Vapor–Liquid Equilibria of Mixtures of Propane and Isomeric Hexanes

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Vapor–liquid equilibrium data extending to critical pressures are reported for mixtures of propane with each of the hexane isomers, *n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. Dew–bubble curves for five different compositions are tabulated for each of the five mixtures. The data in pressure, temperature, and density are successfully correlated by the Leung–Griffiths model as modified by Moldover, Rainwater, and co-workers. The coexistence surfaces are all quite similar with only subtle differences due to the different shapes of the isomeric hexane molecules.

Introduction

This is the second in a series of papers that presents hitherto unpublished vapor–liquid equilibrium (VLE) data from the Ohio State University laboratory, together with correlations of that data with a nonclassical model specifically designed for the extended critical region. The previous paper considered the measurements of propane + neopentane by Hissong (*1*); this paper analyzes the data by Chun (*2*) on propane with each of the five hexane isomers.

The hexane isomers vary in shape from the nearly spherical 2,2-dimethylbutane to the elongated normal isomer. While the VLE phase diagram depends largely on the pure component critical points and the hexane isomers all have nearly the same critical temperatures and pressures, there are subtle differences due to molecular shapes. A similar experiment by Genco (*3*), subsequently published with a classical equation-of-state correlation (*4*), consisted of the measurement of the azeotropic mixtures of each of the five hexane isomers with (perfluoromethyl)cyclohexane.

Results due to Chun for the critical loci (*5*) and second virial coefficients (*6*) of these five mixtures have been published previously. In those papers, the source and purity of the components were reported. The excess critical temperatures and pressures were fitted to a function of composition, and the virial coefficients were correlated by the method of Tsonopoulos (*7*).

The mixture propane + *n*-hexane was also measured in the Ohio State University laboratory by Porthouse (*8*), and smoothed data have been previously published by Kay (*9*). The measurements of Chun and of Porthouse collectively were taken along 11 different isopleths (loci of constant composition). Our analysis shows that the Chun and Porthouse data are mutually consistent in pressure–temperature–composition space, but the coexisting densities of the two different data sets cannot be correlated with the same set of parameters.

Chun's experimental apparatus was of identical design to that of Hissong as described in detail in the previous paper (*1*, *10*). Also in that paper was a description, not repeated here, of the Leung–Griffiths model as modified by Moldover, Rainwater, and co-workers (*11–14*). We first present the results for isomeric hexane mixtures, and then discuss the

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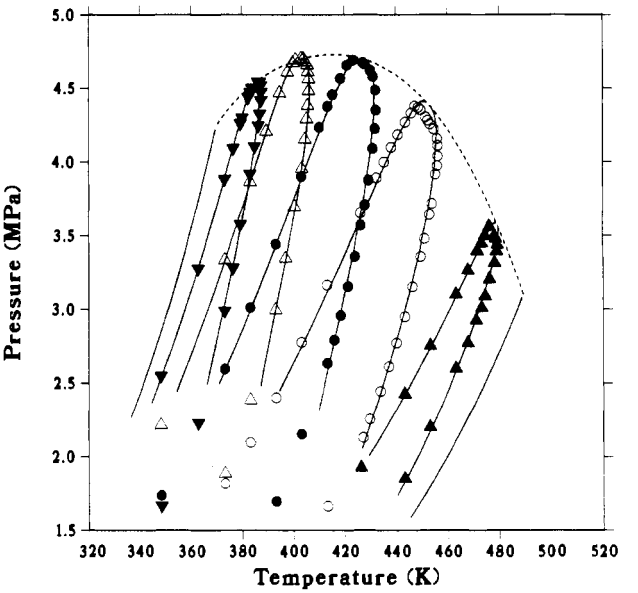

Figure 1. Pressure–temperature phase diagram for the propane + 2,2-dimethylbutane system. In this and subsequent figures, the dashed line is the critical locus and the solid lines are calculated dew–bubble curves from the modified Leung–Griffiths model as optimized to the data of Chun (*2*). Dew–bubble curves are for the following mole fractions of propane, right to left: 0.1527, 0.4490, 0.6587, 0.8205, 0.9194.

Table I. Model Parameters for Hexane Isomers

	22DMB	2MP	23DMB	3MP	nC_6H_{14}
T_c (K)	489.25	498.05	500.23	504.35	507.95
P_c (MPa)	3.102	3.035	3.147	3.124	3.032
ρ_c (kmol/m^3)	2.793	2.718	2.793	2.744	2.718
C_1	1.999	2.037	2.012	2.031	2.071
C_2	−0.896	−0.957	−0.912	−0.916	−0.971
C_3	30.0	30.0	30.0	30.0	30.0
C_4	6.172	6.333	6.192	6.361	6.519
C_5	−23.71	−23.05	−23.64	−22.80	−21.64
C_6	0.0	0.0	0.0	0.0	0.0

normal hexane mixture as measured by Chun with a comparison of the data of Porthouse on the same mixture.

Mixtures of Propane with Isomeric Hexanes

For each of the five hexane isomers, dew–bubble curves, including coexisting densities, have been measured for

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Table II. 2,2-Dimethylbutane (1) + Propane (2) Data

P (MPa)	T (K)	ρ (kmol/m³)	P (MPa)	T (K)	ρ (kmol/m³)
		x_2 = 0.1527			
		Dew Points			
0.2292	348.15	0.09923	2.7727	467.86	
0.4633	373.15	0.17488	2.9282	471.07	
0.5794	383.15	0.21396	3.0102	473.15	
0.7274	393.15	0.27455	3.0909	474.49	
0.8847	403.15	0.32686	3.2043	476.17	
1.0802	413.15	0.40882	3.3165	478.22	
1.3787	426.15	0.52800	3.3951	478.93	2.1447
1.8506	443.15	0.73310	3.4400	479.10	2.2845
2.2022	453.15		3.4818	478.59	2.5970
2.5978	463.15		3.4978	478.22	2.7892
		Bubble Points			
3.5616	476.17	3.6959	2.4243	443.15	5.5189
3.4992	474.42	3.9650	1.9250	426.15	5.9631
3.4491	473.15	4.1092	1.3709	403.15	6.4521
3.3979	471.40	4.2528	1.1721	393.15	6.6518
3.2643	467.86	4.5112	0.9896	383.15	6.8459
3.1012	463.15	4.7734	0.8334	373.15	7.0251
2.7536	453.15	5.1955	0.5230	348.15	7.5974
		x_2 = 0.4490			
		Dew Points			
0.3059	348.15	0.11389	3.3584	449.41	
0.6898	373.15	0.25638	3.4805	450.99	
0.8934	383.15	0.33243	3.6436	452.89	
1.0883	393.15	0.40620	3.7173	453.73	
1.3786	403.15	0.52386	3.9159	455.22	
1.6627	413.15	0.63874	3.9728	455.95	
2.1299	427.09	0.84220	4.0383	456.19	
2.2555	429.67	0.90533	4.1103	456.19	
2.4425	433.72	1.0067	4.1574	455.93	
2.6115	437.12	1.0966	4.2223	454.70	
2.7725	440.14	1.1925	4.2552	453.15	3.0630
2.9501	443.35		4.2814	452.36	3.2502
3.1536	446.29		4.3039	451.46	3.4470
		Bubble Points			
4.3534	449.55	3.8831	3.8902	432.38	5.6235
4.3686	448.63	4.1273	3.6547	426.15	5.9266
4.3782	447.34	4.3966	3.1650	413.15	6.4174
4.3315	445.94	4.5237	2.7762	403.15	6.8001
4.2689	443.59		2.4000	393.15	7.0443
4.1848	440.69	5.0684	2.0968	383.15	7.3228
4.0981	438.08	5.2646	1.8162	373.15	7.5606
3.9978	435.30	5.4545	1.2759	348.15	8.3201
0.5271	348.15	0.20087	3.7068	427.64	
1.0524	373.15	0.39985	3.8748	429.19	
1.3803	383.15	0.53416	4.0891	430.83	
1.6949	393.15	0.66631	4.2241	431.72	
2.1530	403.15	0.87862	4.3504	432.10	
2.6346	413.15	1.1235	4.4865	431.89	2.8159
2.7913	415.86		4.5779	430.98	3.0974
2.9592	418.41		4.6193	429.92	3.3233
3.1537	421.21		4.6646	427.64	3.7815
3.3586	423.88		4.6733	427.07	4.0033
3.5703	426.15				
			Bubble Points		
4.6897	423.24	4.7528	3.8990	403.15	6.6317
4.6562	420.81	5.1971	3.4419	393.15	7.1290
4.5662	418.31	5.4956	3.0122	383.15	7.5458
4.4561	415.30	5.8081	2.5957	373.15	7.9203
4.3758	413.34	5.9680	1.7351	348.15	8.7134
4.2339	410.07	6.2300			
		x_2 = 0.8205			
		Dew Points			
1.0116	348.15		4.3810	405.71	2.8092
1.8846	373.15	0.79654	4.4817	406.12	3.0100
2.3843	383.15	1.0501	4.5634	406.08	3.2273
2.9957	393.15	1.4058	4.6107	405.74	3.4177
3.3473	397.04	1.6622	4.6581	405.50	3.6078
3.6939	400.44	1.9636	4.6797	404.80	3.8294
3.9526	403.40	2.1927	4.6987	404.06	4.0527
4.1532	404.60	2.4455	4.7012	403.14	4.2941
4.2899	405.27	2.6556			
			Bubble Points		
4.6916	400.98	4.9652	4.2057	389.56	6.8979
4.6714	399.87	5.2714	3.8640	383.15	7.4558
4.6089	397.81	5.7740	3.3368	373.15	8.1027
4.4671	394.71	6.2808	2.2143	348.15	9.3517
		x_2 = 0.9194			
		Dew Points			
1.6628	348.15	0.74294	4.2450	386.42	2.8883
2.2292	362.74		4.3229	386.97	3.0316
2.9896	373.15		4.4169	387.42	3.2907
3.2810	376.33	1.7417	4.4710	387.35	3.5429
3.5766	379.31	2.0276	4.5153	387.19	3.8079
3.9177	383.15	2.3996	4.5419	386.09	4.0505
4.1043	384.93	2.6663	4.5418	386.86	4.0964
			Bubble Points		
4.5006	383.86	5.5279	4.0924	376.51	7.0436
4.4709	383.23	5.7380	3.8815	373.15	7.3964
4.4377	382.38	6.0690	3.2745	362.62	8.2750
4.2992	379.94	6.5470	2.5477	348.15	9.1285
4.2617	379.32	6.6553			

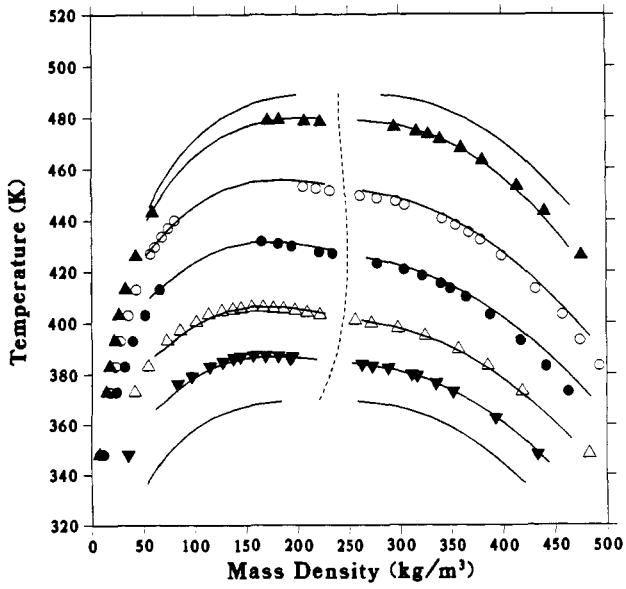

Figure 2. Temperature–density phase diagram for the propane + 2,2-dimethylbutane system. Compositions are the same as in Figure 1.

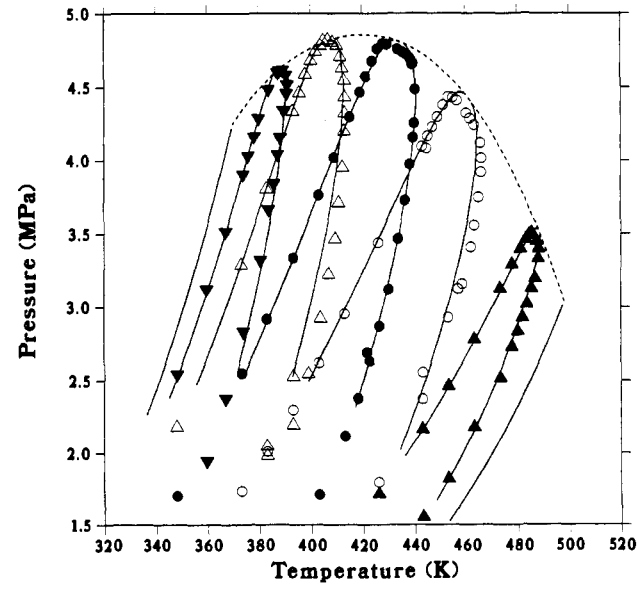

Figure 3. Pressure–temperature phase diagram for the propane + 2-methylpentane system. Dew–bubble curves are for the following mole fractions of propane, right to left: 0.1497, 0.4446, 0.6488, 0.8196, 0.9190.

Table III. 2-Methylpentane (1) + Propane (2) Data

P (MPa)	T (K)	ρ (kmol/m³)	P (MPa)	T (K)	ρ (kmol/m³)
		x_2 = 0.1497			
		Dew Points			
0.1840	348.15	0.06823	2.5164	473.15	
0.3638	373.15	0.11446	2.7298	477.75	
0.4588	383.15	0.16397	2.8354	480.01	
0.5801	393.15	0.21097	2.9288	481.81	
0.7163	403.15	0.25503	3.0206	483.62	
0.8882	413.15	0.32158	3.1253	485.27	
1.1317	426.15	0.41449	3.1937	486.76	1.7290
1.5529	443.15	0.59264	3.3294	487.89	2.0065
1.8206	453.15	0.73527	3.3990	488.06	2.2411
2.1830	463.15		3.4479	487.35	2.6181
		Bubble Points			
3.5055	485.33	3.5312	2.1680	443.15	5.6901
3.4919	484.45	3.7177	1.7153	426.15	6.1056
3.4614	483.13	3.8965	1.4342	413.15	6.3726
3.3975	481.02	4.1068	1.2262	403.15	6.5763
3.2903	477.75	4.3910	1.0531	393.15	6.7686
3.1253	473.15	4.6476	0.8923	383.15	6.9520
2.7806	463.15	5.0816	0.7339	373.15	7.1735
2.4618	453.15	5.4107	0.4846	348.15	7.8356
		x_2 = 0.4446			
		Dew Points			
0.2370	348.15	0.08557	3.1583	458.64	
0.4973	373.15	0.17563	3.4102	461.93	
0.7033	383.15	0.25351	3.5574	463.18	
0.8971	393.15	0.32786	3.7499	465.01	
1.0967	403.15	0.39764	3.9208	465.94	
1.3812	413.15	0.51349	4.0162	466.08	2.1467
1.7968	426.15	0.68233	4.1199	465.78	2.3596
2.3741	443.15		4.2414	463.23	2.7214
2.5543	443.15		4.2869	461.60	2.9612
2.9303	453.15		4.3232	460.23	3.2050
3.1248	456.99				
		Bubble Points			
4.4089	456.60	3.9584	4.0835	444.83	5.3619
4.4298	454.94	4.2714	3.4412	426.15	6.1630
4.4344	453.13	4.6100	2.9570	413.15	6.6084
4.3792	451.30	4.7790	2.6217	403.15	6.9293
4.2970	449.08	4.9310	2.3006	393.15	7.1891
4.2283	447.11	5.1095	2.0119	383.15	7.5489
4.1653	445.33	5.2155	1.7384	373.15	7.6904
4.0949	443.15	5.3486	1.1833	348.15	8.4156
		x_2 = 0.6488			
		Dew Points			
0.3510	348.15	0.12846	3.9748	438.35	
1.0290	383.15	0.37769	4.1564	439.67	
1.3452	393.15	0.50146	4.2546	440.07	
1.7102	403.15	0.64872	4.4853	440.38	
2.1238	413.15	0.82697	4.6561	439.34	
2.3790	418.17	0.94839	4.6620	439.79	
2.6335	422.70	1.07450	4.6866	438.85	
2.6917	421.85	1.11380	4.7034	438.34	
2.8709	426.50	1.20230	4.7226	437.21	3.3611
3.1202	430.06		4.7381	435.69	3.5780
3.4682	433.78		4.7589	433.76	3.8840
3.7291	436.54				
		Bubble Points			
4.7904	429.77	4.5761	4.0209	409.06	6.5293
4.7961	427.97	5.0014	3.7653	403.15	6.8257
4.7610	425.92	5.3105	3.3360	393.15	7.2682
4.6784	423.87	5.5070	2.9186	383.15	7.6419
4.5735	421.41	5.7177	2.5491	373.15	8.0128
4.4664	418.99	5.9019	1.7020	348.15	8.8161
4.2976	415.15	6.1715			
		x_2 = 0.8196			
		Dew Points			
0.7830	348.15	0.30430	3.9537	412.42	1.9841
1.4318	373.15	0.56433	4.2000	413.04	2.2482
1.9822	383.15		4.3238	413.27	2.4112
2.0475	383.15		4.4335	413.21	2.5830
2.5258	393.15		4.5472	413.15	2.7787
2.1984	393.15		4.6296	412.47	2.9894
2.5454	398.94		4.7065	411.67	3.2436
2.9242	403.88		4.7830	410.38	3.6287
3.2232	407.02		4.8039	408.81	3.9588
3.4645	409.53	1.5871	4.8212	406.98	4.8546
3.7113	411.03	1.7729	4.8143	405.12	4.9028
		Bubble Points			
4.7833	403.97	5.1151	4.3340	393.15	6.7016
4.7415	402.05	5.5179	3.8052	383.15	7.4858
4.6803	400.28	5.8395	3.2886	373.15	8.0455
4.5863	398.17	6.1527	2.1844	348.15	9.1540
4.4611	395.61	6.4581			
		x_2 = 0.9190			
		Dew Points			
1.4291	348.15	0.60807	4.1574	388.32	
1.9473	359.69	0.85355	4.3417	389.61	
2.3770	367.04	1.0974	4.4582	390.67	
2.8331	373.97		4.5183	390.93	
3.3204	380.57		4.5821	390.70	
3.6660	384.03		4.6156	389.35	3.9762
3.8434	385.96		4.6135	388.24	4.4006
4.0414	387.38		4.6012	387.39	4.7082
		Bubble Points			
4.4843	383.72	5.8281	3.9055	373.97	7.4363
4.2858	379.92	6.8284	3.5152	367.04	7.9996
4.1626	378.28	6.9928	3.1219	359.69	8.4819
4.0309	375.90	7.2696	2.5416	348.15	9.1049

mixtures with propane at five separate compositions. Critical constants and pure-fluid model parameters (as defined in eqs 3 and 4 of the previous paper) for the hexane isomers are listed in Table I; the equivalent parameters for propane were tabulated previously (*1*). These parameters were obtained from linear fits of the data and correlations of Kay (*15*). The abbreviations in the heading of Table I are 22DMB, 2,2-dimethylbutane; 2MP, 2-methylpentane; 23DMB, 2,3-dimethylbutane; and 3MP, 3-methylpentane.

VLE data for the mixtures are presented in order of increasing critical temperature of the hexane isomer in Tables II–VI and Figures 1–10. Table II lists the VLE data for propane + 2,2-dimethylbutane; the data and Leung–Griffiths correlation are plotted in Figures 1 (pressure–temperature) and 2 (temperature–density). Some of the dew points are without density measurements, as indicated by blank entries in the table. The dew and bubble points have been ordered in the table so that they follow the curves continuously and are monotonic in density, although not in pressure or temperature because of retrograde phenomena.

As seen from Figure 1, the greatest discrepancy between experiment and model prediction is near the critical point for the x = 0.4490 dew–bubble curve. The data appear to form a flat, sloping line near the critical point rather than the expected characteristic rounded shape. It should be emphasized that these experiments are the most difficult very close to critical conditions. Otherwise, the model agrees with the data to within 0.06 MPa in pressure (except in the singular maxcondentherm regions), 0.7 K in temperature, and 13 kg/m³ or 3.5% in density. From Figure 1 of Chun *et al.* (*5*), it is seen that the critical point at x = 0.4490 is slightly discontinuous from the other critical points, which also suggests that the data in the near-critical region for this mixture, and therefore the experimental identification of the critical pressure and temperature, may be slightly in error.

Chun (*2*) has estimated the experimental errors to be 0.004 MPa (0.6 psi) in pressure, 0.1 K in temperature, and 0.25% in measured volumes. Compared with the propane + neopentane correlation, the model discrepancies for this and subsequent mixtures are larger relative to the stated exper-

Table IV. 2,3-Dimethylbutane (1) + Propane (2) Data

P (MPa)	T (K)	ρ (kmol/m³)	P (MPa)	T (K)	ρ (kmol/m³)
		x_2 = 0.1516			
		Dew Points			
0.2004	348.15	0.07729	2.1954	463.15	
0.3873	373.15	0.14598	2.6118	473.15	
0.4811	383.15	0.17430	2.9561	483.15	1.3851
0.6070	393.15	0.22044	3.2389	487.37	1.6900
0.7489	403.15	0.27307	3.4037	488.72	1.9869
0.9090	413.15	0.32986	3.4787	489.14	2.1893
1.1716	426.15	0.43341	3.5375	489.23	2.4130
1.5696	443.15		3.5794	489.18	2.6464
1.8745	453.15				
		Bubble Points			
3.6318	487.84	3.3373	2.5194	453.15	5.5908
3.6409	487.34	3.5089	2.2143	443.15	5.8827
3.6338	486.83	3.6545	1.7702	426.15	6.2809
3.6158	485.98	3.8036	1.4707	413.15	6.5524
3.5881	484.73	3.9968	1.2655	403.15	6.7410
3.4963	481.95	4.2869	1.0808	393.15	6.9409
3.3308	477.26	4.6179	0.9202	383.15	7.1057
3.1845	473.15	4.8517	0.7807	373.15	7.3235
2.8331	463.15	5.2767	0.4969	348.15	7.8849
		x_2 = 0.4522			
		Dew Points			
0.2978	348.15	0.11030	3.0367	453.15	
0.5924	373.15	0.22008	3.4779	459.36	
0.7456	383.15	0.27073	3.6986	461.01	
0.9508	393.15	0.35430	4.0279	463.51	2.1525
1.1562	403.15	0.42339	4.1637	463.64	2.3745
1.4165	413.15	0.52372	4.3033	462.95	2.7057
1.8709	426.15	0.72301	4.3755	461.91	2.9634
2.5362	443.15				
		Bubble Points			
4.4870	457.83	3.8053	3.5253	426.15	6.2815
4.5103	456.31	4.1265	3.0344	413.15	6.7372
4.5097	454.82	4.3917	2.6792	403.15	7.0024
4.4828	453.15	4.6014	2.3484	393.15	7.3196
4.3995	449.66	4.9679	2.0495	383.15	7.5805
4.3143	446.92	5.2059	1.7691	373.15	7.8255
4.1841	443.15	5.4516	1.1902	348.15	8.4923
		x_2 = 0.6508			
		Dew Points			
0.3516	348.15	0.12891	3.7748	434.90	
0.8245	373.15	0.30179	4.1297	437.59	
1.1500	383.15	0.42976	4.3771	438.80	
1.4209	393.15	0.53445	4.5871	439.13	
1.7971	403.15	0.69310	4.6806	438.48	
2.2478	413.15	0.89839	4.7311	437.89	3.1743
2.8211	423.15		4.7622	437.21	3.3279
3.3277	430.23		4.8079	434.95	3.6508
			Bubble Points		
4.8488	430.30	4.5888	3.8403	403.15	6.9140
4.8570	428.40	4.9724	3.3682	393.15	7.3434
4.8075	426.15	5.3235	2.9985	383.15	7.7325
4.6955	423.15	5.6154	2.5642	373.15	8.0802
4.5464	419.15	5.9696	1.7192	348.15	8.8744
4.2777	413.15	6.3716			
		x_2 = 0.8257			
		Dew Points			
0.8325	348.15	0.32993	4.1216	407.77	2.2751
1.3625	364.33		4.3309	408.91	2.5471
1.7251	373.15		4.4967	410.13	2.7650
2.1458	383.15		4.6646	409.86	3.1366
2.7746	393.15		4.7985	408.39	3.7088
3.5543	403.15	1.7523	4.8267	406.20	4.2682
3.8843	406.11	2.0394			
		Bubble Points			
4.8104	403.15	5.0129	3.8738	383.15	7.5150
4.7679	401.01	5.5398	3.3547	373.15	8.1816
4.6110	397.26	6.1957	2.9287	364.33	8.6396
4.4163	393.15	6.7038	2.2262	348.15	9.3170
		x_2 = 0.9153			
		Dew Points			
1.4624	348.15	0.62976	4.2079	390.70	2.5578
1.8825	356.65	0.84657	4.3864	391.74	2.8426
2.3536	365.51		4.5980	392.77	3.2839
2.8111	373.15		4.6642	391.04	3.8776
3.3642	381.99		4.6369	389.17	4.2924
3.8172	387.04				
			Bubble Points		
4.5735	385.55	5.7750	3.4326	365.51	8.1803
4.4542	383.15	6.3518	2.9386	356.65	8.7346
4.2705	379.79	6.8972	2.5364	348.15	9.1834
3.8693	373.15	7.6054			

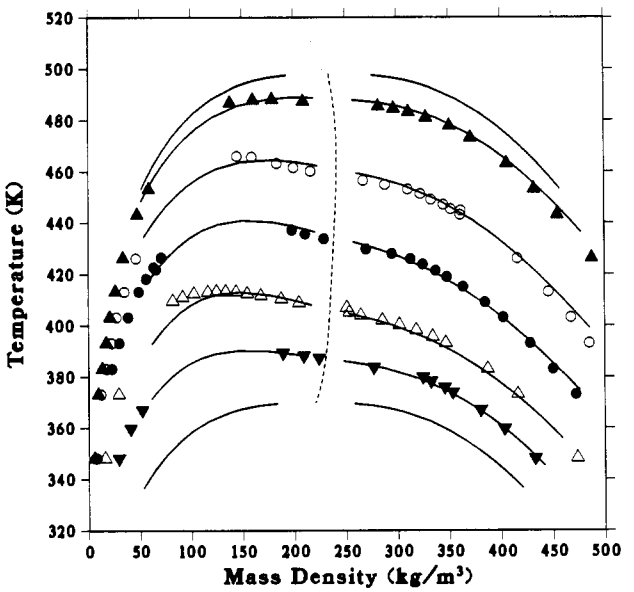

Figure 4. Temperature–density phase diagram for the propane + 2-methylpentane system. Compositions are the same as in Figure 3.

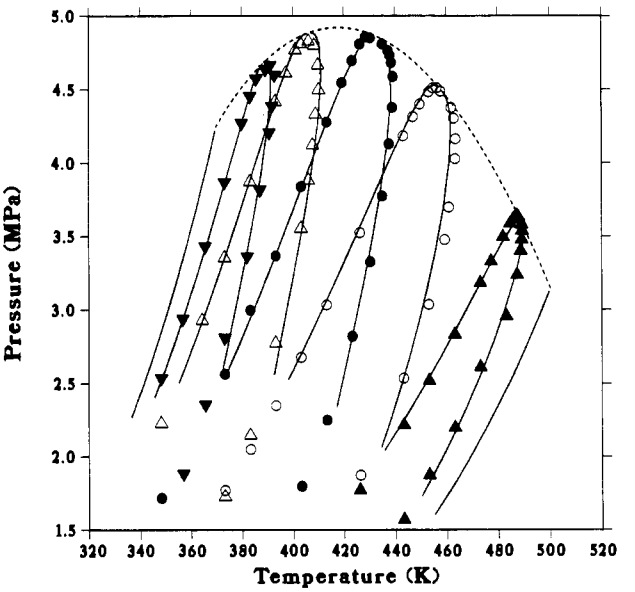

Figure 5. Pressure–temperature phase diagram for the propane + 2,3-dimethylbutane system. Dew–bubble curves are for the following mole fractions of propane, right to left: 0.1516, 0.4522, 0.6508, 0.8257, 0.9153.

imental errors, but such a result is to be expected for mixtures with a greater dissimilarity of component critical temperatures and molecular sizes.

Parameters for the critical locus (eqs 11–14 of the previous paper) and the model mixture parameters are listed in Table VII. For these mixtures, the parameter α_{2m}, which characterizes the dissimilarity of the components, ranges from 0.179 to 0.218. Therefore, according to guidelines developed for the use of the model (*14*), five adjustable mixture parameters

Table V. 3-Methylpentane (1) + Propane (2) Data

P (MPa)	T (K)	ρ (kmol/m^3)	P (MPa)	T (K)	ρ (kmol/m^3)
		$x_2 = 0.1451$			
		Dew Points			
0.1472	348.15	0.05293	1.9788	463.15	
0.3210	373.15	0.11330	2.3235	473.15	
0.4139	383.15	0.14510	2.7170	483.15	
0.5377	393.15	0.20061	3.1336	491.26	1.5489
0.6751	403.15	0.25675	3.3053	493.80	1.7074
0.8323	413.15	0.32333	3.3987	494.83	1.9021
1.0508	426.15	0.37501	3.4504	494.95	2.0329
1.4418	443.15		3.5541	494.37	2.4817
1.7187	453.15				
		Bubble Points			
3.6406	491.71	3.5810	2.0940	443.15	5.9397
3.6128	490.41	3.8193	1.6681	426.15	6.3189
3.5738	488.90	4.0122	1.3938	413.15	6.5719
3.5012	486.98	4.2322	1.2043	403.15	6.7527
3.3657	483.15	4.4964	1.0346	393.15	6.9621
3.0262	473.15	5.0026	0.8827	383.15	7.1556
2.6954	463.15	5.3616	0.7515	373.15	7.3643
2.3810	453.15	5.6690	0.4924	348.15	8.2260
		$x_2 = 0.4453$			
		Dew Points			
0.2421	348.15	0.08737	3.5574	465.08	
0.6487	383.15	0.23020	3.8535	468.19	
0.8431	393.15	0.30877	4.0381	469.32	
1.2928	413.15	0.46970	4.2116	469.73	2.3508
1.6734	426.15		4.3342	468.86	2.6341
2.2995	443.15		4.4384	466.07	3.1172
2.7906	453.15		4.4848	464.46	3.4170
3.1441	459.24				
		Bubble Points			
4.5317	460.99	4.0121	3.4309	426.15	6.3918
4.5649	459.55	4.3477	2.9790	413.15	6.8076
4.5318	456.56	4.7352	2.3476	393.15	7.3742
4.4342	453.15	5.0243	2.0342	383.15	7.6310
4.2993	448.74	5.3539	1.7560	373.15	7.8803
4.0999	443.15	5.6455	1.1913	348.15	8.5425
		$x_2 = 0.6554$			
		Dew Points			
0.8524	373.15	0.33018	4.1150	441.46	
1.0239	383.15	0.37386	4.3678	442.62	
1.5983	403.15	0.59096	4.5250	442.99	
2.0429	413.15	0.78343	4.6488	442.74	
2.4660	421.46	0.97484	4.7224	442.29	
2.8055	427.01	1.1530	4.7997	441.43	
3.1469	431.86	1.3420	4.8379	440.40	
3.4562	435.70		4.8700	439.28	3.4853
3.8037	439.05				
		Bubble Points			
4.9204	433.76	4.3249	4.2792	413.15	6.4919
4.9369	431.07	4.7999	3.8262	403.15	7.0102
4.9291	428.18	5.3590	3.4912	393.15	7.6667
4.8557	426.15	5.5904	3.0656	383.15	8.0818
4.6834	422.17	5.9179	2.6551	373.15	8.4933
4.5020	418.14	6.1849	1.7891	348.15	9.0278
		$x_2 = 0.8336$			
		Dew Points			
0.7882	348.15	0.30642	4.4955	411.52	2.6603
1.1282	362.84	0.43729	4.6458	411.38	2.9502
1.5393	373.15	0.62947	4.7648	410.98	3.2572
2.0204	383.15	0.82934	4.8443	409.79	3.6231
2.5651	393.15		4.8938	408.15	4.0384
3.3994	403.15		4.8829	407.07	4.2431
3.7676	407.14		4.8723	405.45	4.5840
4.0186	408.80		4.8791	406.49	4.5889
4.3078	410.82	2.4076			
		Bubble Points			
4.8372	402.76	5.2513	3.8916	383.15	7.4810
4.7701	400.47	5.7252	3.3667	373.15	8.0747
4.6785	398.16	6.1063	2.8654	362.84	8.5772
4.5586	395.81	6.3872	2.2276	348.15	9.1902
4.4290	393.15	6.6858			
		$x_2 = 0.8850$			
		Dew Points			
1.2027	348.15	0.49466	4.2773	395.17	
1.7559	361.50	0.74562	4.4342	395.71	
2.3892	373.15	1.0693	4.5807	396.27	
2.7892	379.16		4.6578	395.77	3.4021
3.0802	383.15		4.7096	395.40	3.6167
3.5007	387.93		4.7312	394.24	3.9928
3.7412	390.48		4.7182	392.99	4.3034
4.0203	393.25		4.7070	392.10	4.5293
		Bubble Points			
4.6573	389.43	5.4567	3.7589	373.15	7.7160
4.5523	386.74	6.2134	3.1075	361.37	8.4886
4.3422	383.15	6.7371	2.4725	348.15	9.1485
4.1204	379.20	7.1997			

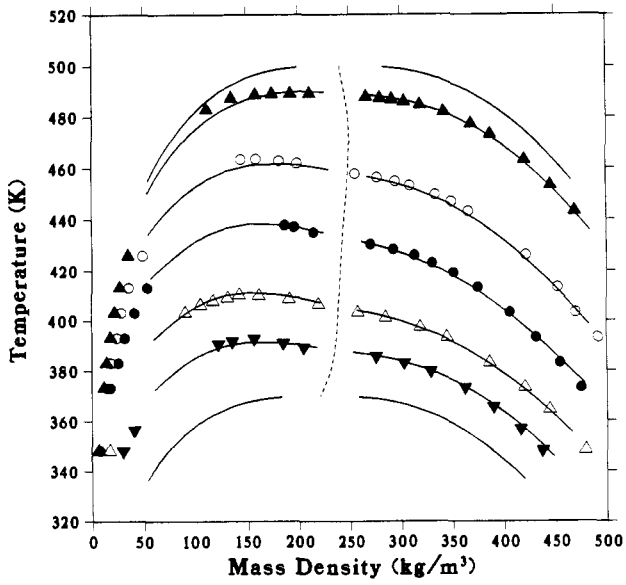

Figure 6. Temperature–density phase diagram for the propane + 2,3-dimethylbutane system. Compositions are the same as in Figure 5.

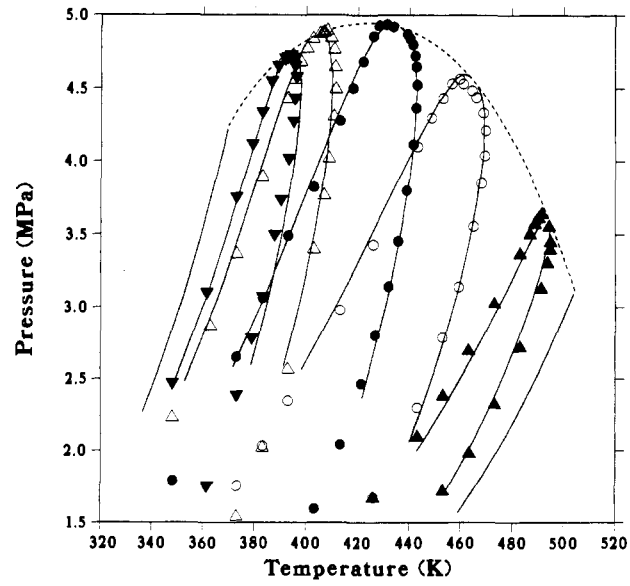

Figure 7. Pressure–temperature phase diagram for the propane + 3-methylpentane system. Dew–bubble curves are for the following mole fractions of propane, right to left: 0.1451, 0.4453, 0.6554, 0.8336, 0.8850.

Table VI. *n*-Hexane (1) + Propane (2) Data

P (MPa)	T (K)	ρ (kmol/m³)	P (MPa)	T (K)	ρ (kmol/m³)	P (MPa)	T (K)	ρ (kmol/m³)	P (MPa)	T (K)	ρ (kmol/m³)
		$x_2 = 0.1435$						$x_2 = 0.6996$			
		Dew Points						Dew Points			
0.1468	348.15	0.05336	2.2025	473.15	0.95287	0.7818	373.15	0.28209	3.0233	426.15	
0.2862	373.15	0.10112	2.6035	483.15		1.0326	383.15	0.37568	3.1142	427.15	
0.3693	383.15	0.12931	3.1449	494.23	1.6699	1.3117	393.15	0.47806	4.2156	439.15	
0.4669	393.15	0.16407	3.1097	494.83		1.6763	403.15	0.62167	4.4071	440.49	2.2598
0.5740	403.15	0.19909	3.2425	495.93	1.7791	2.0682	410.77	0.79368	4.5731	440.81	2.4597
0.7258	413.15	0.25460	3.2945	496.40	1.8847	2.1032	413.15	0.80541	4.7162	440.81	2.6601
0.9418	426.15	0.33495	3.3196	496.70	1.9496	2.2005	413.38	0.85473	4.8090	440.16	2.8414
1.2953	443.15	0.46917	3.3586	497.04	2.0022	2.4880	418.68		4.9033	439.36	3.0697
1.5604	453.15	0.58583	3.4177	497.28	2.2284	2.7966	423.51		4.9574	435.51	3.5033
1.8556	463.15	0.73025	3.4817	497.28	2.5289				Bubble Points		
		Bubble Points				4.9802	428.43	4.6374	4.4561	411.96	6.3780
3.5511	495.35	3.3821	2.2328	453.15	5.5623	4.9731	426.15	5.0122	4.2925	408.54	6.6150
3.5294	494.02	3.6513	1.9625	443.15	5.7990	4.9283	423.78	5.3316	4.1693	405.74	6.7706
3.5447	494.62	3.5514	1.5582	426.15	6.1458	4.9231	423.52	5.3454	4.0509	403.15	6.9109
3.5301	494.23	3.6060	1.2945	413.15	6.3844	4.8625	421.43	5.6065	3.5851	393.15	7.3916
3.5034	493.15	3.7650	1.1211	403.15	6.5744	4.7239	418.06	5.9127	3.1363	383.15	7.8038
3.4080	489.95	4.0942	0.9545	393.15	6.7207	4.5861	414.89	6.1686	2.7225	373.15	8.1707
3.3505	488.15	4.2180	0.8194	383.15	6.9287	4.5055	413.15	6.2947	1.8454	348.15	9.0270
3.1808	483.15	4.5222	0.6908	373.15	7.0683				$x_2 = 0.8201$		
2.8473	473.15	4.9596	0.4497	348.15	7.6395				Dew Points		
2.5309	463.15	5.2767				0.6556	348.15	0.24906	4.3735	415.98	2.4476
		$x_2 = 0.4437$				1.3172	373.15	0.50823	4.4877	416.49	2.5921
		Dew Points				1.7085	383.15		4.5988	416.37	2.7831
0.2160	348.15	0.08091	3.2683	466.03		2.2322	393.15		4.6795	416.29	2.9372
0.4312	373.15	0.15387	3.4420	468.21		2.9003	403.15	1.2636	4.7750	416.04	3.1412
0.5109	383.15	0.17906	3.5578	469.42		3.4295	409.44	1.5923	4.8618	415.54	3.3848
0.5667	383.15	0.20380	3.6648	470.57		3.8635	413.15	1.9204	4.9170	414.71	3.6235
0.7266	393.15	0.25743	3.8712	472.72		4.0875	414.91	2.1116	4.9410	413.35	3.8930
0.9022	403.15	0.31917	3.9065	472.28		4.2170	415.55	2.2488	4.9505	411.32	4.2841
1.1320	413.15	0.40333	3.9911	473.19					Bubble Points		
1.4883	426.15	0.54276	4.0944	473.38		4.9328	409.12	4.7421	4.3238	393.15	6.9797
2.1238	443.15	0.81898	4.1598	473.19		4.9270	408.00	4.9818	3.7971	383.15	7.6849
2.5235	453.15	1.0011	4.3019	472.02	2.6346	4.9062	407.07	5.2525	3.2964	373.15	8.2395
3.0449	462.51	1.3097	4.3330	472.96		4.8889	405.62	5.4850	2.2018	348.15	9.2678
3.0977	463.98	1.3308	4.3445	471.48	2.7584	4.8016	403.15	5.8835			
		Bubble Points						$x_2 = 0.9218$			
4.4546	467.31	3.4320	4.2999	453.15	5.1385			Dew Points			
4.5097	465.21	3.8851	4.2639	452.01	5.2075	1.3526	348.15	0.57383	4.2246	391.59	
4.5159	465.15	3.7346	4.2319	450.91	5.2783	1.8361	359.43	0.79514	4.3902	392.17	
4.5175	462.05	4.3656	4.1489	448.53	5.4110	2.5247	373.15	1.1480	4.4888	392.75	3.0142
4.5237	461.15	4.5026	4.0396	445.54	5.5471	2.7990	377.13	1.3097	4.5936	392.75	3.2994
4.4770	459.38	4.6468	3.9527	443.15	5.6733	3.3132	383.15		4.6234	392.59	3.4513
4.4719	459.15	4.6875	3.3283	426.15	6.3240	3.5843	385.64		4.6550	391.54	3.7400
4.4337	457.39	4.8442	2.8772	413.15	6.7163	3.7906	387.55		4.6799	391.06	3.9637
4.4140	456.86	4.8682	2.5623	403.15	7.0083	4.0254	389.91				
4.3942	456.32	4.9162	2.2528	393.15	7.2357				Bubble Points		
4.3437	454.62	5.0390	1.9822	383.15	7.4998	4.6470	386.86	5.5442	4.4643	383.15	6.3795
4.3420	454.27	5.0599	1.7324	373.15	7.7258	4.6219	386.16	5.5694	3.8848	373.15	7.5729
						4.2375	379.29	6.9417	3.1089	359.43	8.5461
						4.5203	384.22	6.2079	2.5586	348.15	9.1562

Table VII. Parameters of Critical Loci: Mixtures of Propane and Hexane Isomers

	22DMB	2MP	23DMB	3MP	nC_6H_{14}
T_1 (kmol/(m³·MPa))	−0.066 045	−0.074 565	−0.067 793	−0.076 412	−0.083 138
T_2 (kmol/(m³·MPa))	0.020 232	0.026 219	0.029 385	0.019 170	0.031 810
T_3 (kmol/(m³·MPa))	−0.004 986	−0.008 727	−0.021 663	0.000 674	−0.003 303
$\bar{P}_1$ (kmol/m³)	1.103 936	1.271 038	1.272 895	1.322 386	1.408 130
$\bar{P}_2$ (kmol/m³)	0.319 847	0.353 546	0.129 832	0.341 263	0.418 8666
$\bar{P}_3$ (kmol/m³)	0.239 452	0.215 872	0.065 620	0.301 941	0.173 925
$\bar{\rho}_1$ (kmol/m³)	1.938 297	1.454 961	1.496 036	1.702 674	1.844 390
$\bar{\rho}_2$ (kmol/m³)	−0.532 374	0.258 578	−0.272 758	0.791 467	−0.442 113
$\bar{\rho}_3$ (kmol/m³)	0.018 741	0.904 158	1.455 613	1.195 464	0.637 039
α_{2m}	0.179	0.199	0.187	0.211	0.218

Table VIII. Adjustable Mixture Parameters: Mixtures of Propane and Hexane Isomers

	22DMB	2MP	23DMB	3MP	nC_6H_{14}
C_H	−7.0	−6.0	−8.0	−9.0	−8.0
C_X	0.9	0.75	0.8	0.7	0.75
C_Z	0.0	0.2	−0.5	−0.7	−0.2
C_R	3.2	1.5	2.5	1.5	2.9
C_Y	−0.4	−0.6	−0.5	−0.6	0.0

are allowed in contrast to three for the mixture propane + neopentane. Adjustable mixture parameters for our modified Leung–Griffiths correlations are listed in Table VIII.

Data for the other isomeric hexane mixtures are presented similarly: propane + 2-methylpentane in Table III and Figures 3 and 4, propane + 2,3-dimethyl butane in Table IV and Figures 5 and 6, and propane + 3-methylpentane in Table V and Figures 7 and 8. Agreement between experiment and the modified Leung–Griffiths model is comparable to that for propane + 2,2-dimethylbutane with some exceptions, as now noted.

For the 2-methylpentane mixture, the pattern of an overly flattened experimental near-critical region occurs for x = 0.4446 and to a lesser degree for x = 0.6488, as seen in Figure

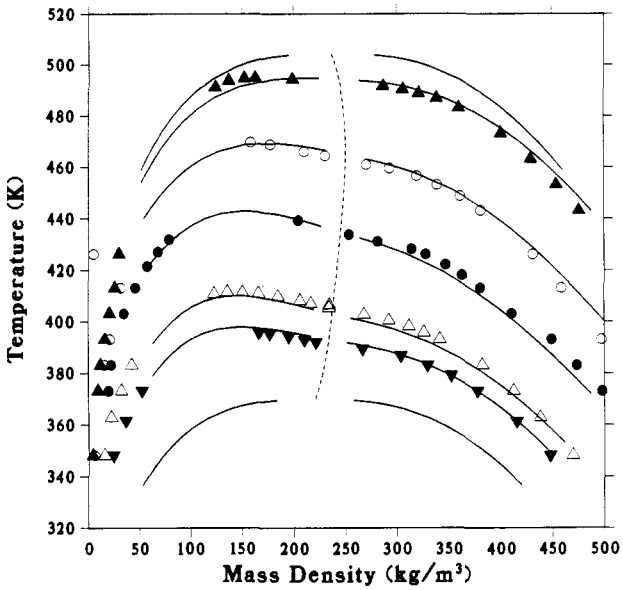

Figure 8. Temperature–density phase diagram for the propane + 3-methylpentane system. Compositions are the same as in Figure 7.

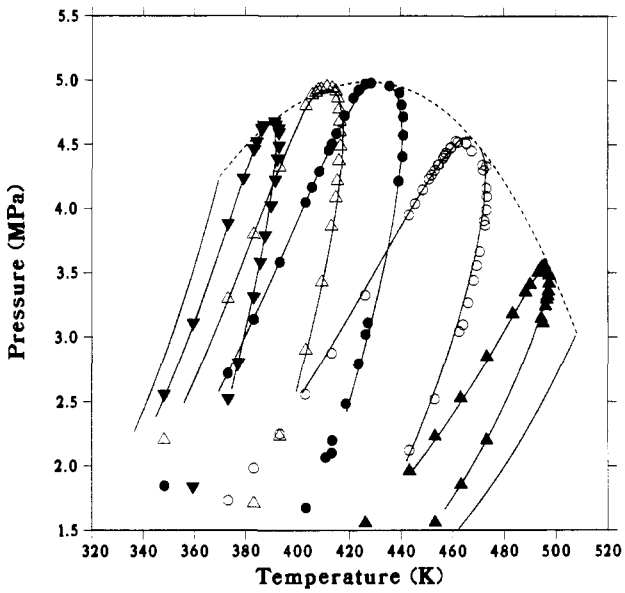

Figure 9. Pressure–temperature phase diagram for the proane + *n*-hexane system. Dew–bubble curves are for the following mole fractions of propane, right to left: 0.1435, 0.4427, 0.6996, 0.8201, 0.9218.

3. Also, on the dew curve for $x = 0.8196$, between 2.5 and 4.0 MPa the experimental points are systematically shifted to higher temperature than the predicted curve, although the two curves appear to rejoin at 2.5 MPa. Figure 4 shows how these dew points appear discontinuous relative to adjacent curves at densities just below the critical density.

The 2,3-dimethylbutane mixture shows the best overall agreement with the theoretical model, as shown in Figures 5 and 6. In ref 5, Figure 1, the 3-methylpentane mixture showed the greatest irregularity in experimentally determined excess critical temperatures, and this is reflected is Figures 7 and 8. In addition to a flattened pattern for the $x = 0.4453$ curve, the data are systematically higher in temperature than the model on the $x = 0.8336$ locus and systematically lower on the $x = 0.8850$ locus. The fit could be made closer to the data with a fourth parameter in the critical temperature equation (eq 11 of the previous paper), but our experience in fitting other mixtures suggests that a fourth parameter is warranted only when $\alpha_{2m} > 0.25$.

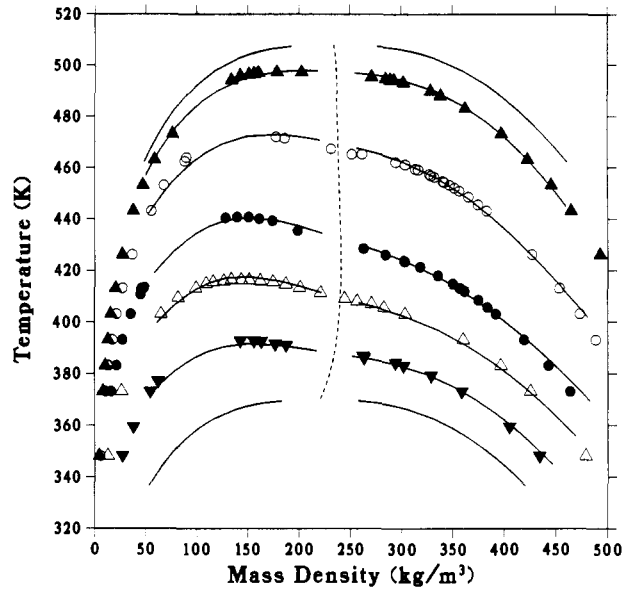

Figure 10. Temperature–density phase diagram for the propane + *n*-hexane system. Compositions are the same as in Figure 9.

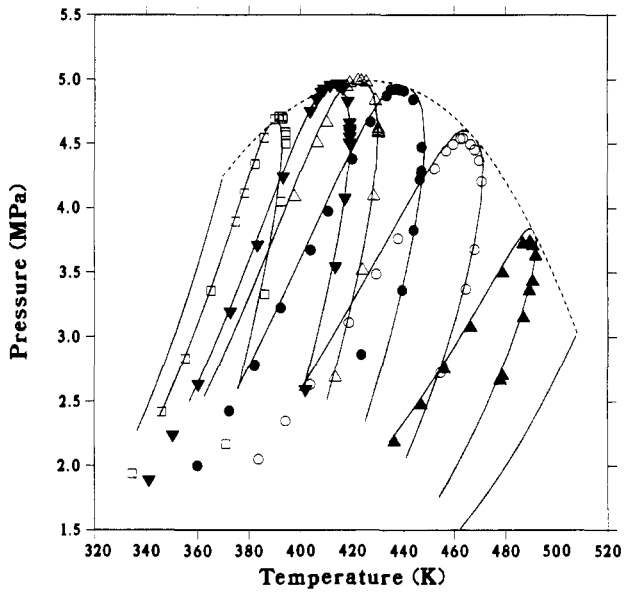

Figure 11. Pressure–temperature phase diagram for the propane + *n*-hexane system with the data of Porthouse (*8*) and with calculated curves from the model as optimized to the data of Chun (*2*). The two data sets are consistent in *P–T* space. Dew–bubble curves are for the following mole fractions of propane, right to left: 0.2198, 0.4598, 0.6487, 0.7599, 0.8129, 0.9176.

Despite these minor discrepancies, overall the modified Leung–Griffiths model provides a correlation that is consistent with the measured dew and bubble points.

Mixtures of Propane with Normal Hexane

As mentioned earlier, VLE for the propane + *n*-hexane mixture has been measured both by Chun (*3*) and by Porthouse (*8*) with apparatus of identical design. The data of Chun and a modified Leung–Griffiths correlation optimized to these data are shown in Figures 9 and 10. Agreement is generally good, within 0.1 MPa in pressure, 1.7 K in temperature, and 7 kg/m³ in density. It is somewhat surprising that the parameter C_Y is zero for this correlation, in contrast to the negative values for the isomeric hexane mixtures and for other normal alkane mixtures of 2/1 carbon number ratio

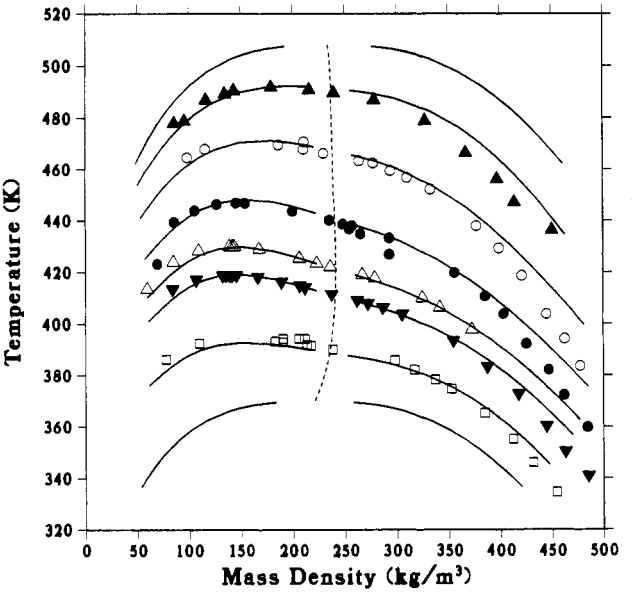

Figure 12. Temperature–density phase diagram for the propane + *n*-hexane system with the data of Porthouse (*8*) and with calculated curves from the model as optimized to the data of Chun (*2*). The two data sets show significant differences in coexisting densities. Compositions are the same as in Figure 11.

such as methane + ethane, ethane + *n*-butane, and *n*-butane + *n*-octane (*14*).

Porthouse (*8*) has measured this mixture for six additional compositions. The raw data of Porthouse (rather than the smoothed data reported in ref 9), together with the predictions of the model as optimized to Chun's data, are displayed in Figures 11 and 12. Agreement in P–T space is acceptable, although Porthouse's results appear systematically lower than those of the model in pressure on the dew curves for x = 0.2198 and x = 0.4598. However, there is some serious disagreement for the coexisting densities, particularly on the liquid side. Above 450 kg/m^3, the same model that agrees well with Chun's densities predicts densities higher than those of Porthouse by as much as 30 kg/m^3. While the trend is less clearly defined, vapor densities below 100 kg/m^3 also appear to be predicted higher than the data. For liquid densities above 400 kg/m^3, the results of Porthouse are lower than those of Chun at equivalent conditions by about 20 kg/m^3, much larger than the stated experimental accuracy.

With a shift in the critical density locus and a new set of mixture parameters, it is possible to construct another Leung–Griffiths correlation that agrees with the coexisting densities of Porthouse (but not with those of Chun). However, this alternate fit requires C_R = 4.3, which is an abnormally large value compared with other normal alkane mixtures with 2/1 carbon number ratio (*14*), and the irregular bubble curve for x = 0.2198 is still not predicted well. Because of these observations and because Chun's second virial coefficients have been accurately correlated (*6*) by the method of Tsonopoulos, we recommend the model optimized to Chun's data as the best estimate of the coexistence surface for the mixture propane + *n*-hexane.

Conclusions

VLE data of Chun (*2*) for the five mixtures of propane with each of the hexane isomers have been presented and correlated with the Leung–Griffiths model as modified by Moldover and Rainwater. In the previous paper, the VLE data on propane + neopentane of Hissong were similarly presented and correlated. With the experiments of Kay (*16*) and others (*17*, *18*) on propane + *n*-pentane and of Vaughan and Collins (*19*) on propane + isopentane, data and critical-region correlations for propane with all of the pentane and hexane isomers are now available.

A motivation for the experimental work was to determine the effects of molecular shape on thermophysical properties. While the model parameters for the five hexane mixtures are roughly of similar values, there is no obvious pattern of dependence of the parameters on the shapes of the hexane molecules, except that C_4, which is closely related to the critical slope of the vapor pressure curve (*14*) and hence the Pitzer acentric factor, is smallest for the most nearly spherical 2,2-dimethylbutane and largest for the most elongated molecule, *n*-hexane. However, computer simulation of molecular fluids is currently making rapid progress (*20*), and the results here should provide a sensitive test of simulation routines in which the molecular shapes are explicitly incorporated into the simulations.

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