Thermodynamics of Octane-Enhancing Additives in Gasolines: Vapor−Liquid Equilibrium of Binary and Ternary Mixtures Containing Di-isopropyl Ether or Heptane and 1-Hexene + Cyclohexane at 313.15 K

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Experimental isothermal $P-x-y$ data for the ternary systems di-isopropyl ether (DIPE) + 1-hexene + cyclohexane and 1-hexene + heptane + cyclohexane and for the binary system DIPE + 1-hexene at 313.15 K are reported. Data reduction by Barker's method provides correlations for G^E, using the Margules equation for the binary system and the Wohl expansion for the ternaries. Wilson, NRTL, and UNIQUAC models have been applied successfully to both the binary and ternary system data.

Introduction

Di-isopropyl ether (DIPE) could be used as a blending agent in the formulation of new gasolines for enhancing the octane number, as a substitute for traditional leaded products. To better understand and model the new formulated gasolines, we started a research program on the thermodynamic characterization of ternary mixtures, as the simplest multicomponent system, containing oxygenated additives (ethers and alcohols), and different types of hydrocarbons (paraffins, cycloparaffins, aromatics, and olefins), methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and DIPE were chosen as additives. We have chosen four hydrocarbons for the purpose of modeling an actual gasoline: paraffins are represented by *n*-heptane, cycloparaffins by cyclohexane, olefins by 1-hexene, and aromatics by benzene.

In previous papers, we published the study of binary and ternary systems containing MTBE[1−6] and these substitution hydrocarbons at 313.15 K. Also, some results with TAME[7−10] and DIPE[11−14] have already been published.

In this paper, two new ternary systems DIPE + 1-hexene + cyclohexane and 1-hexene + heptane + cyclohexane and the binary system DIPE + 1-hexene at 313.15 K are presented.

Experimental Section

Materials. All of the chemicals used here were purchased from Fluka Chemie AG of the highest purity available: chromatography quality reagents (of the series puriss. p.a.) with a purity of >99.5% (by gas chromatography, GC) for heptane and cyclohexane, >99.0% (GC) for DIPE, and >98% (GC) for 1-hexene; the indicated assessments were checked in our laboratory by GC with the following results: >99.8% (GC) for heptane, cyclohexane, and 1-hexene; and >99.5% (GC) for DIPE. All liquids were thoroughly degassed before measurements according to a modified distillation method based on the one suggested by Van Ness and Abbott[15] and kept in glass balloons equipped with leak-proof valves.

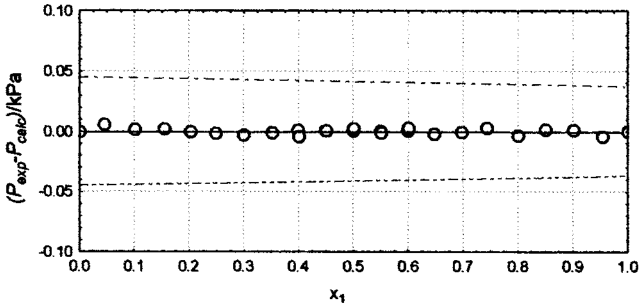

Figure 1. Comparison for the binary system [DIPE (1) + 1-hexene (2)] at 313.15 K of the pressure residuals, defined as differences between experimental and calculated pressures; a ±0.1% band of the experimental pressure in each point is indicated on the diagram.

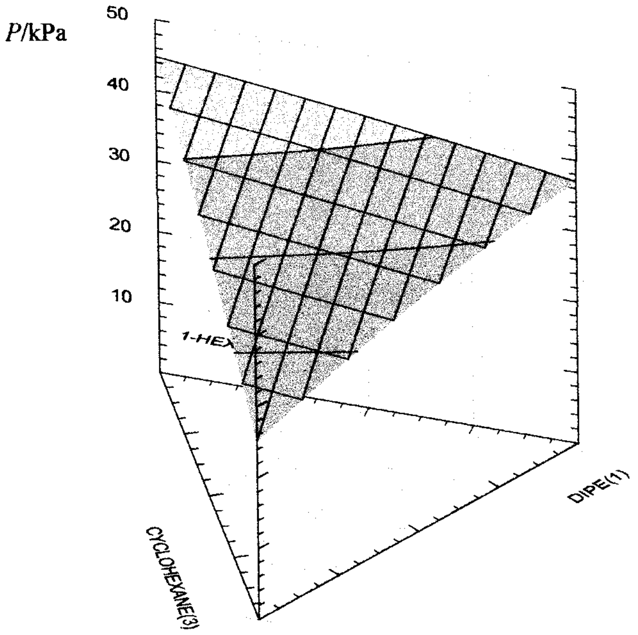

Figure 2. Oblique view of the constant pressure, *P*/kPa, for the DIPE (1) + 1-hexene (2) + cyclohexane (3) system at 313.15 K.

Apparatus and Procedure. A static VLE apparatus, consisting of an isothermal total pressure cell, has been employed for measuring the vapor−liquid equilibrium of

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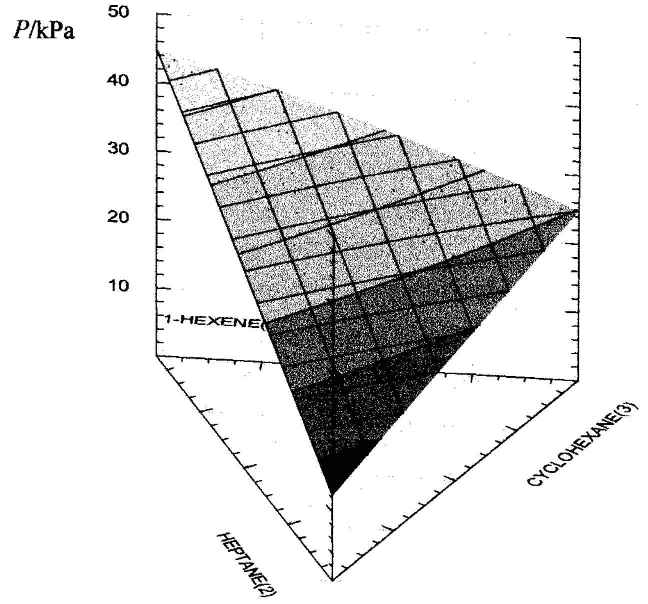

Figure 3. Oblique view of the constant pressure, *P*/kPa, for the 1-hexene (1) + heptane (2) + cyclohexane (3) system at 313.15 K.

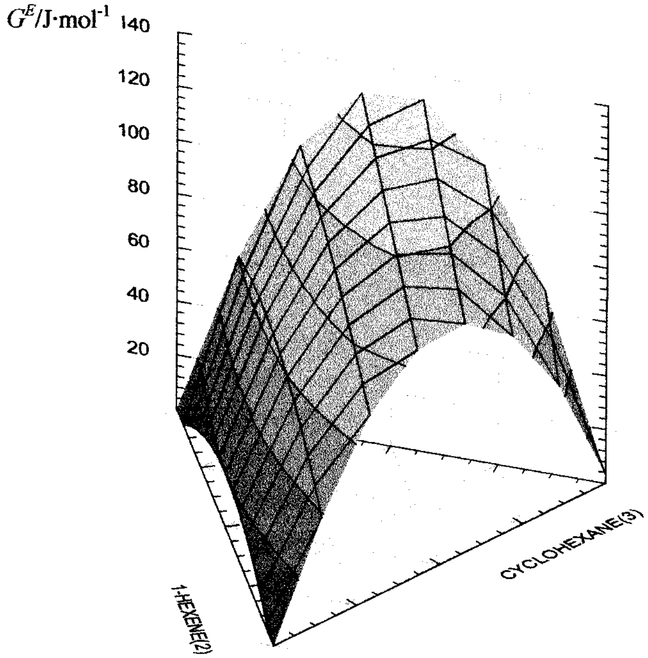

Figure 4. Oblique view of the constant excess Gibbs energy, G^E/J·mol^{-1}, for the DIPE (1) + 1-hexene (2) + cyclohexane (3) system at 313.15 K.

binary and ternary mixtures. The apparatus and measuring technique are based on that by Van Ness and coworkers,[16,17] the performance of which has been described in a previous paper.[18]

The sample injectors were three 100 cm^3 positive displacement pumps (Ruska, model 2200-801) with a resolution of 0.01 cm^3 and an estimated total uncertainty of ±0.03 cm^3. These allowed the injection of known volumes of the pure degassed components into the cell which was immersed in a high-precision water bath (Hart Scientific model 6020) that assured a stability of ±0.5 mK when thermostated at $T = 313.15$ K.

The cell was a cylindrical stainless steel piece with a volume of ~180 cm^3 fitted with a magnetic stirrer coupled to an external drive. An initial volume of ~50 cm^3 of one component was injected into the evacuated cell, and the vapor pressure was measured. Successive injections of a second or third component were made over a desired composition range until the cell was nearly full. The total mass injected was determined accurately from the volumetric displacement of the pistons, the temperature of the injectors, and the known densities for the pure components. This resulted in uncertainties in mole fraction of ±0.0005.

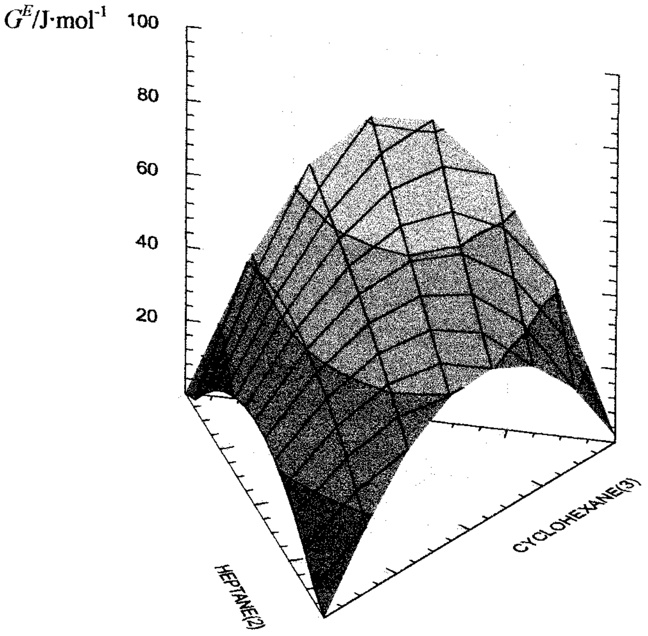

Figure 5. Oblique view of the constant excess Gibbs energy, G^E/J·mol^{-1}, for the 1-hexene (1) + heptane (2) + cyclohexane (3) system at 313.15 K.

Experimental values of total vapor pressure for the binary mixtures were obtained in two overlapping runs starting from opposite ends of the composition range. For the ternary mixtures, data were obtained by addition of a pure species to a mixture of the other two at a fixed temperature. Six runs (dilution lines) were made starting from the corresponding binary system at mole fractions close to 0.3 or 0.7 and adding the third pure component up to a mole fraction of 0.5.

Temperature was measured by means of a calibrated platinum resistance thermometer (SDL model 5385/100) and an ac resistance bridge (ASL model F250) with a resolution of 1 mK and an estimated overall uncertainty of ±10 mK. The measurement of pressure was done indirectly through a differential pressure cell and indicator (Ruska models 2413-705 and 2416-711, respectively). Air was used on the reference side of the differential pressure cell, and the pressure required to obtain a null indication was measured with a fused quartz Bourdon pressure gauge (Texas Instruments model 801). The overall uncertainty of the pressure was estimated to be ±5 Pa.

Experimental Results and Correlations

The use of the measuring technique described above allows a static equilibrium between phases, ensuring a true thermodynamic equilibrium. Direct sampling, particularly of the vapor phase, upsets the equilibrium because the mass of vapor in the cell is very small; however, an appreciable mass must be withdrawn to yield an amount of condensate suitable for accurate analysis. However, as a consequence of Duhem's theorem, sampling of the phases is not necessary. Given a set of equilibrium *x*, *P* data at constant *T*, thermodynamics allows calculation of the *y* values. Thus, the equilibrium vapor need not be sampled

Table 1. Total Pressure Data for DIPE (1) + 1-Hexene (2) at 313.15 K

V_i	T				P	V_i	T				P
cm^3	°C	z_1	x_1	y_1(calcd)	kPa	cm^3	°C	z_1	x_1	y_1(calcd)	kPa
Dilution Line $V_2 = 44.53$ cm^3											
0.00	22.8	0.0000	0.0000	0.0000	44.907	27.19	23.2	0.3508	0.3512	0.3121	42.498
2.39	22.9	0.0453	0.0454	0.0393	44.623	33.56	23.2	0.4001	0.4006	0.3581	42.127
5.67	23.1	0.1013	0.1014	0.0880	44.254	41.22	23.2	0.4503	0.4508	0.4058	41.750
9.18	23.0	0.1543	0.1545	0.1346	43.898	50.24	23.4	0.4996	0.5002	0.4535	41.370
12.76	23.1	0.2023	0.2026	0.1772	43.565	61.35	23.3	0.5494	0.5500	0.5025	40.975
16.66	23.1	0.2487	0.2491	0.2188	43.237	75.36	23.1	0.5996	0.6002	0.5530	40.575
21.52	23.2	0.2996	0.3000	0.2649	42.871						
Dilution Line $V_1 = 51.56$ cm^3											
68.72	23.3	0.3991	0.3988	0.3564	42.145	15.73	23.2	0.7437	0.7437	0.7034	39.387
55.75	23.2	0.4502	0.4499	0.4049	41.757	11.37	23.3	0.8006	0.8006	0.7658	38.894
45.70	23.2	0.4997	0.4995	0.4528	41.373	8.04	23.3	0.8502	0.8503	0.8218	38.467
37.25	23.2	0.5506	0.5505	0.5030	40.970	5.03	23.2	0.9007	0.9008	0.8803	38.020
30.48	23.2	0.5996	0.5995	0.5523	40.579	2.22	23.3	0.9536	0.9537	0.9432	37.540
24.80	23.2	0.6479	0.6479	0.6019	40.182	0.00	23.4	1.0000	1.0000	1.0000	37.120
19.79	23.3	0.6976	0.6975	0.6539	39.772						

Table 2. Total Pressure Data for DIPE (1) + 1-Hexene (2) + Cyclohexane (3) at 313.15 K

V_i	T							P	V_i	T							P
cm^3	°C	z_1	z_2	x_1	x_2	y_1(calcd)	y_2(calcd)	kPa	cm^3	°C	z_1	z_2	x_1	x_2	y_1(calcd)	y_2(calcd)	kPa
Dilution Line $V_1 = 48.56$ cm^3 + $V_2 = 18.49$ cm^3																	
0.00	22.4	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	37.124	16.68	22.6	0.5323	0.2289	0.5321	0.2287	0.5431	0.2797	36.906
0.00	22.4	0.6993	0.3007	0.6994	0.3006	0.6558	0.3442	39.760	22.81	22.7	0.4893	0.2104	0.4891	0.2102	0.5126	0.2626	36.130
1.14	22.3	0.6846	0.2944	0.6847	0.2943	0.6462	0.3386	39.526	28.62	22.7	0.4545	0.1955	0.4543	0.1953	0.4872	0.2485	35.480
2.50	22.4	0.6679	0.2872	0.6679	0.2871	0.6351	0.3322	39.249	35.44	22.7	0.4195	0.1804	0.4193	0.1802	0.4610	0.2341	34.830
5.96	22.6	0.6288	0.2704	0.6288	0.2703	0.6091	0.3173	38.585	43.57	22.7	0.3843	0.1653	0.3840	0.1651	0.4338	0.2193	34.150
9.26	22.6	0.5955	0.2561	0.5955	0.2560	0.5867	0.3044	38.020	53.17	22.6	0.3496	0.1503	0.3493	0.1502	0.4061	0.2043	33.453
13.40	22.6	0.5585	0.2402	0.5584	0.2400	0.5613	0.2900	37.371									
Dilution Line $V_1 = 21.47$ cm^3 + $V_2 = 43.97$ cm^3																	
0.00	22.9	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	44.909	18.37	23.1	0.2257	0.5220	0.2257	0.5216	0.2226	0.6030	38.902
0.00	22.9	0.3018	0.6982	0.3020	0.6980	0.2667	0.7333	42.855	23.52	22.9	0.2108	0.4875	0.2107	0.4871	0.2132	0.5756	38.106
1.17	22.8	0.2955	0.6835	0.2957	0.6833	0.2632	0.7229	42.534	29.59	23.0	0.1955	0.4523	0.1955	0.4518	0.2032	0.5469	37.283
2.65	23.0	0.2878	0.6658	0.2880	0.6655	0.2590	0.7103	42.150	36.50	23.1	0.1807	0.4179	0.1806	0.4175	0.1931	0.5179	36.469
6.10	22.9	0.2714	0.6278	0.2715	0.6275	0.2498	0.6829	41.299	44.87	22.9	0.1654	0.3827	0.1654	0.3822	0.1823	0.4872	35.622
9.70	22.9	0.2562	0.5926	0.2563	0.5922	0.2410	0.6569	40.511	54.82	22.9	0.1504	0.3478	0.1503	0.3474	0.1710	0.4557	34.758
13.79	22.9	0.2408	0.5570	0.2409	0.5567	0.2319	0.6301	39.706									
Dilution Line $V_1 = 46.32$ cm^3 + $V_3 = 15.20$ cm^3																	
0.00	20.9	0.7000	0.0000	1.0000	0.0000	1.0000	0.0000	37.117	19.85	21.2	0.4907	0.2990	0.5227	0.2530	0.5285	0.3065	37.240
0.00	20.8	0.6802	0.0282	0.6997	0.0000	0.7616	0.0000	34.451	25.01	21.9	0.4544	0.3508	0.4904	0.2991	0.4898	0.3574	37.735
1.70	21.8	0.6661	0.0484	0.6800	0.0282	0.7337	0.0367	34.771	31.68	21.4	0.4202	0.3997	0.4542	0.3509	0.4476	0.4129	38.291
2.98	21.3	0.6276	0.1034	0.6659	0.0483	0.7140	0.0625	35.001	39.04	21.3	0.3848	0.4503	0.4199	0.3999	0.4087	0.4640	38.806
6.76	21.3	0.5967	0.1475	0.6274	0.1034	0.6618	0.1312	35.612	48.03	21.2	0.3492	0.5011	0.3845	0.4505	0.3696	0.5154	39.341
10.14	21.2	0.5586	0.2020	0.5965	0.1474	0.6212	0.1846	36.093	58.88	20.9	0.7000	0.0000	0.3490	0.5013	0.3315	0.5655	39.873
14.84	21.4	0.5229	0.2529	0.5584	0.2020	0.5726	0.2486	36.688									
Dilution Line $V_1 = 20.74$ cm^3 + $V_3 = 37.31$ cm^3																	
0.00	22.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.654	20.71	22.2	0.2233	0.2518	0.2232	0.2517	0.2599	0.3395	33.889
0.00	22.1	0.2984	0.0000	0.2982	0.0000	0.4045	0.0000	29.875	26.15	21.9	0.2094	0.2982	0.2093	0.2982	0.2380	0.3927	34.605
1.15	22.1	0.2930	0.0183	0.2927	0.0183	0.3921	0.0283	30.183	33.56	22.1	0.1931	0.3529	0.1930	0.3529	0.2135	0.4525	35.442
3.50	22.0	0.2824	0.0538	0.2821	0.0538	0.3692	0.0812	30.755	41.12	22.1	0.1789	0.4005	0.1788	0.4006	0.1933	0.5022	36.165
7.25	22.3	0.2670	0.1054	0.2668	0.1053	0.3379	0.1542	31.589	50.56	22.2	0.1638	0.4510	0.1637	0.4511	0.1730	0.5528	36.926
10.69	22.0	0.2543	0.1480	0.2541	0.1479	0.3137	0.2112	32.263	61.53	22.3	0.1492	0.5000	0.1491	0.5001	0.1542	0.5999	37.660
15.18	22.1	0.2394	0.1979	0.2392	0.1978	0.2870	0.2746	33.057									
Dilution Line $V_2 = 40.27$ cm^3 + $V_3 = 14.80$ cm^3																	
0.00	22.2	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	44.947	21.56	22.7	0.2495	0.5266	0.2497	0.5261	0.2433	0.6026	39.293
0.00	22.2	0.0000	0.7016	0.0000	0.7011	0.0000	0.8000	39.523	27.69	22.9	0.2992	0.4917	0.2995	0.4912	0.2912	0.5639	39.212
1.45	22.4	0.0219	0.6863	0.0219	0.6858	0.0217	0.7823	39.530	34.72	22.8	0.3487	0.4570	0.3490	0.4565	0.3389	0.5255	39.124
3.43	22.5	0.0502	0.6664	0.0503	0.6659	0.0497	0.7595	39.513	43.27	22.8	0.4002	0.4209	0.4005	0.4204	0.3886	0.4856	39.020
7.29	22.3	0.1010	0.6307	0.1011	0.6303	0.0995	0.7190	39.475	52.96	22.7	0.4495	0.3862	0.4499	0.3858	0.4364	0.4472	38.912
11.46	22.4	0.1502	0.5963	0.1503	0.5958	0.1473	0.6802	39.427	64.50	22.7	0.4986	0.3518	0.4990	0.3513	0.4842	0.4090	38.796
16.23	22.4	0.2002	0.5612	0.2003	0.5607	0.1957	0.6410	39.364									
Dilution Line $V_2 = 17.59$ cm^3 + $V_3 = 37.80$ cm^3																	
0.00	22.6	0.0000	0.0000	1.0000	0.0000	1.0000	0.0000	37.117	23.08	22.1	0.2500	0.2151	0.5227	0.2530	0.5285	0.3065	37.240
0.00	22.8	0.0000	0.2868	0.6997	0.0000	0.7616	0.0000	34.451	29.76	22.1	0.3006	0.2006	0.4904	0.2991	0.4898	0.3574	37.735
1.76	22.6	0.0248	0.2797	0.6800	0.0282	0.7337	0.0367	34.771	37.16	22.1	0.3493	0.1866	0.4542	0.3509	0.4476	0.4129	38.291
3.76	22.6	0.0515	0.2720	0.6659	0.0483	0.7140	0.0625	35.001	46.04	22.1	0.3994	0.1722	0.4199	0.3999	0.4087	0.4640	38.806
7.75	22.5	0.1007	0.2579	0.6274	0.1034	0.6618	0.1312	35.612	56.56	22.1	0.4487	0.1575	0.3845	0.4505	0.3696	0.5154	39.341
12.22	22.4	0.1500	0.2438	0.5965	0.1474	0.6212	0.1846	36.093	69.05	22.0	0.4984	0.1433	0.3490	0.5013	0.3315	0.5655	39.873
17.39	22.2	0.2008	0.2292	0.5584	0.2020	0.5726	0.2486	36.688									

for analysis, and the data are thermodynamically consistent per se.[19,20]

Data reduction for the binary and ternary mixtures was done by Barker's method[21] according to well-established procedures.[22,23]

The nonideality of the vapor phase was taken into account with the virial equation of state, truncated after the second term. The pure-component and interaction second virial coefficients (B_{ij}) were calculated according to the Hayden and O'Connell method[24] using the parameters given by Dymond and Smith.[25]

The ternary systems DIPE + 1-hexene + cyclohexane and 1-hexene + heptane + cyclohexane and the binary system DIPE + 1-hexene were measured at 313.15 K. Data for these ternary systems were adequately correlated by the three-parameter Wohl equation,[26] which also includes the parameters of the corresponding binaries.

$$g_{123} = \frac{G^{\mathrm{E}}}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \tag{1}$$

Table 3. Total Pressure Data for 1-Hexene (1) + *n*-Heptane (2) + Cyclohexane (3) at 313.15 K

V_i/cm^3	T/°C	z_1	z_2	x_1	x_2	y_1(calcd)	y_2(calcd)	P/kPa
Dilution Line $V_1 = 43.63$ cm^3 + $V_2 = 22.06$ cm^3								
0.00	23.4	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	45.004
0.00	23.4	0.6986	0.3014	0.6979	0.3021	0.8895	0.1105	35.222
1.46	23.3	0.6802	0.2935	0.6795	0.2942	0.8720	0.1080	34.989
2.94	23.3	0.6625	0.2859	0.6618	0.2865	0.8550	0.1057	34.777
6.11	23.2	0.6275	0.2708	0.6268	0.2714	0.8209	0.1010	34.365
9.61	23.2	0.5929	0.2559	0.5923	0.2564	0.7865	0.0963	33.945
13.57	23.2	0.5582	0.2409	0.5575	0.2413	0.7512	0.0915	33.516
18.05	23.2	0.5234	0.2259	0.5228	0.2263	0.7153	0.0868	33.084
23.18	23.2	0.4886	0.2109	0.4880	0.2112	0.6785	0.0819	32.638
29.13	23.2	0.4536	0.1958	0.4530	0.1960	0.6408	0.0770	32.177
36.04	23.1	0.4188	0.1807	0.4182	0.1809	0.6024	0.0721	31.715
44.18	23.1	0.3841	0.1657	0.3835	0.1659	0.5632	0.0670	31.234
53.94	23.1	0.3493	0.1507	0.3488	0.1509	0.5229	0.0619	30.750
Dilution Line $V_1 = 18.85$ cm^3 + $V_2 = 49.70$ cm^3								
0.00	23.0	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	12.363
0.00	23.0	0.3077	0.6923	0.3071	0.6929	0.6155	0.3845	22.516
1.27	23.0	0.3005	0.6761	0.2999	0.6767	0.5992	0.3742	22.600
3.07	23.0	0.2908	0.6543	0.2903	0.6549	0.5775	0.3605	22.721
5.84	23.0	0.2771	0.6235	0.2766	0.6241	0.5472	0.3412	22.886
9.28	22.9	0.2618	0.5890	0.2613	0.5895	0.5140	0.3200	23.062
13.20	23.0	0.2463	0.5541	0.2458	0.5546	0.4810	0.2989	23.234
17.64	22.9	0.2308	0.5193	0.2304	0.5196	0.4487	0.2783	23.403
22.67	22.9	0.2154	0.4847	0.2150	0.4850	0.4173	0.2581	23.557
28.50	22.9	0.2000	0.4500	0.1996	0.4503	0.3862	0.2383	23.708
35.75	22.9	0.1837	0.4132	0.1833	0.4134	0.3539	0.2176	23.863
43.61	22.9	0.1687	0.3796	0.1684	0.3797	0.3247	0.1991	23.997
52.98	23.0	0.1538	0.3460	0.1535	0.3461	0.2960	0.1808	24.120
Dilution Line $V_1 = 39.39$ cm^3 + $V_3 = 14.58$ cm^3								
0.00	22.8	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	44.986
0.00	22.9	0.7002	0.0000	0.6997	0.0000	0.7991	0.0000	39.559
1.92	22.9	0.6804	0.0283	0.6798	0.0284	0.7919	0.0093	38.752
3.54	22.9	0.6645	0.0510	0.6639	0.0511	0.7859	0.0170	38.137
7.41	22.9	0.6294	0.1010	0.6288	0.1013	0.7720	0.0350	36.788
11.70	22.9	0.5947	0.1507	0.5939	0.1511	0.7571	0.0542	35.437
16.60	22.9	0.5594	0.2011	0.5586	0.2016	0.7408	0.0751	34.073
22.02	22.9	0.5249	0.2503	0.5241	0.2509	0.7235	0.0972	32.721
28.35	23.0	0.4897	0.3007	0.4889	0.3013	0.7043	0.1216	31.367
35.54	23.0	0.4550	0.3502	0.4542	0.3509	0.6838	0.1478	30.028
43.99	23.0	0.4200	0.4002	0.4193	0.4009	0.6611	0.1764	28.670
54.01	23.0	0.3849	0.4503	0.3842	0.4510	0.6362	0.2080	27.320
65.99	23.1	0.3500	0.5002	0.3493	0.5009	0.6087	0.2425	25.966
Dilution Line $V_1 = 17.06$ cm^3 + $V_3 = 35.05$ cm^3								
0.00	23.4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.652
0.00	23.5	0.2960	0.0000	0.2956	0.0000	0.4408	0.0000	31.630
1.68	23.4	0.2888	0.0243	0.2884	0.0243	0.4358	0.0099	31.137
3.68	23.2	0.2807	0.0517	0.2802	0.0518	0.4300	0.0215	30.584
7.59	23.2	0.2661	0.1011	0.2656	0.1013	0.4194	0.0432	29.641
11.90	23.2	0.2517	0.1499	0.2512	0.1502	0.4084	0.0661	28.694
16.89	23.2	0.2368	0.2002	0.2363	0.2005	0.3965	0.0913	27.724
22.71	23.2	0.2215	0.2518	0.2211	0.2522	0.3837	0.1189	26.763
28.93	23.1	0.2072	0.3000	0.2068	0.3005	0.3710	0.1466	25.805
36.42	23.1	0.1923	0.3505	0.1919	0.3510	0.3569	0.1776	24.838
45.07	23.1	0.1775	0.4004	0.1772	0.4009	0.3420	0.2108	23.877
55.22	23.1	0.1628	0.4500	0.1625	0.4505	0.3261	0.2464	22.924
67.47	23.1	0.1480	0.4999	0.1478	0.5004	0.3090	0.2852	21.965
Dilution Line $V_2 = 47.35$ cm^3 + $V_3 = 14.90$ cm^3								
0.00	23.2	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	12.348
0.00	23.2	0.0000	0.7009	0.0000	0.7012	0.0000	0.5367	16.252
1.40	23.2	0.0237	0.6843	0.0237	0.6846	0.0641	0.5021	16.980
3.27	23.1	0.0537	0.6633	0.0536	0.6636	0.1376	0.4624	17.868
6.92	23.0	0.1072	0.6258	0.1070	0.6262	0.2515	0.4010	19.466
9.89	23.0	0.1465	0.5983	0.1462	0.5987	0.3236	0.3621	20.626
14.34	23.0	0.1992	0.5613	0.1989	0.5617	0.4085	0.3164	22.178
19.29	22.9	0.2508	0.5252	0.2504	0.5255	0.4805	0.2777	23.676
24.75	22.9	0.3004	0.4904	0.3001	0.4907	0.5416	0.2449	25.129
31.01	22.9	0.3498	0.4557	0.3495	0.4561	0.5958	0.2158	26.563
39.15	22.9	0.4045	0.4174	0.4043	0.4177	0.6494	0.1871	28.132
47.72	23.0	0.4529	0.3834	0.4528	0.3837	0.6921	0.1642	29.523
57.93	23.0	0.5013	0.3496	0.5012	0.3497	0.7310	0.1434	30.908
Dilution Line $V_2 = 21.65$ cm^3 + $V_3 = 37.09$ cm^3								
0.00	22.8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.659
0.00	22.8	0.0000	0.3009	0.0000	0.3012	0.0000	0.1817	21.181
1.61	22.8	0.0255	0.2933	0.0255	0.2935	0.0558	0.1710	21.894
3.36	22.9	0.0519	0.2853	0.0518	0.2856	0.1092	0.1608	22.598
6.49	22.8	0.0956	0.2722	0.0954	0.2725	0.1901	0.1455	23.753
10.60	22.8	0.1472	0.2566	0.1470	0.2569	0.2750	0.1295	25.086
15.25	22.9	0.1989	0.2411	0.1987	0.2414	0.3507	0.1154	26.401
20.35	23.0	0.2489	0.2260	0.2487	0.2263	0.4167	0.1032	27.652
26.28	23.0	0.2997	0.2107	0.2995	0.2110	0.4776	0.0920	28.900
33.00	23.0	0.3496	0.1957	0.3494	0.1960	0.5324	0.0820	30.109
40.88	23.0	0.3997	0.1807	0.3995	0.1808	0.5832	0.0728	31.308
50.18	23.1	0.4497	0.1656	0.4496	0.1658	0.6302	0.0644	32.492
61.81	23.1	0.5016	0.1500	0.5016	0.1501	0.6757	0.0563	33.711

Table 4. Average Values of Experimental Vapor Pressures (P_i^{sat}) for the Pure Compounds Measured in This Work and Literature Values (P_i^{sat}), Molar Volumes of Pure Liquids (V_i^L), and the Second Virial Coefficients (B_{ii}, B_{ij}) at 313.15 K Used for the Reduction of the Systems

	DIPE (1)	heptane (2)	cyclohexane (3)	1-hexene (4)
P_i^{sat}/kPa	37.125	12.355	24.653	44.959
P_i^{sat} (lit.)/kPa	37.081[a] 37.090[b]	12.331[c] 12.348[d] 12.335[e] 12.300[f]	24.635[c] 24.630[d] 24.634[e] 24.670[f]	44.979[c] 44.989[d] 45.050[e] 45.030[f]
V_i^L/cm^3·mol^{-1}	145.4	150.3	110.8	128.6
B_{ii}/cm^3·mol^{-1}	−1688	−2521	−1554	−1510
B_{12}/cm^3·mol^{-1}	−2025			
B_{13}/cm^3·mol^{-1}	−1604			
B_{14}/cm^3·mol^{-1}	−1581			
B_{23}/cm^3·mol^{-1}		−1975		
B_{24}/cm^3·mol^{-1}		−1918		
B_{34}/cm^3·mol^{-1}			−1521	

[a] Calculated from the Antoine equation using constants reported by Riddick et al.[31] [b] Reported by Ambrose et al.[32] [c] Reported by Segovia.[1] [d] Reported by Montero.[33] [e] Calculated from the Antoine equation using constants reported in TRC tables.[34] [f] Calculated from the Antoine equation using constants reported by Reid et al.[35]

Parameters C_0, C_1, and C_2 were found by regression of the ternary data, and correlations for g_{ij} were given by the equation

$$g_{ij} = \frac{G^E}{RT} = [A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j]x_ix_j \qquad (2)$$

which is the Margules equation up to four parameters.[27] It was chosen for fitting the binary mixtures.

Table 5. Summary of Results of the Correlation for the Binary System DIPE (1) + 1-Hexene (2) at 313.15 K

	Margules[a]	Wilson	NRTL	UNIQUAC
A_{12}	0.0391	0.8004	−0.2560	1.0739
A_{21}	0.0314	1.1842	0.3148	0.9191
$\lambda_{12} = \lambda_{21}$	0.0053			
α_{12}			0.3	
rms ΔP/kPa	0.003	0.003	0.003	0.003
max $\lvert\Delta P\rvert$/kPa	0.006	0.007	0.007	0.007

[a] Three parameters.

Binary and ternary systems were correlated using Wilson,[28] NRTL,[29] and UNIQUAC[30] models, which express the excess Gibbs energy as

$$\frac{G^E}{RT} = -\sum_i x_i \ln(\sum_j x_j A_{ij}) \qquad (3)$$

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j A_{ji}G_{ji}x_j}{\sum_k G_{ki}x_k} \qquad (4)$$

$$\frac{G^E}{RT} = \sum_i x_i \ln\frac{\varphi_i}{x_i} + \frac{z}{2}\sum_i q_i x_i \ln\frac{\vartheta_i}{q_i} - \sum_i q_i x_i \ln(\sum_j \vartheta_j A_{ji}) \qquad (5)$$

where $G_{ji} = \exp(-\alpha_{ji}A_{ji})$, $\alpha_{ji} = 0.3$,

Table 6. Summary of Results for the Other Binary Systems Involved in the Ternary Systems at 313.15 K

	Margules[a]	Wilson	NRTL	UNIQUAC
	DIPE (1) + Cyclohexane (2)[b]			
A_{12}	0.2402	0.6236	−0.3644	1.1293
A_{21}	0.1694	1.2322	0.6438	0.8370
λ	0.0306			
α_{12}			0.3	
rms ΔP/kPa	0.003	0.004	0.005	0.004
max $\lvert\Delta P\rvert$/kPa	0.007	0.007	0.011	0.006
	1-Hexene (2) + Cyclohexane (3)[c]			
A_{23}	0.15676	0.63162	−0.41347	1.28529
A_{32}	0.10554	1.30477	0.62019	0.72725
λ	0.03151			
α_{23}			0.3	
rms ΔP/kPa	0.014	0.014	0.015	0.014
max $\lvert\Delta P\rvert$/kPa	0.032	0.033	0.033	0.033
	1-Hexene (1) + *n*-Heptane (2)[d]			
A_{12}	0.03553	0.94507	−0.04050	1.13779
A_{21}	0.03598	1.01664	0.08086	0.85778
λ	0.01313			
α_{12}			0.3	
rms ΔP/kPa	0.022	0.022	0.022	0.022
max $\lvert\Delta P\rvert$/kPa	0.052	0.057	0.057	0.056
	n-Heptane (2) + Cyclohexane (3)[c]			
A_{23}	0.07485	0.65278	−0.44393	1.13037
A_{32}	0.04796	1.35389	0.57937	0.86418
λ	0.02355			
α_{23}			0.3	
rms ΔP/kPa	0.009	0.009	0.009	0.009
max $\lvert\Delta P\rvert$/kPa	0.017	0.017	0.018	0.017

[a] Three parameters. [b] Chamorro et al.[11] [c] Segovia et al.[5] [d] Segovia et al.[3]

$$\vartheta_i = \frac{q_i x_i}{\sum_j q_j x_j}$$

$$\varphi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

and $z = 10$.

Table 1 gives experimental values of total pressure and the corresponding compositions of the liquid and vapor phases for the binary systems. Tables 2 and 3 give the same information for the ternary systems. In these tables, the compositions of the vapor phases were reduced by the Margules equation for the binary system and the Wohl expansion for the ternary systems. In addition, these three tables also contain the original injected volumes, the temperature during the injection, and the total cell composition z_i.

The average values of the experimental vapor pressures (P_i^{sat}) for the pure compounds, molar volumes of pure liquids (V_i^{L}), and second virial coefficients (B_{ii} and B_{ij}) are indicated in Table 4, which includes literature vapor pressures (P_i^{sat}, lit.) for comparison.

Table 7. Summary of the Results Obtained for the Ternary System DIPE (1) + 1-Hexene (2) + Cyclohexane (3) at 313.15 K

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.2454			
C_1	0.0636			
C_2	0.0644			
A_{12}		0.8594	−0.1714	1.0183
A_{21}		1.1148	0.2172	0.9719
A_{13}		0.5645	−0.4403	1.2263
A_{31}		1.3162	0.7516	0.7565
A_{23}		0.7042	−0.3121	1.2033
A_{32}		1.2121	0.4796	0.7929
$\alpha_{12} = \alpha_{23} = \alpha_{13}$			0.3	
rms ΔP/kPa	0.020	0.016	0.016	0.016
max $\lvert\Delta P\rvert$/kPa	0.053	0.035	0.035	0.035

Table 8. Summary of the Results Obtained for the Ternary System 1-Hexene (1) + Heptane (2) + Cyclohexane (3) at 313.15 K

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.6152			
C_1	0.1196			
C_2	0.0960			
A_{12}		1.2897	0.4629	0.9769
A_{21}		0.7196	−0.3776	1.0103
A_{13}		0.5450	−0.3182	0.8857
A_{31}		1.1668	0.7801	1.0202
A_{23}		0.4185	−0.4131	0.8151
A_{32}		1.1980	1.1249	1.0361
$\alpha_{12} = \alpha_{23} = \alpha_{13}$			0.3	
rms ΔP/kPa	0.020	0.014	0.015	0.015
max $\lvert\Delta P\rvert$/kPa	0.069	0.033	0.031	0.042

Results of data correlation for the binary system are summarized in Table 5. The results of the correlation of the other binaries that form the ternary systems have been published previously, and these are summarized in Table 6. For the ternary systems, the results of the correlation are given in Tables 7 and 8. All of these tables contain values of the adjustable parameters of the different models which lead to the results using Barker's method, the root-mean-square of the difference between the experimental and the calculated pressures (rms ΔP) and the maximum value of this difference (max $|\Delta P|$).

As an example of the fits of models to the data, Figure 1 shows a plot of ($P_{\mathrm{exptl}} - P_{\mathrm{calcd}}$) versus x_1 for the binary system DIPE + 1-hexene using the Margules equation with three parameters. It can be seen that both branches, necessary to cover the entire composition range, exhibit good agreement close to equimolar concentrations. Furthermore, all deviations are <0.1% of the total pressure.

Discussion

We have not found literature data available for comparison for any of the binary and ternary systems at 313.15 K, presented in this paper.

The binary system studied presents a slight positive deviation from ideality, and the results of the correlation gave root-mean-square pressure residuals of 3 Pa for all of the models with a maximum value of the absolute deviation of 7 Pa.

The measurements for the ternary DIPE + 1-hexene + cyclohexane system were well correlated by all of the models, showing root-mean-square pressure residuals of 16 Pa, with maximum values of the absolute deviation in pressure of 35 Pa for the Wilson, NRTL, and UNIQUAC models and of up to 53 Pa for the Wohl equation, within a maximum range of pressure close to 45 kPa.

For the system 1-hexene + heptane + cyclohexane, again all of the models closely correlated the experimental values. The value of the root-mean-square pressure residuals was 17 Pa, with a maximum value of the absolute deviation in pressure of 41 Pa for the Wilson, NRTL, and UNIQUAC models. The Wohl equation gives a little poorer calculations with root-mean-square pressure residuals of 25 Pa, and the maximum absolute deviation in pressure was 82 Pa.

Graphical results for the ternary systems are in Figures 2−5. They show the oblique view of the pressure and of the excess Gibbs energy surface for the ternary systems.

The total equilibrium pressure always increases from the value of the saturation pressure of less volatile compound to the saturation pressure of more volatile compounds. The two measured ternary systems show slight positive deviations from ideality, and the molar excess Gibbs energy also increases up to a maximum value, which corresponds to a less ideal binary system. The ternary system DIPE + 1-hexene + cyclohexane is the least ideal ternary system because the binary (DIPE + cyclohexane) is also the least ideal binary system, with a maximum value of G^E of 130 J·mol^{-1}. On the other hand, the highest value of G^E for the ternary system 1-hexene + heptane + cyclohexane is ∼82 J·mol^{-1}, which corresponds to the binary 1-hexene + cyclohexane.

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