somewhat surprising, and it is perhaps related to the simultaneous existence of anisotropy of shape and multipolar interactions.

Registry No. CF_4, 75-73-0; CF_3H, 75-46-7.

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Isobaric Vapor–Liquid Equilibrium Data for the Binary Systems 1,2-Dimethoxyethane + Alcohols

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Vapor–liquid equilibrium data are reported at 101.32 kPa for the binary systems formed by 1,2-dimethoxyethane with the following alcohols: methanol, ethanol, 1-propanol, and 1-butanol. An azeotrope was observed for the systems ethanol + 1,2-dimethoxyethane and 1,2-dimethoxyethane + 1-propanol. Experimental data, activity coefficients, fugacity coefficients, and correlation parameters for the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations are reported.

Introduction

Experimental data of vapor–liquid equilibrium (VLE) are useful for designing some types of separation processes. When experimental data are not available, estimations are made, based mainly on group contribution models (*1*). Hank et al. (*2*) proposed a method for predicting VLE data from excess molar enthalpies H^E at different temperatures.

In this paper we report VLE data for 1,2-dimethoxyethane (2,5-dioxahexane) + 1-alkanol (methanol through butanol) systems. Excess molar enthalpy data at 298.15 K are available for all these systems (*3*), but no VLE measurements have been published. The data reported here will be used as part of a program to determine the applicability of liquid models for the calculation of activity coefficients (*4*).

Experimental Section

Apparatus and Procedure. Vapor–liquid equilibrium measurements were carried out in an all-glass equilibrium still of the Gillespie type (*5*) as modified by Röck and Sieg (*6*). It is a commercial unit manufactured by Fritz GmbH (Normag, Hofheim, Germany), and its features have been described previously (*7*). The apparatus allows good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium, and it prevents entrainment of liquid drops and partial condensation in the vapor phase.

The boiling point temperature T in the equilibrium still was measured with a mercury-in-glass thermometer (0.1 K divisions),

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Table I. Density ρ, Refractive Index n_D, and Normal Boiling Point T_b of Compounds

compound	ρ(298.15 K)/(kg m^{-3}) this work	ρ(298.15 K)/(kg m^{-3}) lit.	n_D(298.15 K) this work	n_D(298.15 K) lit.	T_b/K this work	T_b/K lit.
1,2-dimethoxyethane	861.3	863.70 (7)	1.3774	1.37811 (7)	358.22	357.65 (7), 358.31 (8)
methanol	786.7	786.37 (7)	1.3265	1.32652 (7)	337.85	337.70 (7)
ethanol	785.0	784.93 (7)	1.3594	1.35941 (7)	351.45	351.44 (7)
1-propanol	799.5	799.60 (7)	1.3835	1.38370 (7)	370.31	370.30 (7)
1-butanol	805.9	805.75 (7)	1.3973	1.39741 (7)	390.75	390.88 (7)

Table II. Refractive Index n_D for the Binary Systems Methanol (1) + 1,2-Dimethoxyethane (2) and Ethanol (1) + 1,2-Dimethoxyethane (2) as a Function of the Mole Fraction x_1, of the Alcohol

methanol + 1,2-dimethoxyethane x_1	methanol + 1,2-dimethoxyethane n_D(298.15 K)	ethanol + 1,2-dimethoxyethane x_1	ethanol + 1,2-dimethoxyethane n_D(298.15 K)
0.0000	1.3774	0.0000	1.3774
0.0767	1.3760	0.1085	1.3764
0.0905	1.3758	0.1587	1.3759
0.2468	1.3729	0.2947	1.3743
0.3706	1.3697	0.3439	1.3739
0.4874	1.3657	0.3597	1.3735
0.6233	1.3598	0.4567	1.3721
0.7156	1.3547	0.5106	1.3713
0.8037	1.3482	0.6035	1.3697
0.8384	1.3451	0.6961	1.3678
0.9134	1.3380	0.7915	1.3656
0.9489	1.3338	0.8843	1.3631
1.0000	1.3265	0.9541	1.3610
		1.0000	1.3594

Table III. Density ρ for the Binary Systems 1,2-Dimethoxyethane (1) + 1-Propanol (2) and 1,2-Dimethoxyethane (1) + 1-Butanol (2) as a Function of the Mole Fraction x_1, of 1,2-Dimethoxyethane

1,2-dimethoxyethane + 1-propanol x_1	1,2-dimethoxyethane + 1-propanol ρ(298.15 K)/(g cm^{-3})	1,2-dimethoxyethane + 1-butanol x_1	1,2-dimethoxyethane + 1-butanol ρ(298.15 K)/(g cm^{-3})
0.0000	0.7995	0.0000	0.8059
0.0533	0.8040	0.0843	0.8109
0.0566	0.8044	0.1768	0.8166
0.0881	0.8070	0.2669	0.8221
0.1678	0.8132	0.3776	0.8282
0.2335	0.8184	0.4595	0.8331
0.3319	0.8251	0.5667	0.8389
0.4164	0.8308	0.6711	0.8447
0.5299	0.8378	0.6982	0.8463
0.6287	0.8434	0.7847	0.8506
0.7543	0.8498	0.8987	0.8565
0.7584	0.8501	1.0000	0.8613
0.8962	0.8569		
1.0000	0.8613		

Table IV. Antoine Equation Parameters, Equation 1

compound	A	B	C
1,2-dimethoxyethane	6.965 15	1246.334	220.000
methanol	8.078 37	1582.271	239.726
ethanol	8.112 17	1592.864	226.184
1-propanol	7.744 22	1437.686	198.463
1-butanol	7.835 61	1558.190	196.881

Table V. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 2, for Methanol (1) + 1,2-Dimethoxyethane (2) at 101.32 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	358.30		1.0000
0.040	0.163	354.05	2.2126	1.0095
0.067	0.220	352.65	1.8740	1.0121
0.115	0.300	350.70	1.5970	1.0196
0.185	0.394	348.25	1.4257	1.0384
0.244	0.462	346.40	1.3573	1.0567
0.265	0.486	345.80	1.3443	1.0595
0.290	0.514	345.15	1.3312	1.0599
0.346	0.557	343.95	1.2650	1.0923
0.435	0.623	342.50	1.1890	1.1305
0.513	0.669	341.45	1.1271	1.1939
0.579	0.715	340.65	1.1007	1.2226
0.623	0.739	340.25	1.0737	1.2678
0.681	0.773	339.70	1.0496	1.3284
0.760	0.818	339.10	1.0188	1.4457
0.836	0.873	338.60	1.0079	1.5025
0.851	0.882	338.50	1.0043	1.5419
0.893	0.913	338.25	1.0005	1.5971
0.952	0.962	338.05	0.9976	1.5661
1.000	1.000	337.85	1.0000	

calibrated against a standard thermometer. The adjustment of the local pressure to the pressure of 101.32 kPa was measured with a dibutyl phthalate manometer (±0.003 kPa).

Vapor and liquid compositions, x and y, were determined, by using a Perkin-Elmer gas chromatograph (Model 990, flame ionization detector). For the methanol + 1,2-dimethoxyethane and ethanol + 1,2-dimethoxyethane systems, the column was a 200 × 0.3 cm, 10% UCC on 982 Chromosorb W (AWDMCS), and nitrogen was used as carrier gas with a flow rate of 9×10^{-4} m^3 s^{-1} and an oven temperature of 343.15 K. For the 1,2-dimethoxyethane + 1-propanol and 1,2-dimethoxyethane + 1-butanol systems, the column was a 300 × 0.6 cm, 15% Carbowax 1500 on Chromosorb 60/80 mesh; the nitrogen flow rate was 3.6×10^{-3} m^3 s^{-1}, and the oven temperature, 393.15 K. Besides chromatography, duplicate analysis was used for each sample by measuring either the density (with an Ostwald type pycnometer) or the refractive index (PZO-RL2 refractometer of the Abbe type). Compositions found by gas chromatography and either pycnometry or refractometry were in good agreement. The accuracies for the different measurements were, for densities, ±0.2 kg m^{-3} and, for refractive indices, ±0.0001 at (298.15 ± 0.1) K, and chromatography gave an accuracy of composition to within ±(0.002–0.004) mole fraction, depending on the composition range; the temperature accuracy was ±0.1 K.

Materials. All the materials were reagent grade purity, supplied by Fluka. The 1,2-dimethoxyethane was handled, taking care to avoid sun light, in order to prevent the formation of peroxides. It was used without further purification, as the chromatographic analysis did not show any evidence of impurities. The alcohols were further purified by distillation in a packed column and stored over 3-Å molecular sieves, to prevent any water impurity, after the aforementioned treatment. The physical properties of these compounds appear in Table I.

Experiments were started by evacuating the equilibrium still and filling it with dried nitrogen. Then, the still was filled with the system under investigation. Once the system reached steady-state conditions, about 45 min were allowed before the first sample was taken. For each data point 30 min were allowed before samples of both phases were drawn.

Results and Discussion

Refractive indexes, n_D, at 298.15 K for the methanol + 1,2-dimethoxyethane and ethanol + 1,2-dimethoxyethane systems are listed in Table II. Densities, ρ, at 298.15 K for the systems 1,2-dimethoxyethane + 1-propanol and 1,2-dimethoxyethane + 1-butanol are shown in Table III.

Table VI. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 2, for Ethanol (1) + 1,2-Dimethoxyethane (2) at 101.32 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	358.30		1.0000
0.043	0.100	357.05	1.8708	0.9911
0.078	0.147	356.25	1.5632	0.9996
0.078	0.153	356.15	1.6332	0.9956
0.125	0.218	355.35	1.4975	0.9932
0.155	0.260	354.25	1.5029	1.0076
0.210	0.298	353.75	1.2964	1.0387
0.235	0.333	353.10	1.3279	1.0405
0.285	0.378	352.60	1.2675	1.0549
0.307	0.403	352.20	1.2743	1.0581
0.333	0.442	351.95	1.3013	1.0358
0.375	0.460	351.60	1.2193	1.0819
0.405	0.493	351.40	1.2196	1.0739
0.435	0.515	351.10	1.2004	1.0923
0.465	0.532	350.95	1.1669	1.1186
0.523	0.576	350.80	1.1300	1.1422
0.542	0.584	350.75	1.1077	1.1690
0.553	0.592	350.60	1.1072	1.1805
0.595	0.617	350.60	1.0725	1.2230
0.627	0.639	350.55	1.0561	1.2537
0.647	0.661	350.55	1.0587	1.2440
0.675	0.682	350.50	1.0491	1.2695
0.692	0.697	350.50	1.0458	1.2764
0.731	0.724	350.55	1.0264	1.3291
0.757	0.745	350.60	1.0178	1.3572
0.787	0.775	350.60	1.0185	1.3661
0.826	0.811	350.65	1.0134	1.4025
0.857	0.842	350.85	1.0061	1.4174
0.887	0.867	350.90	0.9969	1.5050
0.893	0.875	350.90	0.9994	1.4938
0.925	0.904	351.15	0.9889	1.6262
0.953	0.935	351.25	0.9888	1.7514
1.000	1.000	351.45	1.0000	

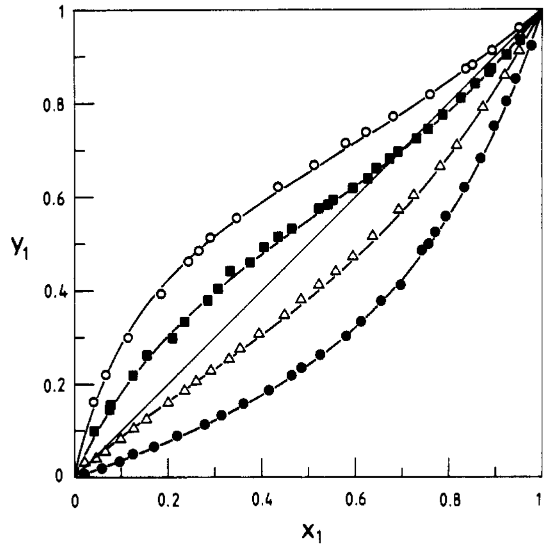

Figure 1. x–y diagram at 101.32 kPa for the following binary systems: (○) methanol (1) + 1,2-dimethoxyethane (2); (■) ethanol (1) + 1,2-dimethoxyethane (2); (△) 1,2-dimethoxyethane (1) + 1-propanol (2); (●) 1,2-dimethoxyethane (1) + 1-butanol (2). The continuous lines represent data calculated with the NRTL equation for the four systems.

The vapor pressure data of pure compounds P_i^s were obtained from the Dortmund Data Bank (DDB). The parameters A, B, and C of the Antoine equation

$$\log (P_i^s/\mathrm{mmHg}) = A - B/[(t/^\circ\mathrm{C}) + C] \qquad (1)$$

are listed in Table IV.

The experimental data (x, y, T) at a pressure P = 101.32 kPa are given in Tables V–VIII. Figure 1 shows the y–x diagrams.

Table VII. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 2, for + 1,2-Dimethoxyethane (1) + 1-Propanol (2) at 101.32 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	370.30		1.0000
0.050	0.090	369.35	1.3137	0.9932
0.081	0.143	368.75	1.3109	0.9894
0.127	0.211	367.80	1.2680	0.9945
0.184	0.292	366.70	1.2506	0.9962
0.219	0.337	366.10	1.2341	0.9977
0.275	0.398	365.20	1.1918	1.0109
0.308	0.429	364.65	1.1658	1.0265
0.364	0.486	363.85	1.1443	1.0376
0.406	0.529	363.15	1.1402	1.0467
0.443	0.561	362.70	1.1232	1.0593
0.479	0.589	362.25	1.1055	1.0795
0.517	0.620	361.85	1.0912	1.0940
0.552	0.654	361.45	1.0911	1.0913
0.607	0.694	360.75	1.0755	1.1317
0.648	0.726	360.35	1.0668	1.1499
0.671	0.748	360.10	1.0695	1.1431
0.710	0.773	359.85	1.0526	1.1801
0.741	0.796	359.50	1.0497	1.2045
0.766	0.816	359.25	1.0489	1.2148
0.801	0.842	358.95	1.0446	1.2418
0.847	0.877	358.75	1.0353	1.2677
0.875	0.897	358.45	1.0345	1.3155
0.902	0.920	358.25	1.0357	1.3140
0.935	0.947	358.05	1.0348	1.3233
0.955	0.962	357.95	1.0324	1.3762
0.981	0.971	357.95	1.0144	2.4874
1.000	1.000	358.30	1.0000	

Table VIII. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 2, for + 1,2-Dimethoxyethane (1) + 1-Butanol (2) at 101.32 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	390.75		1.0000
0.023	0.078	389.75	1.4280	0.9733
0.057	0.147	388.05	1.1339	0.9930
0.077	0.195	387.05	1.1424	0.9936
0.103	0.248	385.90	1.1189	0.9969
0.133	0.318	384.45	1.1539	0.9878
0.167	0.380	382.80	1.1468	0.9951
0.207	0.441	381.15	1.1218	1.0041
0.230	0.475	380.10	1.1184	1.0115
0.245	0.500	379.45	1.1247	1.0076
0.258	0.514	379.00	1.1113	1.0143
0.304	0.588	377.10	1.1362	0.9879
0.346	0.622	375.45	1.1050	1.0302
0.388	0.666	373.95	1.0999	1.0333
0.420	0.698	372.75	1.1013	1.0352
0.476	0.737	371.50	1.0735	1.0655
0.516	0.765	369.90	1.0651	1.0856
0.537	0.781	369.25	1.0645	1.0866
0.586	0.812	367.65	1.0622	1.1158
0.640	0.841	366.25	1.0492	1.1517
0.687	0.866	365.05	1.0426	1.1752
0.722	0.886	364.20	1.0409	1.1678
0.781	0.910	362.75	1.0319	1.2465
0.831	0.933	361.55	1.0309	1.2675
0.876	0.950	360.55	1.0263	1.3475
0.905	0.965	359.85	1.0309	1.2701
0.942	0.981	359.25	1.0254	1.1601
0.978	0.993	358.55	1.0215	1.1627
1.000	1.000	358.30	1.0000	

The vapor-phase fugacity coefficients were calculated in terms of the second molar virial coefficients estimated by the Tsonopoulos correlation (*10*). The fugacity coefficients estimated by this method lie between 1.00 (ideal) and 0.96. The Poynting correction can be also taken as unity for the experi-

Table IX. Correlation Parameters A_{12}, A_{21}, and α_{12} for Activity Coefficient Models, Mean Deviations in Temperature $\overline{\Delta T}$, and Vapor-Phase Mole Fraction $\overline{\Delta y_1}$, and Activity Coefficients at Infinite Dilution γ_i^{∞} [a]

	A_{12}	A_{21}	α_{12}	$\overline{\Delta T}$	$\overline{\Delta y_1}$	γ_1^{∞}	γ_2^{∞}
		Methanol (1) + 1,2-Dimethoxyethane (2)					
Margules	0.7276	0.4764		0.26	0.0069	2.07	1.61
Van Laar	0.7741	0.4841		0.26	0.0071	2.17	1.62
Wilson[b]	1266.4475	-718.4422		0.26	0.0073	2.15	1.62
NRTL[b]	-229.0431	782.2020	0.2982	0.26	0.0074	2.11	1.62
UNIQUAC[b]	-284.7047	833.0487		0.31	0.0078	1.99	1.54
		Ethanol (1) + 1,2-Dimethoxyethane (2)					
Margules	0.5407	0.5063		0.27	0.0056	1.72	1.66
Van Laar	0.5438	0.5050		0.27	0.0056	1.72	1.66
Wilson	672.0463	-273.8088		0.28	0.0058	1.72	1.66
NRTL[b]	93.9736	293.1003	0.3005	0.28	0.0058	1.71	1.66
UNIQUAC[b]	-188.7111	449.3529		0.27	0.0058	1.70	1.65
		1,2-Dimethoxyethane (1) + 1-Propanol (2)					
Margules	0.2540	0.4229		0.21	0.0049	1.29	1.53
Van Laar	0.2493	0.4781		0.16	0.0059	1.28	1.61
Wilson[b]	-476.0809	864.2285		0.16	0.0059	1.29	1.62
NRTL[b]	725.2431	-348.4411	0.3079	0.18	0.0053	1.29	1.57
UNIQUAC[b]	519.1184	-306.1896		0.19	0.0054	1.29	1.57
		1,2-Dimethoxyethane (1) + 1-Butanol (2)					
Margules	0.2081	0.2345		0.32	0.0063	1.23	1.26
Van Laar	0.2106	0.2330		0.32	0.0063	1.23	1.26
Wilson[b]	-13.0480	182.4822		0.33	0.0059	1.24	1.26
NRTL[b]	75.8336	92.1383	0.3021	0.34	0.0059	1.24	1.26
UNIQUAC[b]	73.8075	-19.6265		0.34	0.0059	1.24	1.26

[a] The definitions of the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations are given in ref 17. [b] A_{12} and A_{21} in cal mol^{-1}.

mental conditions in this study. Thus the liquid-phase activity coefficients γ_i were calculated by the equation

$$\gamma_i = y_i P / x_i P_i^{s} \qquad (2)$$

and are listed in Tables V-VIII.

Thermodynamic consistency was tested by using the Herington integral (*11*) and the point-to-point methods as described by Fredenslund (*1*).

The activity coefficients were correlated using the Margules (*12*), Van Laar (*13*), Wilson (*14*), NRTL (*15*), and UNIQUAC (*16*) equations. The definitions of the equations and the pure component parameters are given in ref 17. The following objective function was minimized (*15*)

$$Q = \sum_n \sum_i \left[\left(\frac{\gamma_{i,\mathrm{expt}} - \gamma_{i,\mathrm{calc}}}{\gamma_{i,\mathrm{expt}}} \right)_{i,n} \right]^2 \qquad (3)$$

where n is the number of experimental data points.

The parameters A_{12}, A_{21}, and $\underline{a}_{12}$ for the correlation equations, the mean deviations in y, $\overline{\Delta y}$ and T, $\overline{\Delta T}$ (*17*) and the activity coefficients at infinite dilution, γ_1^{∞} and γ_2^{∞}, are listed in Table IX.

According to the data reported in Tables V-VIII, the four systems studied in this work show positive deviations from the ideal behavior. An azeotrope exists in the ethanol (1) + 1,2-dimethoxyethane (2) system for a molar fraction of ethanol of $x_1 = 0.715$ at $T = 350.50$ K.

Molecular interactions in the 1-alkanol + 1,2-dimethoxyethane mixtures are fairly complex. There are some molecular interactions that contribute to the positive deviation from ideality, such as the interactions resulting from polar forces and hydrogen bonds between alkanol molecules. These contributions decrease as the number of C atoms increases in the 1-alkanol. The association of the 1,2-dimethoxyethane molecules, due to its polar nature, contributes also to the positive deviation. These two positive deviations are compensated for by the negative contribution due to the alkanol OH/ether O interactions and the polar interactions alkanol/ether. These negative contributions also decrease as the number of C atoms increases in the 1-alkanol. Therefore, the final deviation from ideality depends on the actual values of the different contributions. From the experimental results obtained in this work, we can conclude that interactions contributing to positive deviations in this work, we can conclude that interactions contributing to positive deviations are stronger than those contributing to negative ones in the series 1-methanol/1-butanol. Further work is needed to reach some conclusion about interactions with higher alkanols.

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Glossary

A,B,C	Antoine equation parameters, eq 1
n_D	refractive index
P	total Pressure, kPa
P_i^{s}	pure component saturation pressure, kPa
t	temperature, °C
T	temperature, K
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i

Greek Letters

ρ	density, kg m^{-3}
γ_i	Liquid-phase activity coefficient of component i
γ_i^{∞}	Infinite dilution activity coefficient of component i

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Vapor–Liquid Equilibrium in the System Carbon Dioxide + Cyclopentane from 275 to 493 K at Pressures to 12.2 MPa

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Isothermal vapor-liquid equilibrium data have been measured for the carbon dioxide + cyclopentane system at 15 temperatures from 276.64 to 493.11 K and at pressures to 12.2 MPa. The mixture critical line has been located and is shown to be continuous in p-T-x space between the critical points of the pure components. The results are compared with the only other set of measurements on this system in the literature, which were made at temperatures below 333 K. The data sets are also correlated by using two cubic equations of state, the Soave–Redlich–Kwong and Peng–Robinson equations. Both equations provide phase compositions in good agreement with experiment except near the critical points of mixtures. Binary interaction parameters for the system are reported for both equations of state over the entire temperature range.

Introduction

This study is a continuation of a research program to provide vapor–liquid equilibrium (VLE) data on binary systems of interest to the petroleum and natural gas industry. VLE data for CO_2 + n-pentane (*1*), CO_2 + n-butane (*2*), and CO_2 + 2,2-dimethylpropane (*3*) have been reported previously. There is a recent report of VLE data for the binary system CO_2 + cyclopentane at three temperatures by Eckert and Sandler (*4*). Their work did not include measurement of mixture critical points, and it covers only a small portion of the temperature range of vapor–liquid equilibrium for this system. This paper presents VLE data at temperatures to within 20 K of the critical temperature of cyclopentane and at pressures to the critical line of the mixture.

Experimental Section

The apparatus and the procedure used in this study are essentially the same as those used by Shah et al. (*3*) and the studies mentioned in that paper. It is a vapor recirculation system designed for the measurement of liquid- and vapor-phase compositions as a function of pressure at fixed temperature. The details of the method have been given in earlier papers (*5–7*).

Two sets of apparatus were used in this study, depending on the temperature. A high-temperature apparatus was used for temperatures greater than 320 K. One change was made in the apparatus for this study. The glass-windowed equilibrium cell was replaced by a stainless steel cell fitted with eight small windows of synthetic sapphire. This cell was used earlier by Pozo and Streett (*5*) to study the dimethyl ether + water system. More details about the cell are available there. The low-temperature apparatus used for the isotherms below 320 K was the same as that described by Shah et al. (*3*).

Temperature was measured on IPTS-68 using a platinum resistance thermometer and Mueller bridge with an accuracy of 0.02 K. Pressures were measured with an uncertainty of 0.007 MPa or 0.5% (whichever is greater) by using a digital pressure gauge (Autoclave Engineers, Inc., Model DPS-0021) calibrated in this laboratory against a Ruska DDR-6000 direct-reading quartz spiral gauge that was in turn calibrated against a Ruska dead-weight gauge.

The phase compositions were determined by withdrawing samples through capillary lines and analyzing them with a Hewlett-Packard Model 5840A gas chromatograph equipped with a thermal conductivity detector. A stainless steel column (0.312-cm o.d., 50.8-cm length) packed with 100/120 mesh Porapak Q was used for separation of CO_2 and cyclopentane. The gas chromatograph was calibrated by using mixtures of known composition that were prepared gravimetrically. The phase compositions reported here are estimated to be accurate within 0.3 mol % near the middle of the mole fraction range and better near the extremes. In the immediate vicinity of the critical line, the uncertainty may be as large as 0.5 mol %.

The CO_2 used in this work was supplied by Air Products and Chemicals Inc. and had a purity of 99.99 mol %. The cyclopentane was supplied by Phillips Petroleum Co. with a minimum purity of 99 mol %. These chemicals were used without further purification.

Results

Vapor and liquid compositions have been measured at 15 temperatures from 276.64 to 493.11 K and pressures to 12.2 MPa. The experimental results are presented in Table I, and the isotherms are plotted on a pressure–composition (p–x) diagram in Figure 1. The system exhibits large positive deviations from Raoult's law at low pressures. The pressure–temperature (p–T) extent of the region covered by this study, together with a few isopleths, is shown in Figure 2. AB and CD are the vapor pressure curves for CO_2 and cyclopentane, respectively, with critical points B and D. BED is the mixture critical line. Data for the critical line are listed in Table II. The critical pressure and composition for each isotherm were located by performing an extrapolation using the equilibrium values at the four or five highest pressures in an algorithm that uses the assumption that the variation of composition with pressure about the critical value is cubic. Phase compositions were measured at pressures within ~0.3 MPa of the critical

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