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High Pressure Solubility of Carbon Dioxide and Carbon Monoxide in Dimethyl Ether

Ari Jónasson,* Ole Persson, and Aage Fredenslund

Engineering Research Centre IVC-SEP, Institut for Kemiteknik, The Technical University of Denmark, DK-2800 Lyngby, Denmark

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An apparatus has been constructed for precisely measuring the solubility of gases in liquids. The equipment is designed for use at temperatures from 0 to 200 °C and pressures up to 18 MPa. Measurements were made on carbon dioxide (1) + dimethyl ether (2) at three isotherms in order to verify the apparatus and techniques by comparing with data from the literature. Measurements were also made on the system carbon monoxide (1) + dimethyl ether (2) which has not been previously studied. The results have been correlated using the Soave−Redlich−Kwong equation of state. Two different local composition mixing rules have been used: the MHV2 mixing rule in combination with the modified UNIFAC model and the MHV2 mixing rule in combination with the original UNIQUAC model.

Introduction

One of the most important methods in producing olefins is by cracking naphtha or natural gas condensates. The method is important due to the low cost of the feed materials. One of the most promising routes for producing olefins is from dimethyl ether. Optimization of a dimethyl ether plant production requires accurate phase equilibrium data for the components of the feed and the product as well as reliable models for calculating phase equilibria. An apparatus has been built to accurately determine the high pressure solubility of gases in dimethyl ether.

Apparatus and Procedures

The apparatus consists of a 700 mL cell with 6 mm thick walls made of stainless steel (Figure 1). The apparatus is designed to investigate vapor−liquid equilibrium in the temperature range from 0 to 200 °C and in the pressure range from 0.02 to 18 MPa. The temperature in the cell is measured by a S1220 Systemteknik AB digital thermometer equipped with a platinum resistance probe, with a resolution of ±0.001 K. The thermometer was checked by measuring the ice point and the normal boiling point of distilled water. The pressure is measured by a digital HBM Uberdruck gage pressure meter with a resolution of ±0.1 bar. The pressure meter was calibrated against a Desgranges Et Huot 26000 dead weight tester. The cell is equipped with a medimex MRK 30 stirrer head with permanent magnet coupling to a gas stirrer. The stirrer is driven by a Ingersoll-Rand MOO2R multivane air motor which can operate up to 1520 rpm.

The cell is surrounded by a jacket connected to a water bath for controlling the temperature of the cell. The oven is used to control the temperature of the sample lines.

The sampling system is shown in Figure 2. It consists of 1/16 in. o.d. tubes (ca. 0.01 in. i.d.). The use of small diameter tubing keeps the dead volume to a minimum.

The sampling valve for the liquid phase is a Rheodyne Model 7010 with a 0.5 μL sample loop. The sampling valve for the gas phase is a Rheodyne Model 7013 with a 500 μL sample loop. The composition of the liquid phase and the gas phase is measured using a Hewlett-Packard 5840A gas cromatograph. The line from the oven to the gas chromatograph is heated by electrical tape to avoid condensation of the sample.

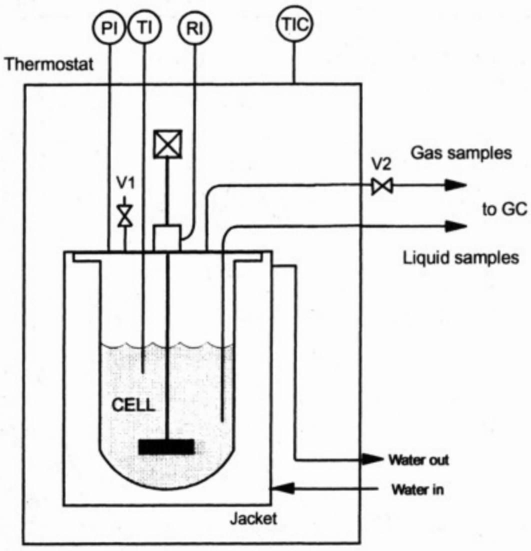

Figure 1. Equipment: TIC, temperature control; PI, pressure meter; TI, temperature meter; RI, rotator.

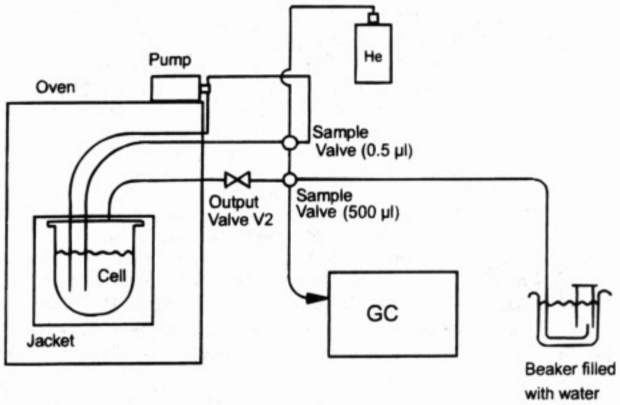

Figure 2. Sampling system.

A measurement is carried out as follows: (1) First the cell is evacuated by means of a vacuum pump. The less volatile component is then added to the cell. The temperature of the jacket is regulated until the cell has reached the desired temperature. (2) The more volatile compoment is added until the desired pressure is reached. The mixture

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Table 1. Source and Purity of the Compounds

substance	supplier	min purity, %
dimethyl ether	Fluka	99.2
carbon dioxide	AGA	99.0
carbon monoxide	AGA	99.0

Table 2. Vapor Pressure of CO_2 and Comparison with Calculated Values

t/°C	P_{exp}/MPa	P_{calc}/MPa	δP/MPa
−3.01	3.22	3.220	0.000
0.31	3.54	3.519	0.021
4.32	3.92	3.908	0.012
9.05	4.42	4.406	0.014
14.13	4.98	4.993	−0.013
15.69	5.16	5.185	−0.025
21.17	5.88	5.903	−0.023
21.50	5.94	5.948	−0.008
23.56	6.22	6.238	−0.018
26.65	6.68	6.694	−0.014
29.66	7.16	7.163	−0.003
30.52	7.31	7.302	0.008

is stirred for 5−10 min at about 1300 rpm. The cell is then left undisturbed until the desired temperature has been reached again. (3) For sampling of the liquid phase, the pump is started, and the liquid phase is recirculated for about 1 min to flush the dead volume in the tube to the sample valve. The sampling valve is then turned, and 0.5 μL of the liquid phase is transferred directly to the gas chromatograph. (4) For sampling of the gas phase, the temperature of the oven is kept higher than the temperature of the cell to ensure no condensation of the less volatile component. The output valve V2 is turned, and about 20 mL of the gas phase is transferred to a beaker filled with water. The sampling valve is then turned, and 500 μL of the gas phase is then transferred to the gas chromatograph. (5) The composition of the gas phase and the liquid phase is calculated using a prepared calibration curve. (6) A new mixture is measured by starting again at step 2.

The accuracy of the temperature was ±0.02 K, and the accuracy of the pressure was ±0.01 MPa. Measurements on the mole fraction of the liquid phase were reproduced within 0.0030 which gives an accuracy of x_1 of ±0.0015. For the gas phase the reproduction was within 0.0050 which gives an accuracy of y_1 of ±0.0025.

Materials

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

Results and Discussion

The first system to be measured was that of carbon dioxide and dimethyl ether in order to compare the results with data from the literature. First the vapor pressures of the pure components were measured. The results are shown in Tables 2 and 3 along with values calculated from an equation given in the DIPPR data bank (*5*). Deviations from these calculated values are shown in Figures 3 and 4. As can be seen the calculated values are in good agreement with the experimental data. The standard deviation for carbon dioxide is 0.016 MPa, and that for dimethyl ether is 0.011 MPa.

In order to determine the compositions of the mixtures of carbon dioxide and dimethyl ether, a calibration curve for the gas chromatograph was needed. The calibration curve was prepared by weighing a certain amount of dimethyl ether into a 10 mL cylinder and then adding some carbon dioxide and weighing again. The cylinder was then put on the gas sample line in the oven and warmed to about 100 °C to ensure that the entire mixture would be gaseous. This mixture of known composition was then injected into the gas chromatograph, and the peak areas A were noted. The results are shown in Figure 5 where the known composition x_{CO_2} is drawn against A' which is the peak area of CO_2 divided by the total peak area, i.e., $A' = (A_{CO_2}/(A_{CO_2} + A_{DME}))$. A third-order polynomial, drawn to fit the points,

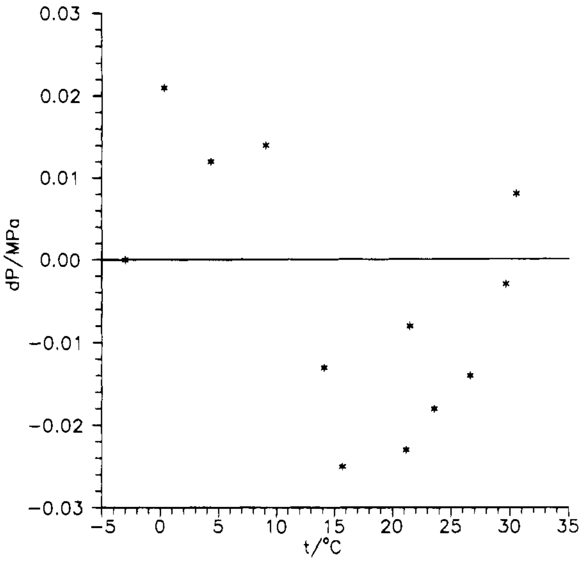

Figure 3. Deviation between experimental and calculated values of vapor pressure for carbon dioxide.

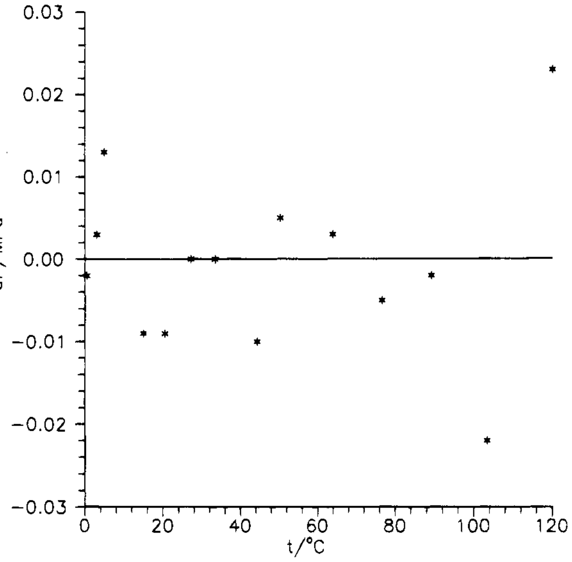

Figure 4. Deviation between experimental and calculated values of vapor pressure for dimethyl ether.

Table 3. Vapor Pressure of Dimethyl Ether and Comparison with Calculated Values

t/°C	P_{exp}/MPa	P_{calc}/MPa	δP/MPa
0.51	0.27	0.272	−0.002
3.07	0.30	0.297	0.003
4.97	0.33	0.317	0.013
15.01	0.43	0.439	−0.009
20.50	0.51	0.519	−0.009
27.11	0.63	0.630	0.000
33.39	0.75	0.750	0.000
44.39	0.99	1.000	−0.010
50.25	1.16	1.155	0.005
63.94	1.59	1.587	0.003
76.67	2.08	2.085	−0.005
89.25	2.68	2.682	−0.002
103.77	3.50	3.522	−0.022
120.12	4.72	4.697	0.023

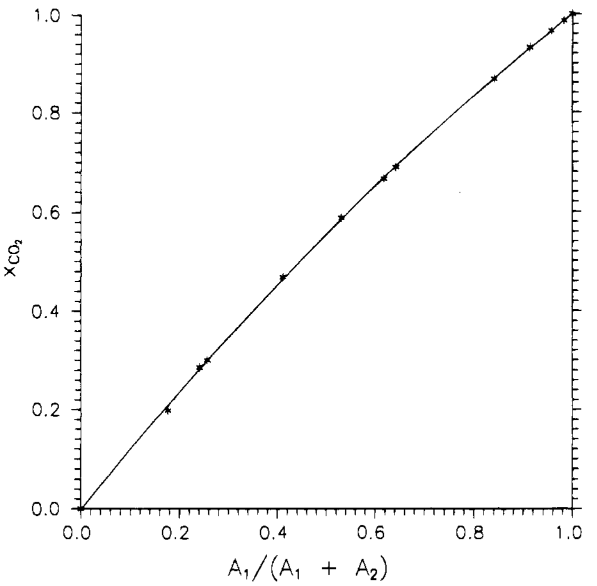

Figure 5. GC calibration curve for the system CO_2 (1) + dimethyl ether (2).

Table 4. Composition of the Liquid Phase (x_1) and the Vapor Phase (y_1) at the Pressure P for the System CO_2 (1) + Dimethyl Ether (2) at 15.05 °C

x_1	y_1	P/MPa	x_1	y_1	P/MPa
0.0000	0.0000	0.42	0.4030	0.7888	1.77
0.0149	0.1733	0.50	0.4782	0.8322	2.10
0.0541	0.3061	0.60	0.5526	0.8639	2.46
0.1019	0.4312	0.72	0.6284	0.8937	2.84
0.1518	0.5242	0.86	0.7079	0.9161	3.27
0.2022	0.6047	1.02	0.7822	0.9391	3.73
0.2663	0.6794	1.24	0.8501	0.9580	4.12
0.3240	0.7365	1.48			

Table 5. Composition of the Liquid Phase (x_1) and the Vapor Phase (y_1) at the Pressure P for the System CO_2 (1) + Dimethyl Ether (2) at 35.50 °C

x_1	y_1	P/MPa	x_1	y_1	P/MPa
0.0000	0.0000	0.78	0.5055	0.8171	3.43
0.0212	0.1230	0.87	0.5602	0.8417	3.76
0.0689	0.2783	1.06	0.6266	0.8710	4.28
0.1094	0.3828	1.24	0.6582	0.8808	4.52
0.1569	0.4773	1.46	0.6934	0.8839	4.80
0.2067	0.5468	1.70	0.7291	0.8922	5.11
0.2583	0.6103	1.96	0.7596	0.9149	5.39
0.3061	0.6633	2.23	0.7917	0.9186	5.66
0.3575	0.7035	2.50	0.8395	0.9271	6.12
0.4050	0.7465	2.80	0.8516	0.9294	6.25
0.4585	0.7839	3.11	0.8577	0.9335	6.33

gives for the mole fraction of CO_2

$$x_{CO_2} = -0.00247793 + 1.24338A' - 0.279869A'^2 + 0.0394022A'^3$$

The standard deviation is found to be 0.0038. This polynomial is found suitable for calculation of the vapor and the liquid compositions.

The system CO_2 (1) + dimethyl ether (2) was measured at three isotherms, 15.05, 33.50, and 46.97 °C. The results are shown in Tables 4–6 and in Figures 6–8. This system has previously been measured by Tsang and Streett (*1*) at the same temperatures. In Figure 6 the experimental values are seen to be in good agreement with the literature results. In Figure 7 some systematic differences in the vapor phase occur. In an intermediate composition range the composition of Y_1 is about 0.02 higher than values from the literature. However, in Figure 8 this systematic difference is seen to be in an opposite direction; that is, the composition of y_1 is about 0.02 lower than values from the literature. The results are therefore considered to be in agreement with the literature. From this one may conclude that the equipment can be used to obtain accurate gas solubilities.

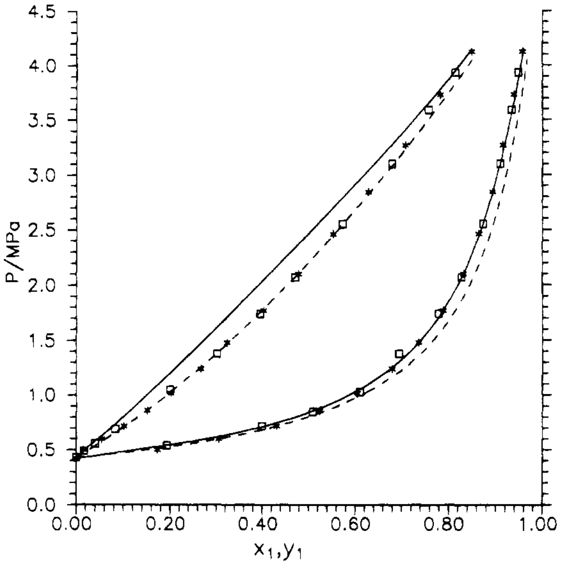

Figure 6. Isothermal pressure–composition data for CO_2 (1) + dimethyl ether (2) at 15.05 °C: (□) literature, (*) experimental data, (—) MHV2/UNIFAC, (- - -) MHV2/UNIQUAC.

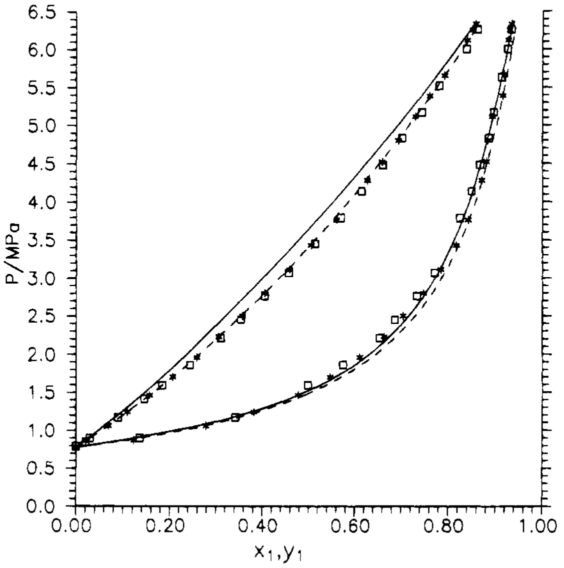

Figure 7. Isothermal pressure–composition data for CO_2 (1) + dimethyl ether (2) at 35.50 °C: (□) literature, (*) experimental data, (—) MHV2/UNIFAC, (- - -) MHV2/UNIQUAC.

Table 6. Composition of the Liquid Phase (x_1) and the Vapor Phase (y_1) at the Pressure P for the System CO_2 (1) + Dimethyl Ether (2) at 46.97 °C

x_1	y_1	P/MPa	x_1	y_1	P/MPa
0.0000	0.0000	1.04	0.3770	0.6798	3.30
0.0177	0.0817	1.12	0.4209	0.7140	3.62
0.0386	0.1538	1.24	0.4606	0.7416	3.92
0.0706	0.2527	1.40	0.5128	0.7632	4.32
0.1230	0.3930	1.70	0.5614	0.7855	4.72
0.1772	0.4670	1.99	0.6132	0.8060	5.22
0.2300	0.5394	2.32	0.6650	0.8315	5.72
0.2800	0.5969	2.64	0.7097	0.8439	6.16
0.3253	0.6552	2.96	0.7744	0.8688	6.79

The SRK equation of state has been used to correlate the results. The mixing rules used are the MHV2 (modified

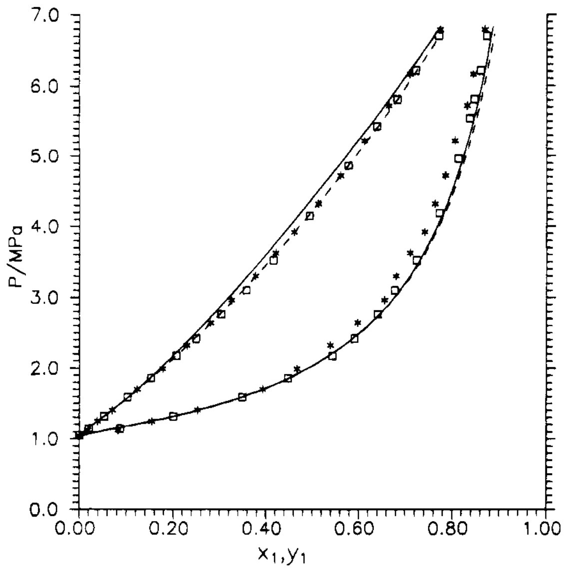

Figure 8. Isothermal pressure–composition data for CO_2 (1) + dimethyl ether (2) at 46.97 °C: (□) literature, (*) experimental data, (—) MHV2/UNIFAC, (- - -) MHV2/UNIQUAC.

Table 7. Interaction Parameters for the CO_2 (1) + Dimethyl Ether (2) System

model	interaction parameters	
MHV2/UNIFAC	$A_{10,26,1} = 97.165$	$A_{10,26,2} = 4.392$
	$A_{26,10,1} = 64.647$	$A_{26,10,2} = -3.794$
MHV2/UNIQUAC	$u(1,2) = -192.612$	$u(2,1) = 217.053$

Huron Vidal second order) mixing rule in combination with the modified UNIFAC model and the MHV2 in combination with the original UNIQUAC model. The mixing rule combines the SRK equation of state with a model for the excess Gibbs energy (*2–4*). The advantage of this mixing rule is its capability of predicting vapor–liquid equilibrium compositions for mixtures with polar components.

The first model is based on interactions between the ether group (CH_3O) and the carbon dioxide group (CO_2) (group numbers 10 and 26 in the UNIFAC model). The second model is based on interactions between the carbon dioxide molecule (1) and the dimethyl ether molecule (2) in the UNIQUAC model. The estimated interaction parameters are shown in Table 7.

The results of the correlations of the two models are shown in Figures 6–8. For the first isotherm at 15.05 °C of Figure 6, the MHV2/UNIFAC model is seen to correlate the results well in the vapor phase, but for the liquid phase there is considerable deviation. The MHV2/UNIQUAC model is seen to correlate the liquid phase results quite well, but the vapor phase results only fairly well. In the second isotherm at 35.50 °C (Figure 7) the MHV2/UNIQUAC model correlates the data very well, but again the results obtained with the MHV2/UNIFAC model show larger deviation from the experimental values in the liquid phase. In the third isotherm at 46.97 °C (Figure 8) both models show fair representation of the experimental data.

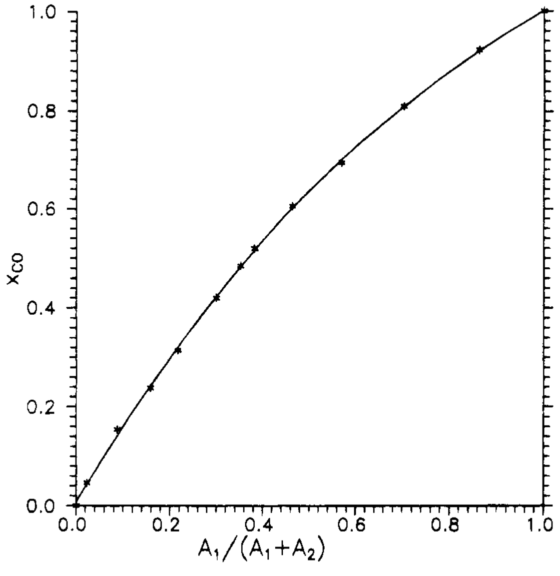

Figure 9. GC calibration curve for the system CO (1) + dimethyl ether (2).

Table 8. Composition of the Liquid Phase (x_1) and the Vapor Phase (y_1) at the Pressure P for the System CO (1) + Dimethyl Ether (2) at 15.00 °C

x_1	y_1	P/MPa	x_1	y_1	P/MPa
0.0000	0.0000	0.42	0.0493	0.8063	2.51
0.0072	0.2093	0.50	0.0555	0.8230	2.95
0.0098	0.3584	0.62	0.0661	0.8402	3.46
0.0134	0.4823	0.78	0.0772	0.8547	4.06
0.0169	0.5711	0.95	0.0887	0.8667	4.72
0.0192	0.6156	1.07	0.1036	0.8737	5.45
0.0245	0.6618	1.24	0.1186	0.8817	6.16
0.0277	0.7042	1.47	0.1322	0.8849	6.82
0.0333	0.7465	1.77	0.1441	0.8861	7.44
0.0404	0.7782	2.12	0.1515	0.8870	7.70

Table 9. Composition of the Liquid Phase (x_1) and the Vapor Phase (y_1) at the Pressure P for the System CO (1) + Dimethyl Ether (2) at 33.00 °C

x_1	y_1	P/MPa	x_1	y_1	P/MPa
0.0000	0.0000	0.71	0.0449	0.6943	2.58
0.0092	0.1589	0.83	0.0555	0.7291	3.14
0.0119	0.2604	0.95	0.0670	0.7600	3.77
0.0146	0.3455	1.08	0.0810	0.7850	4.47
0.0177	0.4282	1.25	0.0898	0.7997	5.20
0.0226	0.5118	1.48	0.1106	0.8069	5.94
0.0280	0.5809	1.78	0.1253	0.8126	6.64
0.0358	0.6411	2.14	0.1391	0.8179	7.35

Table 10. Composition of the Liquid Phase (x_1) and the Vapor Phase (y_1) at the Pressure P for the System CO (1) + Dimethyl Ether (2) at 43.00 °C

x_1	y_1	P/MPa	x_1	y_1	P/MPa
0.0000	0.0000	0.93	0.0412	0.6169	2.64
0.0101	0.1539	1.07	0.0503	0.6596	3.09
0.0110	0.2335	1.19	0.0609	0.7014	3.61
0.0144	0.3052	1.31	0.0725	0.7307	4.17
0.0190	0.3939	1.49	0.0869	0.7489	4.83
0.0226	0.4587	1.69	0.0996	0.7670	5.55
0.0281	0.5110	1.95	0.1133	0.7793	6.24
0.0346	0.5712	2.27	0.1286	0.7926	6.92

Three isotherms have been measured for the system CO (1) + dimethyl ether (2) at 15.00, 33.00, and 43.00 °C. First a calibration curve for the gas chromatograph was prepared. The results are shown in Figure 9 where the known composition x_{CO} is drawn against A, which is the peak area of CO divided by the total peak area of CO and dimethyl ether. A third-order polynomial was used to fit the points which gave the following equation for calculating the composition:

$$x_{CO} = 0.00692573 + 1.61828A - 0.823568A^2 + 0.200002A^3$$

This gave a standard deviation of 0.00602, and the equation is therefore found suitable for calculating the compositions.

The measured isothermal pressure–composition data for CO (1) + DME (2) are given in Tables 8–10. The three isotherms were used to calculate interaction parameters

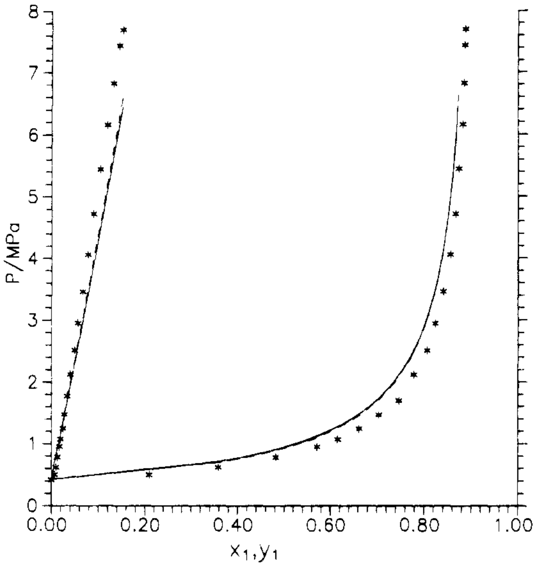

Figure 10. Isothermal pressure–composition data for CO (1) + dimethyl ether (2) at 15.00 °C: (*) experimental data, (—) MHV2/UNIFAC, (- - -) MHV2/UNIQUAC.

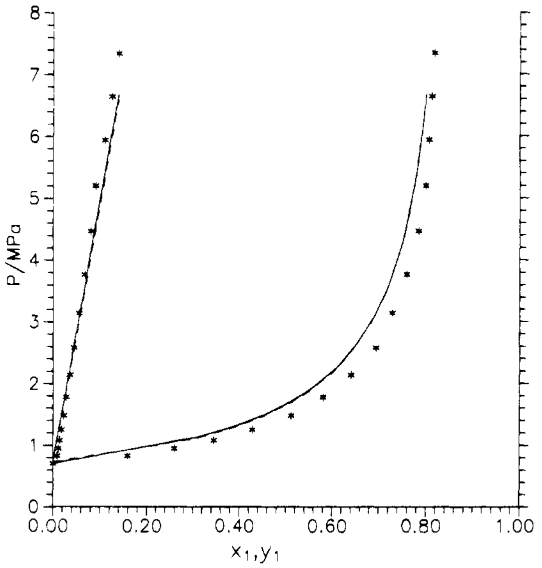

Figure 11. Isothermal pressure–composition data for CO (1) + dimethyl ether (2) at 33.00 °C: (*) experimental data, (—) MHV2/UNIFAC, (- - -) MHV2/UNIQUAC.

Table 11. Interaction Parameters for the CO (1) + Dimethyl Ether (2) System

model	interaction parameters	
MHV2/UNIFAC	$A_{10,25,1} = 125.720$	$A_{10,25,2} = 4.584$
	$A_{25,10,1} = 90.468$	$A_{25,10,2} = -3.550$
MHV2/UNIQUAC	$u(1,2) = 236.233$	$u(2,1) = -131.382$

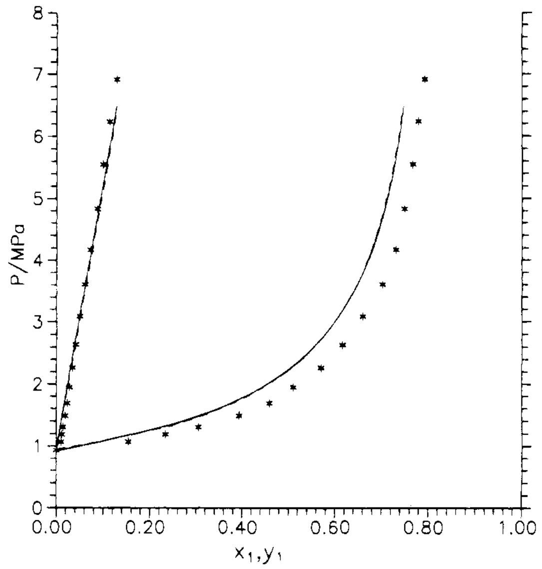

Figure 12. Isothermal pressure–composition data for CO (1) + dimethyl ether (2) at 43.00 °C: (*) experimental data, (—) MHV2/UNIFAC, (- - -) MHV2/UNIQUAC.

in the MHV2/UNIFAC and the MHV2/UNIQUAC models. In the MHV2/UNIFAC model, the interaction parameters between the ether group (CH_3O) and the carbon monoxide group (CO) were calculated (group numbers 10 and 25 in the UNIFAC model). In the MHV2/UNIQUAC model the interaction parameters between the carbon monoxide molecule (1) and the dimethyl ether molecule (2) were calculated. The calculated parameters are shown in Table 11. The results of the correlations of the two models are shown in Figures 10–12. The two models are seen to correlate the experimental data very similarly at all three isotherms. At 15.00 °C both models correlate quite well the vapor phase and the liquid phase at lower pressures. At 33.00 °C the models correlate the liquid phase well, but they do not correlate the curvature of the vapor phase completely. At 43.00 °C the models again correlate the liquid phase quite well, but there is some deviation in the representation of the vapor phase.

Conclusions

Equipment has been built in order to accurately measure the high pressure solubility of gases in liquids.

Three isotherms have been measured for the system CO_2 (1) + dimethyl ether (2) at 15.05, 35.5, and 46.97 °C. The measured data show good agreement with data from the literature, and one can therefore conclude that the equipment is suitable for this type of measurement. Three isotherms at 15.00, 33.00, and 43.00 °C have been measured for the system CO (1) + dimethyl ether (2). This system has not been measured previously.

Two models have been used to correlate the experimental data, the MHV2/UNIFAC and MHV2/UNIQUAC models. For the first system the MHV2/UNIQUAC is seen to correlate the experimental data slightly better than MHV2/UNIFAC, but for the second system the two models are seen to correlate the experimental data equally well.

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