for the binary system CO_2 + 1,2-epoxycyclohexane are reported in Table 3 per isopleth and in Figure 1 as isothermal series.

These results are compared with previously reported data on the phase behavior of this system in Figure 2.[11] As can be seen in this figure, there seems to bee a discrepancy between the two data sets. In general we find lower bubble-point pressures. It should be noted that our results are within the margins of the experimental uncertainty of 0.7 MPa as reported by the group of Beckman.[11] However, the experimental uncertainty as reported by these authors is substantial and the deviation seems to be systematic. It should be noted that for low concentrations of 1,2-epoxycyclohexane these authors report anomalous phase behavior, which was suggested to originate from the

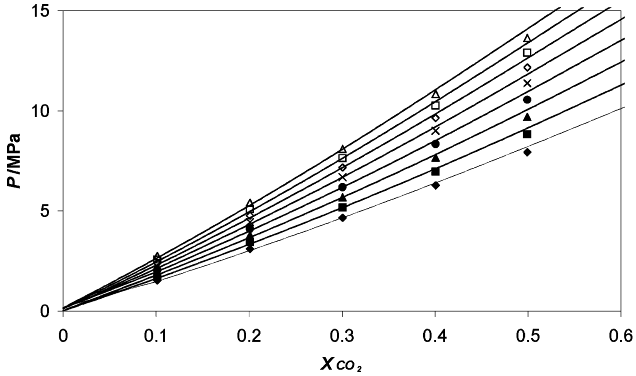

Figure 1. Bubble points for the binary system CO_2 + 1,2-epoxycylohexane, measured at ◆, 353.8 K; ■, 363.8 K; ▲, 373.9 K; ●, 383.9 K; ×, 393.9 K; ◇, 403.9 K; □, 413.9 K; △, 423.9 K. Lines are calculated using the Peng−Robinson equation of state and van der Waals one-fluid mixing rules with T_c, P_c, acentric factor, and k_{ij} (T) as reported in Tables 4 and 5.

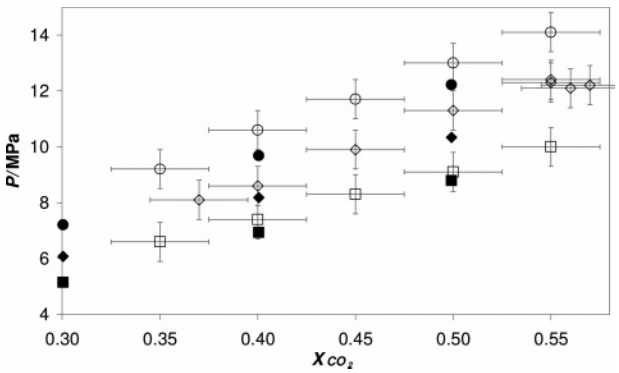

Figure 2. Comparison between the data reported in this work: ■, 363 K; ◆, 382 K; ●, 405 K; and previously reported data:[11] □, 363 K; ◇, 382 K; ○, 405 K.

formation of poly(cyclohexene ether). Trace amounts of water are known to catalyze polyether formation.[11] In our work, this particular problem is avoided by extensively drying the 1,2-epoxycyclohexane before use, thus explaining the difference between the two data sets.

Table 5. Temperature-Dependent and -Independent Interaction Parameter k_{ij} (T) and k_{ij} Used for Correlation of Binary Experimental Data (see Table 3) with the Peng−Robinson Equation of State, van der Waals One-Fluid Mixing Rules, and 1,2-Epoxycyclohexane Parameters According to the Joback and Reid Method[a]

T/K	k_{ij} (T)	k_{ij}
353.8	0.05415	0.05536
363.8	0.05381	0.05536
373.9	0.05360	0.05536
383.9	0.05369	0.05536
393.9	0.05429	0.05536
403.9	0.05550	0.05536
413.9	0.05749	0.05536
423.9	0.06037	0.05536
ΔX	1.5 %	1.6 %

[a] The temperature-dependent interaction parameter k_{ij} (T) has been determined by minimizing the average relative deviation in calculated liquid composition (ΔX) at all temperatures (T).

Modeling. The experimental data presented in the previous section have been correlated using the PR equation of state.[13] The values of the model parameters for pure CO_2 and 1,2-epoxycyclohexane are summarized in Table 4. The critical temperature and pressure for 1,2-epoxycyclohexane have been estimated using the group contribution method as proposed by Joback and Reid[14] and the bond contribution method as proposed by Marrero-Morejon and Pardillo-Fontdevila.[15] For the Joback and Reid method, the contribution by the epoxide group is estimated using an ether group contribution. In general, the method of Joback and Reid is more reliable for estimates of the critical temperature than for the critical pressure, while the method of Marrero-Morejon and Pardillo-Fontdevila provides even higher accuracies for the critical temperature and slightly worse estimates for the critical pressure when an experimental boiling point is used.[22] Both these methods require a value for the boiling point, for which the value has been determined from vapor pressure data as described in the previous section. To estimate the acentric factor, the vapor pressure at $T_r = 0.7$ has been interpolated from the vapor pressure data of 1,2-epoxycyclohexane using eq 1. The results of these estimates are summarized in Table 4 including the average relative deviation (ΔP_{sat} and $\Delta\rho$) for the description of the pure component experimental data from Tables 1 and 2 with the PR equation of state. The Joback and Reid method describes the experimental vapor pressures almost as accurately as the Antoine equation. Because the deviation using the Marrero-Morejon and Pardillo-Fontdevila method is significantly larger, these parameters have not been used for further calculations. It should be noted that the deviations for the description of the liquid densities are similar for the two methods.

For the description of the binary data, the PR equation of state has been used in combination with the van der Waals one-fluid mixing rules with only one binary interaction parameter (k_{ij}) for the attractive parameter (a_{ij}). Since this parameter is found to be temperature-dependent, the interaction parameter (k_{ij}) is optimized to match the experimental data at each temperature separately. Optimization is achieved by minimizing the average relative deviation (ΔX) between the calculated (x_{cal}) and the experimental composition (x_{exp}) at given pressure and temperature:

$$\Delta X = \frac{1}{n}\sum_{i}^{n}\left|\frac{x^{i}_{cal} - x^{i}_{exp}}{x^{i}_{exp}}\right| \tag{2}$$

The results are presented in Table 5 with the average relative deviation (ΔX) between the experimental data from Table 3 and calculations using the pure component pa-

Table 4. Pure Component Parameters (a, b, T_c, P_c, and ω) Used for Correlation of Experimental Data with the Peng−Robinson Equation of State[a]

	method	a $Pa\cdot m^6\cdot mol^{-1}$	b $cm^3\cdot mol^{-1}$	T_c K	P_c kPa	ω	ΔP_{sat} %	$\Delta\rho$ %
CHO	Marrero-Morejon and Pardillo-Fontdevila[15]	2.9037	97.767	607.80	4021.0	0.3639	3.3	8.8
CHO	Joback and Reid[14]	2.8222	92.780	622.51	4339.7	0.2902	0.6	3.5
CO_2	Poling et al.[22]	0.3964	26.675	304.12	7374	0.225		

[a] Average relative deviations between calculated and experimental data are reported for vapor pressures (ΔP_{sat}) and liquid density data ($\Delta\rho$). CHO refers to 1,2-epoxycyclohexane.

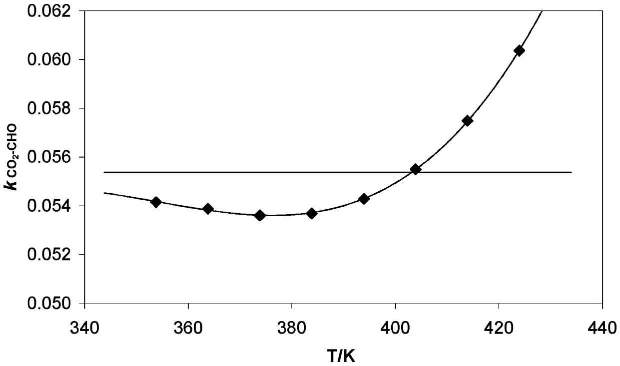

Figure 3. Temperature dependency of interaction parameter k_{ij} (T) determined by minimizing ΔX (see Table 5).

rameters as reported in Table 4. Additionally, Table 5 presents the effect of using one temperature-independent value for k_{ij} in the complete temperature range. This temperature-independent k_{ij} is the arithmetic average of the temperature-dependent k_{ij} values (see Figure 3).

Clearly there is little increase in deviation in the description of the phase behavior when a temperature-independent value for k_{ij} is used in the temperature range of interest. However, it should be noted that the average relative deviation increases when the difference between temperature and mean temperature increases. This indicates that extrapolations are probably more reliable if a correlation for the temperature-dependent interaction parameters is used (see Figure 3).

Super et al. also reported data in the critical region.[11] Using the above-described approach, our results lead to an overprediction of the mixture critical point of approximately 2 MPa, while the predicted critical compositions agree within the reported experimental uncertainty.

Conclusions

VLE data relevant to the copolymerization of carbon dioxide and 1,2-epoxycyclohexane are reported in this paper. Experimental bubble point isopleths for the binary system carbon dioxide + 1,2-epoxycyclohexane have been measured. These data are believed to be more accurate than previously reported data. Additionally, vapor pressures and liquid densities of 1,2-epoxycyclohexane have been measured. The data are successfully correlated using the PR equation of state. The experimental data and parameters that are reported in this work are important for the design and the further development of this CO_2-based solvent-free alternative to polycarbonate synthesis.

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