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Vapor−Liquid Equilibria of Systems Containing Dichloromethane and Gaseous Components

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Isothermal pressure−composition data were measured for three binary systems: carbon monoxide + dichloromethane; propene + dichloromethane; 1-butene + dichloromethane. Each system was measured at three temperatures (30.0, 60.0, and 90.0 °C) and pressures up to 70 bar. The experimental data were correlated with the SRK equation of state using the MHV2 mixing rule and the UNIQUAC method for the expression of the excess Gibbs energy.

Introduction

Dichloromethane is a colorless, highly volatile liquid, which is an important solvent for the chemical and the food industry. About 40% of the annual production of dichloromethane is used as a cleaning agent and paint remover, and another 25% as a pressure mediator in areosols. Other uses of dichloromethane include extraction technologies such as decaffeination of coffee, extraction of hops and paraffin, and recovery of pharmaceuticals. A small amount is used as an intermediate in the chemical industry.

The dichloromethane used as a solvent in extraction or absorption processes has to be recycled in order to keep the consumption of dichloromethane to a minimum. By using dichloromethane as an intermediate, the remaining dichloromethane has to be separated in order to reach the needed purity of the product. Because of the low boiling temperature of dichloromethane (40.2 °C at atmospheric pressure) it is economical to recycle and separate it by distillation. Therefore vapor−liquid equilibrium data are needed. Gas solubility data are also important when using dichloromethane as an absorption solvent.

Apparatus and Procedures

The measurements were performed on an existing 700 cm^3 cell made of steel. This apparatus has previously been used to measure gas solubility in dimethyl ether[1,2] and gas solubility in acetic acid[3] with good results. Pressure and temperature meters are attached to the cell, and the compositions of the gas and the liquid phases are measured by a gas chromatograph. A more detailed description[1] of the apparatus and the experimental method is available.

Table 1 lists the compounds, their suppliers, and minimum guaranteed purity. The compounds were all used without further purification.

To analyze samples which are taken from the liquid and the vapor phases of the binary mixtures, calibration curves for the gas chromatograph are needed. This is done by injecting binary mixtures of gas + dichloromethane with known compositions into the gas chromatograph and registering the peak areas (gas: carbon monoxide, propene, or 1-butene). A plot of the known concentrations versus the peak area fractions of gas is made, and a second-order polynomial is used to fit the points. Results of the calibrations are presented in Table 2.

Table 1. Source and Purity of the Compounds

compd	source	minimum purity/%
dichloromethane	Merck	99.5
carbon monoxide	Hede Nielsen A/B	99.97
propene	AGA	99.5
1-butene	AGA	99.0

Table 2. Calibration Results for the Gas Chromatograph

system	mean deviation in composn
carbon monoxide + dichloromethane	0.0096
propene + dichloromethane	0.0055
1-butene + dichloromethane	0.0074

Table 3. Composition of the Liquid (x_1) and Vapor (y_1) Phases at the Pressure *P* for the System Carbon Monoxide (1) + Dichloromethane (2)

x_1	y_1	P/bar	x_1	y_1	P/bar
		t = 30.0 °C			
0.0000	0.000	0.71[a]	0.0126	0.957	23.1
0.0018	0.819	4.0	0.0165	0.967	29.9
0.0031	0.868	6.3	0.0214	0.979	40.1
0.0048	0.889	9.1	0.0254	0.974	49.2
0.0071	0.909	12.7	0.0303	0.984	59.8
0.0098	0.940	16.7			
		t = 60.0 °C			
0.0000	0.000	1.98[a]	0.0179	0.900	30.4
0.0061	0.790	10.1	0.0230	0.915	40.1
0.0087	0.836	14.9	0.0290	0.920	49.4
0.0117	0.867	20.1	0.0346	0.927	59.8
0.0139	0.885	24.5			
		t = 90.0 °C			
0.0000	0.000	4.58[a]	0.0245	0.848	40.4
0.0028	0.391	8.4	0.0309	0.886	49.8
0.0056	0.512	11.8	0.0382	0.902	59.6
0.0115	0.756	21.0	0.0442	0.916	70.2
0.0179	0.791	30.1			

[a] Obtained from DIPPR.[6]

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Table 4. Composition of the Liquid (x_1) and Vapor (y_1) Phases at the Pressure *P* for the System Propene (1) + Dichloromethane (2)

x_1	y_1	P/bar	x_1	y_1	P/bar
		t = 30.0 °C			
0.0000	0.000	0.70[a]	0.2553	0.901	5.0
0.0596	0.688	2.0	0.3401	0.926	6.0
0.1182	0.803	3.0	0.5201	0.942	8.0
0.1887	0.866	4.0	1.0000	1.000	13.15[a]
		t = 60.0 °C			
0.0000	0.000	1.98[a]	0.1411	0.763	5.9
0.0332	0.403	2.9	0.1820	0.809	6.9
0.0656	0.662	3.9	0.2677	0.855	8.9
0.1022	0.721	4.9	1.0000	1.000	25.42[a]
		t = 90.0 °C			
0.0000	0.000	4.58[a]	0.2233	0.942	13.7
0.0445	0.490	6.5	0.3234	0.963	17.4
0.0967	0.712	8.8	0.4284	0.976	20.9
0.1471	0.771	10.9	1.0000	1.000	44.45[a]

[a] Obtained from DIPPR.[6]

Table 5. Composition of the Liquid (x_1) and Vapor (y_1) Phases at the Pressure *P* for the System 1-Butene (1) + Dichloromethane (2)

x_1	y_1	P/bar	x_1	y_1	P/bar
		t = 30.0 °C			
0.0000	0.000	0.70[a]	0.4136	0.759	2.1
0.1558	0.500	1.3	0.6347	0.858	2.6
0.2939	0.665	1.7	0.6834	0.927	2.8
0.3677	0.697	1.9	1.0000	1.000	3.49[a]
		t = 60.0 °C			
0.0000	0.000	1.98[a]	0.4371		4.7
0.1249	0.357	3.1	0.6284	0.871	5.6
0.2988		4.1	0.6951		6.1
0.3695	0.714	4.4	1.0000	1.000	7.73[a]
		t = 90.0 °C			
0.0000	0.000	4.58[a]	0.5842	0.843	10.7
0.1545	0.502	6.5	0.6240	0.870	11.1
0.2986	0.639	8.0	0.6997	0.897	11.8
0.3679	0.722	8.8	1.0000	1.000	14.86[a]
0.4329	0.755	9.3			

[a] Obtained from DIPPR.[6]

Table 6. *m* Parameters in the α Expression, Critical Parameters, Volume, and Surface Area Parameters for All Compounds

compd	m_1	m_2	T_c/K	P_c/bar	R	Q
dichloromethane	0.8453	1.1030	510.00	63.00	2.2564	1.988
carbon monoxide	0.5614	0.8072	132.91	35.01	2.094	2.120
propene	0.6957	1.2025	364.85	46.05	2.2465	2.024
1-butene	0.7649	1.4090	419.57	40.18	2.9209	2.564

Table 7. Interaction Parameters C_{ij} and D_{ij} between Gas and Dichloromethane

gas	C_{ij}/K	D_{ij}/K^2	gas	C_{ij}/K	D_{ij}/K^2
carbon monoxide	−51.713	45840	1-butene	−83.284	37599
propene	−69.288	34840			

Table 8. Overview of the Correlation Results for the Three Systems That Have Been Measured

system	ΔP/bar[a]	Δy[b]
carbon monoxide + dichloromethane	0.93	0.026
propene + dichloromethane	0.15	0.110
1-butene + dichloromethane	0.09	0.050

[a] $\Delta P = \sum|P^{\text{calc}} - P^{\text{exp}}|/N_{\text{data}}$. [b] $\Delta y = \sum|y^{\text{calc}} - y^{\text{exp}}|/N_{\text{data}}$.

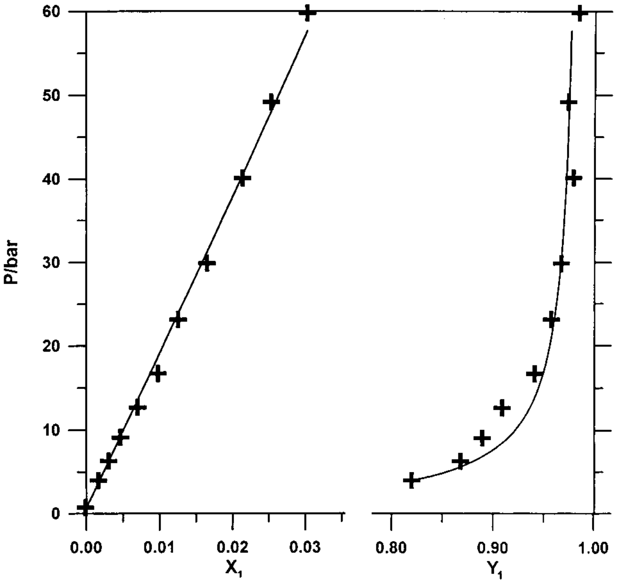

Figure 1. Isothermal pressure composition data for carbon monoxide (1) + dichloromethane (2) at 30.0 °C: +, experimental data; —, MHV2 model.

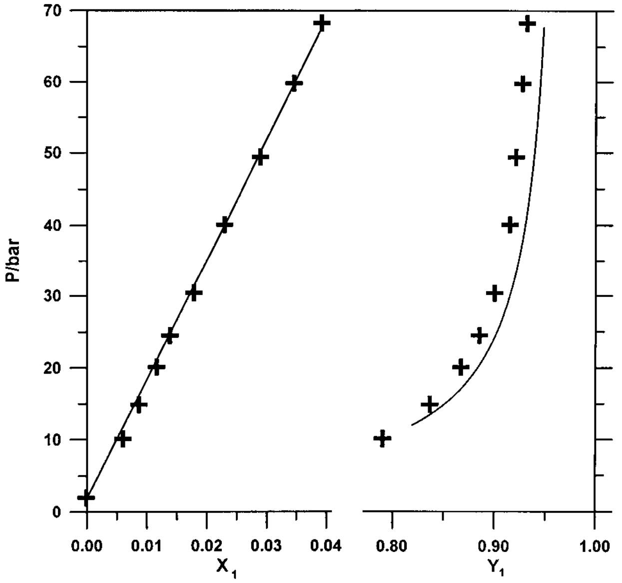

Figure 2. Isothermal pressure composition data for carbon monoxide (1) + dichloromethane (2) at 60.0 °C: +, experimental data; —, MHV2 model.

Experimental Data Section

The systems carbon monoxide + dichloromethane, propene + dichloromethane, and 1-butene + dichloromethane were measured at three temperatures (30.0, 60.0, 90.0 °C). The accuracy of the pressure meter is 0.1 bar, which is also the estimated accuracy of the pressure measurements. The accuracy of the temperature meter is 0.01 °C, and the estimated accuracy of the temperature measurements is 0.05 °C. The mean deviation of the calibration curve (Table 2) can be used as an estimate for the accuracy of the composition in the vapor and the liquid phase. For the first two systems the measurements with the gas chromatograph were repeated within 0.003 area fraction for the liquid phase and 0.005 area fraction for the vapor phase (area fraction corresponds approximately to mole fraction). For the last system 1-butene + dichloromethane the measurements were repeated within 0.006 area fraction for the liquid phase and 0.011 area fraction for the vapor phase. For three of the vapor phase measurements at 60.0 °C the values could not be repeated within reasonable limits. The results of the measurements are presented in

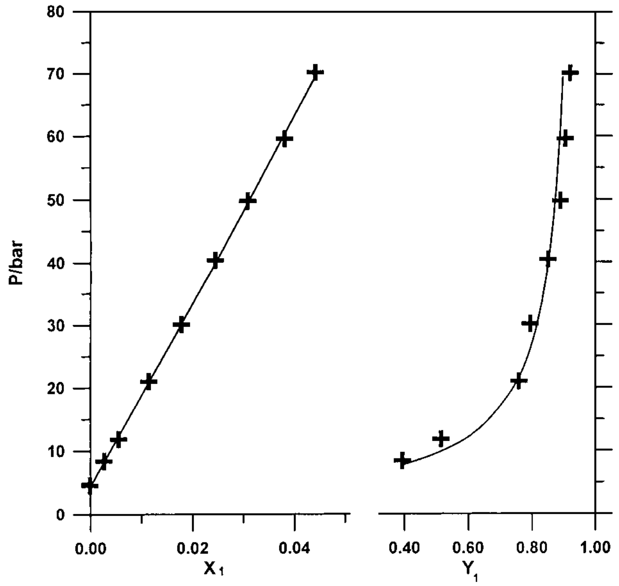

Figure 3. Isothermal pressure composition data for carbon monoxide (1) + dichloromethane (2) at 90.0 °C: +, experimental data; —, MHV2 model.

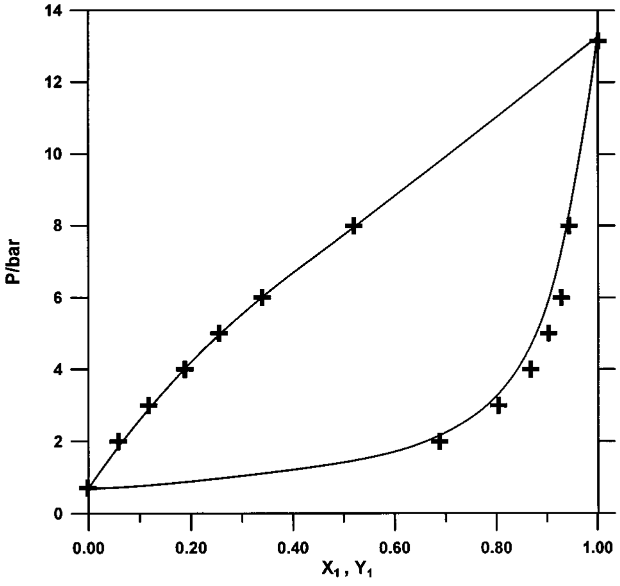

Figure 4. Isothermal pressure composition data for propene (1) + dichloromethane (2) at 30.0 °C: +, experimental data; —, MHV2 model.

Tables 3−5. The liquid-phase compositions (x_i) are considered somewhat more accurate than the vapor phase compositions (y_i). The values of x_i and y_i are, therefore, given with a different number of significant digits in Tables 3−5.

Correlations of the VLE Data

The experimental data have been correlated with the MHV2 model by Dahl et al.[4] The model combines the SRK equation of state with a model for the excess Gibbs energy, the UNIQUAC[5] model. For the temperature dependence of the a parameter ($a_i = a_{ci}\alpha_i$) we used the model of Jónasson et al.,[3]

$$\alpha_i = 1 + m_{1i}(1 - T_{ri}) + m_{2i}(1 - \sqrt{T_{ri}})^2 \qquad (1)$$

For the temperature dependence of the binary interaction parameters τ_{ij} in the UNIQUAC model we used the

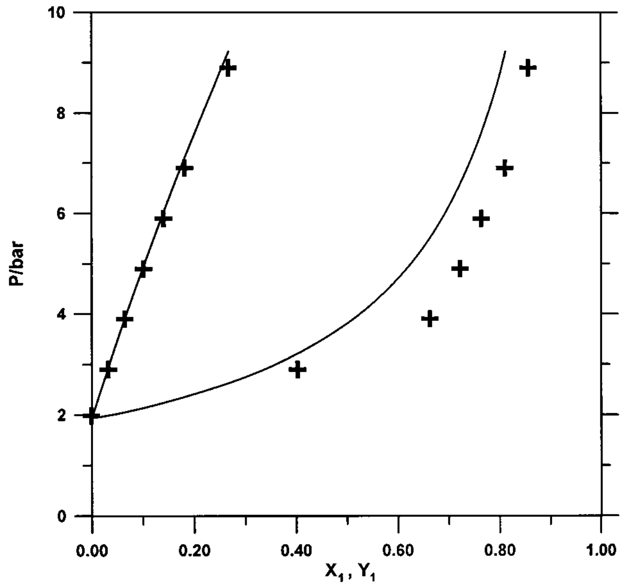

Figure 5. Isothermal pressure composition data for propene (1) + dichloromethane (2) at 60.0 °C: +, experimental data; —, MHV2 model.

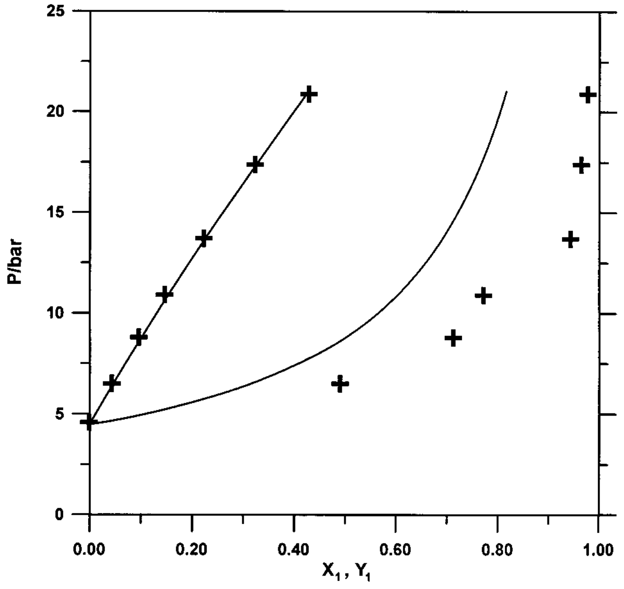

Figure 6. Isothermal pressure composition data for propene (1) + dichloromethane (2) at 90.0 °C: +, experimental data; —, MHV2 model.

following expression:

$$\tau_{ij} = \frac{C_{ij}}{T} + \frac{D_{ij}}{T^2} \qquad (2)$$

Here the parameters C_{ij} and D_{ij} are symmetrical, i.e., $C_{ij} = C_{ji}$ and $D_{ij} = D_{ji}$. When estimating the interaction parameters, we minimized the following objective function:

$$\mathrm{SSQ} = \sum_{i=1} (P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}})^2 \qquad (3)$$

The pure component parameters used in the model are presented in Table 6. The results of the correlations are shown in Figures 1−9 and in Tables 7 and 8.

For the system carbon monoxide + dichloromethane at 30.0 °C (Figure 1) the model correlates both phases very well. At 60.0 °C (Figure 2) the model correlates the liquid

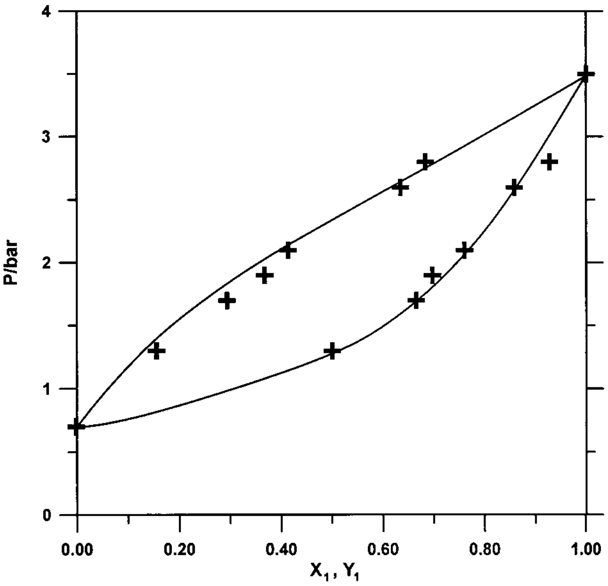

Figure 7. Isothermal pressure composition data for 1-butene (1) + dichloromethane (2) at 30.0 °C: +, experimental data; —, MHV2 model.

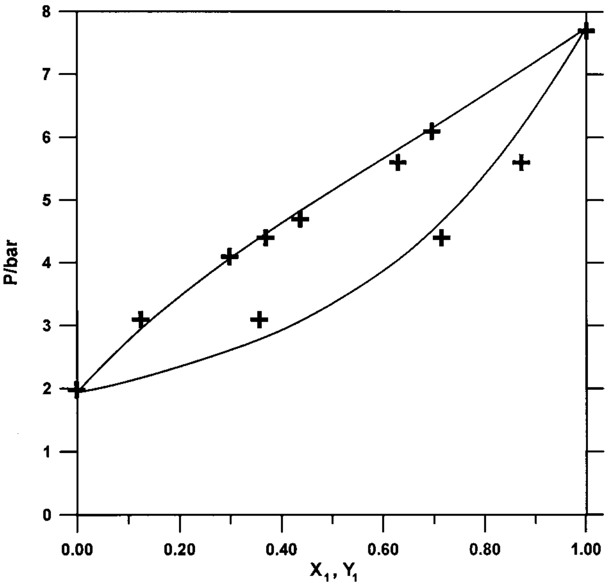

Figure 8. Isothermal pressure composition data for 1-butene (1) + dichloromethane (2) at 60.0 °C: +, experimental data; —, MHV2 model.

phase very well, but for the vapor phase the calculated values are around 0.01−0.02 mole fraction higher than the experimental data. At 90.0 °C (Figure 3) the model correlates both phases well.

For the system propene + dichloromethane at 30.0 °C (Figure 4) the model correlates both phases well. At 60.0 °C (Figure 5) the calculated values of the vapor phase are 0.04−0.14 mole fraction lower than the experimental data. At 90.0 °C (Figure 6) the calculated values of the vapor phase are 0.15−0.25 mole fraction lower than the experimental data. At 90.0 °C the temperature is very close to the critical temperature of propene (91.7 °C). When we have measured very close to the critical temperature of one component, experience has shown that this can give both experimental and modeling problems.

For the system 1-butene + dichloromethane at 30.0 °C (Figure 7) and 60.0 °C (Figure 8) the model correlates the experimental data well. At 90.0 °C (Figure 9) the calculated values of the vapor phase are 0.05−0.12 mole fraction lower than the experimental ones.

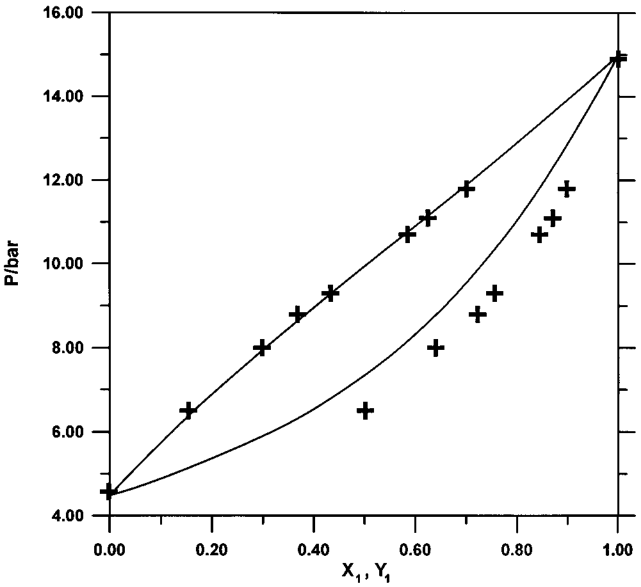

Figure 9. Isothermal pressure composition data for 1-butene (1) + dichloromethane (2) at 90.0 °C: +, experimental data; —, MHV2 model.

As can be seen in Figures 1−9, it appears that the deviations between the experimental data and the model increase with the temperature. No definite reason can be found to explain this behavior, but the deviations are likely to originate from limitations in the model. The main importance for the authors was to produce the experimental data and correlate them with a reasonable model. Other possible models have therefore not been investigated.

Conclusions

Three isothermal binary systems have been measured containing gas + dichloromethane. The gases are carbon monoxide, propene, and 1-butene. The systems have been measured at three temperatures (30, 60, and 90 °C) and pressures up to 70 bar.

The experimental data have been correlated with the MHV2 model. The model correlates the systems carbon monoxide + dichloromethane and 1-butene + dichloromethane well. The model correlates the system 1-propene + dichloromethane reasonably well, but there are some deviations in the vapor phase at 90 °C, which is very close to the critical temperature of propene.

List of Symbols

a	attractive EOS parameter
m_1, m_2	coefficients in the expression for α
P_c	critical pressure
T_c	critical temperature
x_i	liquid-phase composition of component i
y_i	vapor phase composition of component i
τ_{nm}	interaction parameter between components n and m

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