Isothermal Vapor−Liquid Equilibria for Methyl-2,2-dimethylethyl Ether + 2-Methylpropan-2-ol, Diethyl Ether + Ethyl-2,2-dimethylethyl Ether, 2-Methyl-2-butene + (2-Methylbutan-2-ol), and Diisopropyl Ether + Octane

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Isothermal vapor−liquid equilibrium data for four binary systems methyl-2,2-dimethylethyl ether + 2-methylpropan-2-ol, diethyl ether + ethyl-2,2-dimethylethyl ether, 2-methyl-2-butene + 2-methylbutan-2-ol, and diisopropyl ether + octane were collected at two temperatures using a modified Malanowski still. The virial equation truncated at the second virial coefficient was used to calculate the vapor-phase fugacity coefficients. The liquid-phase activity coefficient data were fitted to the van Laar, Wilson, and NRTL equations.

Introduction

As a part of the American Institute of Chemical Engineers Design Institute for Physical Property Data Project 805(B)/92 isothermal vapor−liquid equilibrium measurements *P, x, y* have been made on the following systems: methyl-2,2-dimethylethyl ether + 2-methylpropan-2-ol at 313.15 K and 323.15 K; diethyl ether + ethyl-2,2-dimethylethyl ether 298.15 K and 303.15 K; 2-methyl-2-butene + 2-methylbutan-2-ol at 298.15 K and 303.15 K; diisopropyl ether + octane at 308.15 K and 323.15 K.

Experimental Section

Materials. Methyl-2,2-dimethylethyl ether (methyl *tert*-butyl ether), 2-methylpropan-2-ol (*tert*-butyl alcohol), diethyl ether, ethyl-2,2-dimethylethyl ether (*tert*-butyl ethyl ether), 2-methylbutan-2-ol (*tert*-amyl alcohol), and diisopropyl ether were from Aldrich and were purified using standard procedures as described in Riddick et al. (1986).

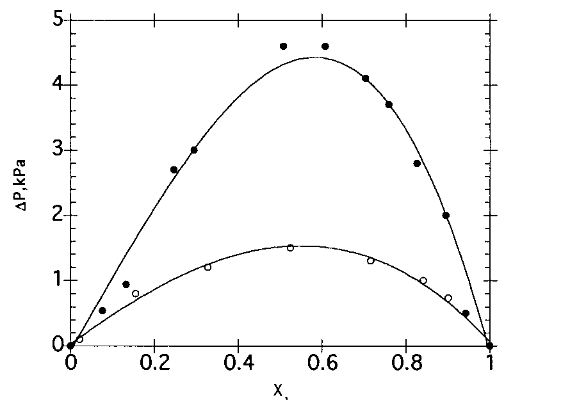

Figure 2. Deviation in pressure for the system methyl-2,2-dimethylethyl ether (1) + 2-methylpropan-2-ol (2): (○) liquid phase; (●) vapor phase.

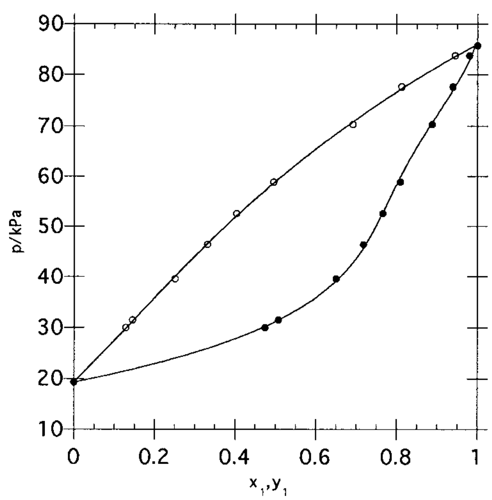

Figure 1. *P*−*x*−*y* diagram for the system methyl-2,2-dimethylethyl ether + 2-methylpropan-2-ol at 313.15 K: (○) liquid phase; (●) vapor phase.

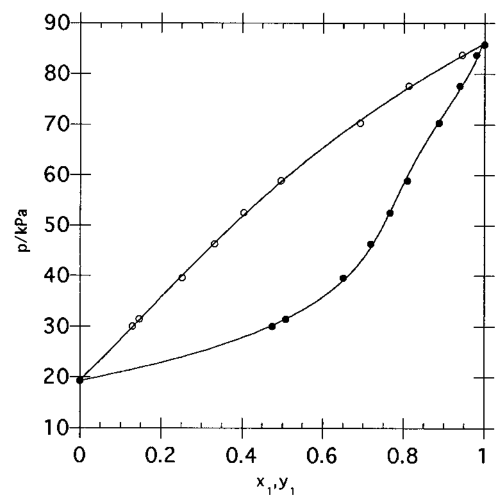

Figure 3. *P*−*x*−*y* diagram for the system diethyl ether + ethyl-2,2-dimethylethyl ether at 303.15 K: (○) liquid phase; (●) vapor phase.

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Table 1. Properties of Pure Chemicals at 298.15 K and 101.325 kPa

chemical	ρ/(g cm^{-3}) exptl	ρ/(g cm^{-3}) lit.	T_b/(K) exptl	T_b/(K) lit.	n_D exptl	n_D lit.
methyl-2,2-dimethylethyl ether	0.7353	0.73566[c]	328.20	328.211[c]	1.3689[a]	1.36892[a]
2-methylpropan-2-ol	0.77541[a]	0.77545[b,d]	355.63	355.497[d]	1.3848[d]	1.3852[d]
diethyl ether	0.7083	0.70782[d]	307.80	307.581[d]	1.3489	1.34954[d]
ethyl-2,2-dimethyl ethyl ether	0.7420[a,c]	0.7420[a,c]	345.72	345.65[c]	1.3728	1.3729[c]
2-methyl-2-butene	0.6620[a,e]	0.6620[a,d]	311.79	311.75[e]	1.3877[a]	1.3878[a,e]
2-methylpropan-2-ol	0.8090[a,d]	0.8096[a,d]	375.31	375.2[d]	1.4050[a,c]	1.4050[a,d]
diisopropyl ether	0.71852	0.71854[d]	341.67	341.66[d]	1.3653	1.3655[d]
octane	0.69833	0.69862[d]	398.99	398.823[d]	1.3950	1.39505[d]

[a] 293.15 K. [b] 303.15 K. [c] Cunningham (1992). [d] Riddick, et al. (1986). [e] Dean (1987).

Table 2. Refractive Index (n_D) Measurements at 298.15 K

methyl-2,2-dimethylethyl (1) ether + 2-methylpropan-2-ol (2) x_1	n_D	diethyl ether (1) + ethyl-2,2-dimethylethyl ether (2) x_1	n_D	2-methyl-2-butene (1) + 2-methylpropan-2-ol (2) x_1	n_D	diisopropyl ether (1) + octane (2) x_1	n_D
0.0000	1.3848	0.0000	1.3728	0.0000	1.4020	0.0000	1.3950
0.0477	1.3842	0.0422	1.3713	0.0451	1.4010	0.0252	1.3943
0.1178	1.3829	0.1132	1.3701	0.1000	1.3999	0.0637	1.3933
0.1502	1.3826	0.1583	1.3696	0.1534	1.3991	0.1214	1.3914
0.1908	1.3818	0.2244	1.3681	0.2112	1.3980	0.1958	1.3895
0.2478	1.3809	0.2858	1.3669	0.2476	1.3973	0.2819	1.3872
0.2986	1.3798	0.4261	1.3643	0.2915	1.3967	0.3659	1.3848
0.3473	1.3791	0.4419	1.3632	0.3478	1.3957	0.4364	1.3826
0.3799	1.3787	0.5075	1.3616	0.3981	1.3947	0.5123	1.3802
0.4513	1.3770	0.5671	1.3606	0.4304	1.3943	0.5816	1.3785
0.4939	1.3763	0.6579	1.3587	0.4825	1.3934	0.6458	1.3765
0.5435	1.3756	0.7194	1.3575	0.5502	1.3918	0.7130	1.3746
0.6037	1.3742	0.7470	1.3567	0.5828	1.3913	0.7794	1.3723
0.6340	1.3734	0.8579	1.3535	0.6587	1.3900	0.8454	1.3702
0.6999	1.3722	0.9160	1.3521	0.6931	1.3892	0.9005	1.3682
0.7478	1.3714	0.9500	1.3505	0.7542	1.3880	0.9538	1.3665
0.8047	1.3703	1.0000	1.3489	0.7871	1.3873	1.0000	1.3653
0.8518	1.3694			0.8410	1.3863		
0.8925	1.3684			0.8778	1.3858		
0.9395	1.3675			0.9522	1.3840		
1.0000	1.3667			1.0000	1.3834		

Table 3. Refractive Index (n_D) of Composition Polynomials at 298.15 K

system	polynomial	SD
methyl-2,2-dimethylethyl ether (1) + 2-methylpropan-2-ol (2)	$n_D = 1.3848 - (1.3895 \times 10^{-2})x_1 - (8.8650 \times 10^{-2})x_1^2 + (4.5161 \times 10^{-3})x_1^3$	1.3×10^{-4}
diethyl ether (1) + ethyl-2,2-dimethylethyl ether (2)	$n_D = 1.3726 -(2.1974 \times 10^{-2})x_1 + (6.9443 \times 10^{-3})x_1^2 - (8.5424 \times 10^{-3})x_1^3$	3.0×10^{-4}
2-methyl-2-butene (1) + 2-methylpropan-2-ol (2)	$n_D = 1.4018 - (1.7521 \times 10^{-2})x_1 - (5.7337 \times 10^{-4})x_1^2(- 5.0033 \times 10^{-4})x_1^3$	1.3×10^{-4}
diisopropyl ether (1) + octane (2)	$n_D = 1.3950 - (2.7843 \times 10^{-2})x_1 + 3.0826 \times 10^{-5})x_1^2 - 2.0864x_1^3$	1.4×10^{-4}

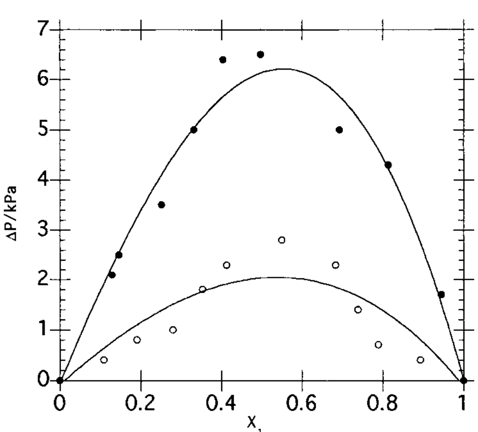

Figure 4. Deviation in pressure for the system diethyl ether (1) + ethyl-2,2-dimethylethyl ether (2): (○) 298.15 K; (●) 303.15 K.

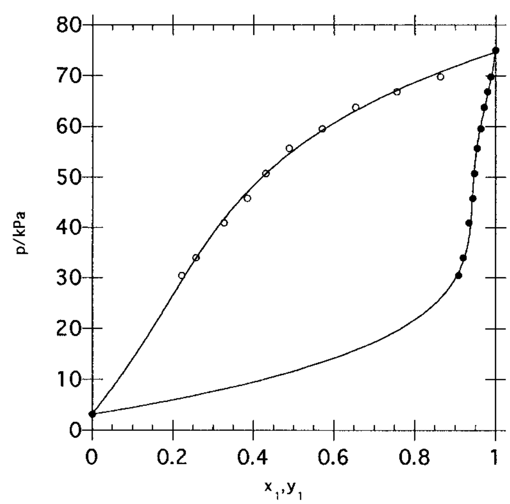

Figure 5. $P-x-y$ diagram for the system 2-methyl-2-butene + 2-methylpropan-2-ol at 303.15 K: (○) liquid phase; (●) vapor phase.

The chemicals were dried and distilled in an all-glass apparatus with a 0.8 m column. The middle $^1/_3$ fraction boiling within ±0.1 K was collected and stored under an

Table 4. Experimental *P*, *x*, *y*, Activity Coefficient γ, and Fugacity Coefficient ϕ for Systems Studied

P/kPa	x_1	y_1	γ_1	γ_2	ϕ_1	ϕ_2
			Methyl-2,2-dimethylethyl Ether (1) + 2-Methylpropan-2-ol (2)			
			T = 313.15 K			
13.90	0.0000	0.0000				
15.04	0.0223	0.1035	1.2075	0.9911	1.0355	0.9990
21.80	0.1554	0.4552	1.0959	1.0068	1.0273	0.9952
30.18	0.3275	0.6728	1.0564	1.0493	1.0199	0.9933
39.53	0.5253	0.8265	1.0524	1.0325	1.0129	0.9933
48.13	0.7168	0.9139	1.0325	1.0464	1.0072	0.9940
53.61	0.8419	0.9493	1.0137	1.2297	1.0038	0.9942
56.06	0.9014	0.9692	1.0092	1.2533	1.0023	0.9948
59.86	1.0000	1.0000				
			T = 323.15 K			
23.53	0.0000	0.0000				
28.76	0.0761	0.3419	1.5612	0.8688	1.0295	0.9979
32.70	0.1334	0.4490	1.3272	0.8797	1.0275	0.9957
41.49	0.2468	0.5969	1.2046	0.9348	1.0229	0.9906
44.70	0.2951	0.6376	1.1575	0.9656	1.0212	0.9888
59.46	0.5085	0.7861	1.0934	1.0780	1.0135	0.9802
65.68	0.6081	0.8438	1.0804	1.0863	1.0103	0.9766
71.10	0.7042	0.8787	1.0490	1.2062	1.0074	0.9435
74.08	0.7597	0.9048	1.0416	1.2120	1.0059	0.9717
77.27	0.8267	0.9262	1.0203	1.3563	1.0042	0.9699
80.72	0.8950	0.9531	1.0112	1.4829	1.0024	0.9679
82.20	0.9427	0.9714	0.9957	1.6859	1.0017	0.9670
85.21	1.0000	1.0000				
			Diethyl Ether (1) + Ethyl-2,2-dimethylethyl Ether (2)			
			T = 298.15 K			
17.28	0.0000	0.0000				
23.52	0.1083	0.4017	1.2584	0.9099	1.0273	0.9964
28.37	0.1910	0.5451	1.1640	0.9178	1.0239	0.9942
33.38	0.2797	0.6399	1.0945	0.9581	1.0207	0.9922
38.14	0.3539	0.7056	1.0869	0.9960	1.0179	0.9903
41.86	0.4134	0.7452	1.0763	1.0406	1.0158	0.9889
50.76	0.5572	0.8211	1.0617	1.1701	1.0109	0.9859
56.48	0.6833	0.8754	1.0239	1.2663	1.0078	0.9847
58.61	0.7396	0.8979	1.0057	1.3092	1.0066	0.9845
60.56	0.7895	0.9184	0.9946	1.3373	1.0055	0.9843
65.82	0.8931	0.9604	0.9966	1.3880	1.0028	0.9837
71.22	1.0000	1.0000				
			T = 303.15 K			
19.29	0.0000	0.0000				
29.97	0.1293	0.4755	1.3240	0.9306	1.0295	0.9943
31.44	0.1455	0.5080	1.3175	0.9325	1.0286	0.9937
39.53	0.2516	0.6518	1.2233	0.9444	1.0237	0.9906
46.33	0.3322	0.7186	1.1928	0.9998	1.0200	0.9879
52.50	0.4044	0.7667	1.1809	1.0508	1.0168	0.9857
8.84	0.4971	0.8094	1.1330	1.1371	1.0135	0.9836
70.29	0.6929	0.8889	1.0602	1.2930	1.0076	0.9809
77.61	0.8133	0.9388	1.0494	1.2922	1.0039	0.9798
83.73	0.9450	0.9804	1.0145	1.5149	1.0009	0.9793
85.70	1.0000	1.0000				
			2-Methyl-2-butene (1) + 2-Methylpropan-2-ol (2)			
			T = 298.15 K			
2.24	0.0000	0.0000				
28.13	0.2631	0.9226	1.6148	1.2887	1.0197	0.9770
31.65	0.3048	0.9348	1.5858	1.2907	1.0176	0.9740
37.90	0.3801	0.9491	1.5406	1.3457	1.0140	0.9687
40.57	0.4150	0.9550	1.5175	1.3464	1.0125	0.9664
43.00	0.4477	0.9589	1.4949	1.3776	1.0111	0.9643
47.72	0.5103	0.9654	1.4614	1.4455	1.0083	0.9603
51.89	0.5825	0.9708	1.3966	1.5502	1.0059	0.9568
56.37	0.6619	0.9759	1.3387	1.7097	1.0034	0.9531
57.30	0.6960	0.9790	1.2976	1.6829	1.0028	0.9524
60.50	0.8863	0.9932	1.0895	1.5344	1.0010	0.9499
62.29	1.0000	1.0000				
			T = 303.15 K			
3.15	0.0000	0.0000				
30.44	0.2232	0.9083	1.6913	1.1150	1.0247	0.9774
33.90	0.2586	0.9203	1.6441	1.1276	1.0228	0.9747
40.90	0.3277	0.9338	1.5822	1.2389	1.0188	0.9690
45.81	0.3856	0.9439	1.5182	1.2816	1.0161	0.9652
50.69	0.4312	0.9480	1.5048	1.4142	1.0134	0.9613
55.68	0.4893	0.9546	1.4628	1.5044	1.0106	0.9574
59.49	0.5720	0.9640	1.3473	1.5162	1.0085	0.9545
63.77	0.6536	0.9714	1.2706	1.5899	1.0062	0.9512
66.79	0.7559	0.9801	1.1591	1.6404	1.0045	0.9490
69.75	0.8640	0.9880	1.0658	1.8499	1.0029	0.9468
69.75	0.8640	0.9880	1.0658	1.8499	1.0029	0.9468
75.05	1.0000	1.0000				

Table 4. (Continued)

P/kPa	x_1	y_1	γ_1	γ_2	ϕ_1	ϕ_2
			Diisopropyl Ether (1) + Octane (2)			
			T = 308.15 K			
3.20	0.0000	0.0000				
5.97	0.1912	0.5196	0.5505	1.1044	0.9967	0.9921
7.03	0.2878	0.6770	0.5608	0.9934	0.9954	0.9917
8.79	0.3989	0.8158	0.6080	0.8380	0.9937	0.9912
11.36	0.4773	0.8836	0.7100	0.7860	0.9917	0.9897
15.02	0.6153	0.9472	0.7779	0.6389	0.9889	0.9878
17.92	0.6949	0.9653	0.8356	0.6304	0.9867	0.9860
23.15	0.8610	0.9913	0.8911	0.4467	0.9828	0.9829
25.72	0.9112	0.9967	0.9386	0.2941	0.9809	0.9812
30.08	1.0000	1.0000				
			T = 323.15 K			
6.56	0.0000	0.0000				
10.72	0.1658	0.4753	0.5907	1.0238	0.9953	0.9883
15.40	0.3103	0.7340	0.6972	0.8996	0.9913	0.9862
18.99	0.3954	0.8229	0.7544	0.8410	0.9888	0.9846
22.54	0.4756	0.8769	0.7912	0.7984	0.9865	0.9830
26.49	0.5708	0.9175	0.8084	0.7668	0.9840	0.9813
31.58	0.6690	0.9456	0.8446	0.7794	0.9809	0.9788
34.71	0.7302	0.9603	0.8620	0.7657	0.9790	0.9773
38.24	0.8000	0.9760	0.8788	0.6867	0.9768	0.9757
42.80	0.8843	0.9916	0.9012	0.4638	0.9741	0.9737
53.64	1.0000	1.0000				

Table 5. Properties of Pure Chemicals for the Calculation of Second Virial Coefficients

chemical	P_c (kPa)	T_c (K)	V_c (m^3/kmol)	μ (D)	ω
methyl-2,2-dimethylethyl ether	3370[a]	496.4[a]	0.329	1.2[a]	0.269[a]
2-methylpropan-2-ol	3970[a]	506.2[a]	0.275[a]	1.7[a]	0.612[a]
diethyl ether	3640[a]	466.7[a]	0.280[a]	1.3[a]	0.281[a]
ethyl-2,2-dimethylethyl ether	3149[b]	512.0[b]	0.382[b]	1.22[b]	0.296[b]
2-methyl-2-butene	3450[a]	470.0[a]	0.292[c]	0.34[d]	0.244[a]
2-methylbutan-2-ol	3950[a]	545.0[a]	0.319[d]	1.9[a]	0.579[d]
diisopropyl ether	2880[a]	500.3[a]	0.386[a]	1.13[d]	0.331[a]
octane	2490[a]	568.8[a]	0.492[d]	0.0	0.398[a]

[a] Reid et al. (1987). [b] Cunningham (1992). [c] Smith and Srivastava (1986). [d] Dean (1987).

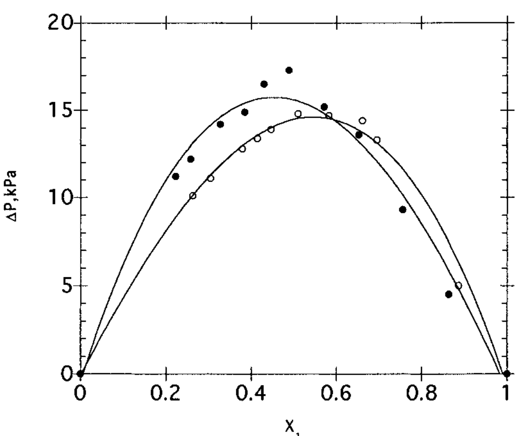

Figure 6. Deviation in pressure for the system 2-methyl-2-butene (1) + 2-methylpropan-2-ol (2): (○) 298.15 K; (●) 303.15 K.

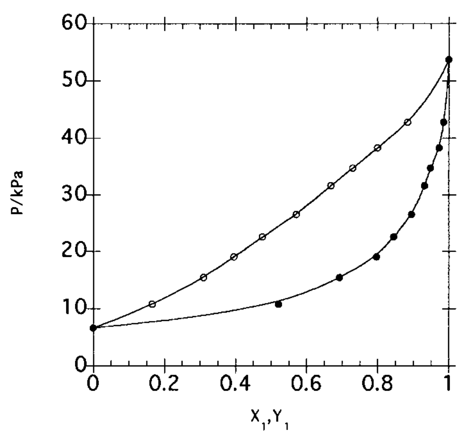

Figure 7. $P-x-y$ diagram for the system diisopropyl ether + n-octane at 323.15 K: (○) liquid phase; (●) vapor phase.

atmosphere of dry nitrogen. The measured density, boiling points, and refractive index are compared with literature values in Table 1.

Refractive index was measured with an Abbe refractometer Mark II model 104828/N with an accuracy of ±0.0001, and density measurements were made in a bicapillary pycnometer (Krishnaiah et al. 1993), with values reproducible to $\pm 5 \times 10^{-5}$ g cm^{-3}.

Apparatus. The apparatus, measuring techniques, and the accuracy of the measured variables were described by Krishnaiah et al. (1994). Modifications to the still were done in the equilibrium chamber, drop counter, and mixing chambers. Pressures were measured using an absolute manometer and a cathetometer accurate to ±0.01 mm. Temperature measurements were made using a Hewlett-Packard quartz thermometer with a resolution of 0.1 mK. Details are too lengthy to be reproduced and are given in an earlier DIPPR paper (Krishnaiah et al., 1994).

Results and Discussion

Refractive index was used to determine the composition of the liquid and the vapor samples. Synthetic mixtures were prepared by mass using a Sartorius analytical balance series R accurate to ±0.1 mg. Precautions were taken to minimize evaporation losses during the preparation and transfer of the mixtures. The refractive index values for

Table 6. Parameters for Activity Coefficient Models

	van Laar			Wilson			NRTL		
	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
Methyl-2,2-dimethylethyl Ether (1) + 2-Methylpropan-2-ol (2)									
T = 313.15 K									
	$A_{12} = 0.2016$			$\Lambda_{12} = 0.6160$		$\tau_{12} = -0.3682$			
	$A_{21} = 0.1320$			$\Lambda_{21} = 1.2839$		$\tau_{21} = 0.6083$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0110	0.0020	0.0077	0.0109	0.0020	0.0077	0.0134	0.0020	0.0082
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.4457	0.0011	0.0047	0.4400	0.0011	0.0047	0.4900	0.0010	0.0049
323.15 K									
	$A_{12} = 0.1348$			$\Lambda_{12} = 1.9750$		$\tau_{12} = 1.8314$			
	$A_{21} = 0.6877$			$\Lambda_{21} = 0.1995$		$\tau_{21} = -0.9635$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0017	0.0095	0.0518	0.0015	0.0081	0.0511	0.0011	0.0061	0.0501
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.0745	0.0045	0.0241	0.0582	0.0037	0.0235	0.0418	0.0030	0.0228
Diethyl Ether (1) + Ethyl-2,2-dimethyl ethyl Ether (2)									
298.15 K									
	$A_{12} = 0.1502$			$\Lambda_{12} = 1.5143$		$\tau_{12} = 1.0705$			
	$A_{21} = 0.3163$			$\Lambda_{21} = 0.4367$		$\tau_{21} = -0.6352$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0125	0.0097	0.0246	0.0124	0.0097	0.0246	0.0124	0.0099	0.0245
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.4370	0.0035	0.0150	0.4340	0.0035	0.0150	0.4310	0.0034	0.0149
303.15 K									
	$A_{12} = 0.2472$			$\Lambda_{12} = 1.6572$		$\tau_{12} = 1.5926$			
	$A_{21} = 0.7387$			$\Lambda_{21} = 0.2506$		$\tau_{21} = -0.7601$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0092	0.0029	0.0217	0.0091	0.0030	0.0216	0.0090	0.0003	0.0214
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.4256	0.0011	0.0128	0.4267	0.0011	0.0127	0.4378	0.0013	0.0125
2-Methyl-2-butene (1) + 2-Methylpropan-2-ol (2)									
298.15 K									
	$A_{12} = 0.5637$			$\Lambda_{12} = 1.4788$		$\tau_{12} = 3.2438$			
	$A_{21} = 2.7899$			$\Lambda_{21} = 0.0006$		$\tau_{21} = -0.7832$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0033	0.0007	0.0099	0.0084	0.0015	0.0094	0.0103	0.0020	0.0105
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.1550	0.0003	0.0094	0.4370	0.0008	0.0089	0.4740	0.0009	0.0100
303.15 K									
	$A_{12} = 0.6394$			$\Lambda_{12} = 1.2365$		$\tau_{12} = 2.1395$			
	$A_{21} = 1.6883$			$\Lambda_{21} = 0.1211$		$\tau_{21} = -0.5118$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0191	0.0000	0.0071	0.0183	0.0000	0.0070	0.0216	0.0000	0.0072
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	1.0250	0.0000	0.0067	0.9810	0.0000	0.0066	1.2040	0.0000	0.0068
Diisopropyl Ether (1) + *n*-Octane (2)									
308.15 K									
	$A_{12} = -1.0126$			$\Lambda_{12} = 3.0908$		$\tau_{12} = -1.7283$			
	$A_{21} = -1.9045$			$\Lambda_{21} = 0.8918$		$\tau_{12} = 7.6643$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0646	0.0050	0.0695	0.0640	0.0051	0.0698	0.0270	0.0171	0.0227
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.7400	0.0025	0.0458	0.7288	0.0025	0.0460	0.4538	0.0120	0.0184
323 K									
	$A_{12} = -0.4542$			$\Lambda_{12} = 3.3473$		$\tau_{12} = -1.9638$			
	$A_{21} = -1.7209$			$\Lambda_{21} = 0.2782$		$\tau_{21} = 3.8866$			
						$\alpha = 0.3000$			
AAD = $\sum\lvert(z - \text{zcal})/z\rvert/(n-2)$	0.0240	0.0020	0.0115	0.0408	0.0040	0.0158	0.0393	0.0120	0.0166
$\sum\lvert z - \text{zcal}\rvert/(n-2)$	0.6333	0.0013	0.0089	1.2011	0.0027	0.0126	1.2522	0.0084	0.0120

the mixtures at 298.15 K are given in Table 2. These results were fitted to a polynomial in the mole fraction, and these equations were used to calculate the compositions. The constants of the polynomial equation are given in Table 3 along with the correlation coefficients and standard deviations.

Isothermal vapor−liquid equilibrium P, x, y values for the four mixtures studied at the temperatures specified are given in Table 4. In all the cases the virial equation truncated at the second virial coefficient was used to calculate the vapor-phase fugacity coefficients. The liquid-phase activity coefficient data were fitted to van Laar, Wilson, and NRTL equations.

The experimental (P, x, y) data at each temperature were fitted to the van Laar, Wilson, and NRTL models (Prausnitz et al., 1987). The generalized least-squares algorithm of Britt and Luecke (1973) was used to correlate the data to these models. The values of the parameters for each model were calculated by minimizing

$$\sum_{i=1}^{k}\sum_{j=1}^{m}\frac{(Z_{m,ij} - Z_{ij})^2}{r_j^{\,2}} \qquad (1)$$

subject to the constraints for each experimental point, $P\phi y_1 - x_1\gamma_1 P_1 = 0$ and $P\phi y_2 - x_2\gamma_2 P_2 = 0$. k is the number of

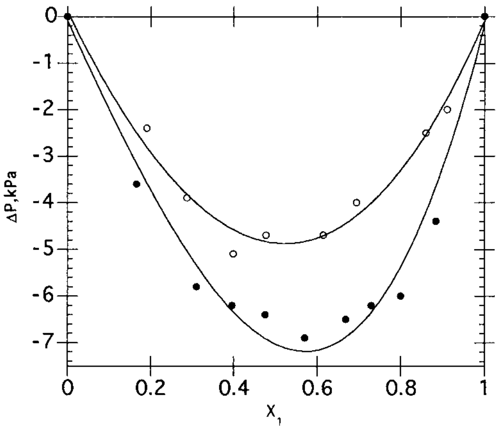

Figure 8. Deviation in pressure for the system diisopropyl ether + *n*-octane: (○) 308.15 K; (●) 323.15 K.

experimental points, *m* is the number of measurements for each experiment, Z_m is the measured value of the variable, *Z* is the estimate of the true value of the variable, and r_j is the uncertainty or error associated with the values. ϕ is the fugacity coefficient, *P* is the pressure, and γ is the mole fraction based activity coefficient.

This method allows for uncertainties in each of the three measured variables. In this analysis it is assumed that all the measured variables are subject to error. The calculated values of the pressure, liquid, and vapor compositions are given in the respective tables for each binary system. The errors associated with the three variables at all experimental conditions are the following: all measurements are ±0.001 kPa in pressure, 0.0005 in liquid composition, and ±0.001 in vapor composition. These values may be optimistic and may reflect in the calculated values of the activity coefficients.

The fugacity coefficients for all the systems were calculated using the virial equation truncated at the second virial coefficient. These values were estimated from the Tsonopoulos (1974) correlation. The fugacity coefficients and the activity coefficients γ_I are given in Table 4. Table 5 gives the property values required to estimate the second virial coefficients, and Table 6 gives the parameters of the van Laar, Wilson, and NRTL equations and the statistical data. All the equations give equally good fits. These models were fitted to predict accurately *P*, *x*, and *y* data.

The higher ΔP values indicate the nonideality of the systems from Raoult's law. The negative departures from ideality for the system diisopropyl ether + octane indicate hydrogen bonding and/or solvation effects. Both effects could be operative, since ether is in the presence of the nonpolar octane. The low vapor pressures of some of the components could have affected the lack of smoothness of $\Delta P - x_1$ data. Figures 1−8 show results in graphical form.

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