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

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

Introduction

Technology for altenative oxygenate additives in unleaded gasoline needs accurate vapor−liquid equilibrium data to design separation processes properly and to predict properties of mixtures of the additives with gasoline hydrocarbons. At this time, our research group is finishing a program of characterization of the fluid phase equilibria of ethers used as octane-enhancing compounds in gasolines.

Di-isopropyl ether (DIPE) could be use as a blending agent in the formulation of the new unleaded gasolines. In previous papers, we published the study of binary and ternary systems containing MTBE[1−6] and the substitution hydrocarbons *n*-heptane, cyclohexane, 1-hexene, and benzene at 313.15 K. Also, some results with TAME[7−10] and DIPE[11−16] have already been published.

In this paper, we present the most recent results related to di-isopropyl ether with two new ternary systems (di-isopropyl ether (DIPE) + 1-hexene + benzene) and (1-hexene + benzene + cyclohexane); both have been measured at 313.15 K.

Experimental Section

Materials. All the chemicals used here were purchased from Fluka Chemie AG. They have the highest purity available and are chromatography quality reagents (of the series puriss. p.a.) with a purity of >99.5%(by gas chromatography, GC) for benzene and cyclohexane, >99.0%-(GC) for DIPE and >98%(GC) for 1-hexene, having checked in our laboratory the indicated assesments by gas chromatography and obtaining the following values, >99.8%-(GC) for benzene and cyclohexane and 1-hexene and >99.5% (GC) for DIPE. All liquids were thoroughly degassed before measurements by using a modified distillation method based on the one suggested by Van Ness and Abbott[17] and kept in glass balloons equipped with leak-proof valves.

Apparatus and Procedure. A static VLE apparatus, consisting of an isothermal total pressure cell, has been employed for measuring the vapor−liquid equilibrium of binary and ternary mixtures. The apparatus and measuring technique are based on that by Van Ness and coworkers[18,19] and whose performance has been described in a previous paper.[20]

The sample injectors were three 100-cm^3 positive displacement pumps (Ruska, mod. 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 l stainless steel cylinder with a volume of about 180 cm^3 fitted with a magnetic stirrer coupled to an external drive. An initial volume of about 50 cm^3 of one component was injected into the evacuated cell, and the vapor pressure was measured. Successive injections of a second or a 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.

Experimental values of total vapor pressure for the ternary mixtures 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 a.c. 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 mod. 801). The overall uncertainties of the pressure were estimated to be ±5 Pa.

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Table 1. Total Pressure Data for DIPE (1) + 1-Hexene (2) + Benzene (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(calc.)	y_2(calc.)	kPa	cm^3	°C	z_1	z_2	x_1	x_2	y_1(calc.)	y_2(calc.)	kPa
		Dilution Line $V_1 = 52.62$ cm^3 + $V_2 = 20.06$ cm^3									Dilution Line $V_1 = 21.97$ cm^3 + $V_3 = 32.24$ cm^3						
0.00	23.2	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	37.124	0.00	22.6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.400
0.00	23.0	0.6990	0.3010	0.6990	0.3010	0.6554	0.3446	39.773	0.00	22.4	0.3001	0.0000	0.2998	0.0000	0.4054	0.0000	29.508
1.02	23.0	0.6842	0.2947	0.6843	0.2946	0.6444	0.3399	39.550	1.58	22.5	0.2930	0.0238	0.2927	0.0237	0.3850	0.0436	30.093
2.50	23.0	0.6639	0.2859	0.6639	0.2858	0.6292	0.3335	39.254	3.58	22.5	0.2844	0.0523	0.2842	0.0522	0.3624	0.0925	30.775
5.30	22.9	0.6286	0.2707	0.6286	0.2706	0.6028	0.3222	38.708	7.19	22.5	0.2701	0.0998	0.2700	0.0997	0.3284	0.1667	31.845
8.42	22.9	0.5934	0.2556	0.5934	0.2554	0.5764	0.3108	38.162	11.69	22.5	0.2543	0.1527	0.2541	0.1526	0.2950	0.2408	32.970
11.88	23.0	0.5587	0.2406	0.5586	0.2405	0.5503	0.2994	37.603	16.20	22.7	0.2401	0.1999	0.2400	0.1997	0.2684	0.3007	33.905
15.80	22.8	0.5240	0.2257	0.5239	0.2255	0.5241	0.2877	37.027	21.64	22.8	0.2250	0.2502	0.2249	0.2501	0.2427	0.3597	34.851
20.30	23.1	0.4892	0.2107	0.4890	0.2105	0.4977	0.2757	36.439	27.78	22.8	0.2101	0.2999	0.2100	0.2998	0.2196	0.4137	35.736
25.62	23.0	0.4535	0.1953	0.4533	0.1951	0.4704	0.2631	35.820	34.78	22.8	0.1953	0.3491	0.1953	0.3490	0.1985	0.4638	36.565
31.57	23.1	0.4193	0.1806	0.4191	0.1804	0.4439	0.2507	35.201	43.57	23.0	0.1795	0.4019	0.1794	0.4019	0.1776	0.5146	37.413
38.77	23.0	0.3842	0.1655	0.3840	0.1653	0.4165	0.2375	34.558	53.60	22.9	0.1643	0.4525	0.1642	0.4526	0.1589	0.5611	38.197
47.32	22.8	0.3495	0.1505	0.3493	0.1504	0.3887	0.2239	33.884	64.69	23.0	0.1502	0.4994	0.1501	0.4995	0.1426	0.6024	38.888
		Dilution Line $V_1 = 22.92$ cm^3 + $V_2 = 47.95$ cm^3									Dilution Line $V_2 = 41.14$ cm^3 + $V_3 = 12.36$ cm^3						
0.00	22.7	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	44.947	0.00	22.3	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	44.922
0.00	22.8	0.2974	0.7026	0.2975	0.7025	0.2626	0.7374	42.907	0.00	22.2	0.0000	0.7028	0.0000	0.7023	0.0000	0.7855	41.005
1.07	22.8	0.2909	0.6875	0.2911	0.6873	0.2577	0.7264	42.664	1.80	22.3	0.0265	0.6841	0.0265	0.6837	0.0240	0.7669	40.912
2.56	22.9	0.2824	0.6674	0.2826	0.6672	0.2512	0.7120	42.329	3.39	22.3	0.0488	0.6685	0.0488	0.6680	0.0443	0.7512	40.824
5.22	22.8	0.2684	0.6343	0.2686	0.6341	0.2406	0.6881	41.772	7.33	22.2	0.0998	0.6326	0.0999	0.6322	0.0910	0.7149	40.624
8.46	22.8	0.2532	0.5982	0.2533	0.5979	0.2292	0.6620	41.148	11.62	22.4	0.1495	0.5977	0.1496	0.5973	0.1370	0.6791	40.426
12.15	22.8	0.2378	0.5618	0.2378	0.5615	0.2178	0.6357	40.495	16.51	22.3	0.1998	0.5623	0.2000	0.5619	0.1840	0.6425	40.225
16.18	22.7	0.2229	0.5268	0.2230	0.5264	0.2070	0.6101	39.835	21.96	22.3	0.2493	0.5275	0.2496	0.5271	0.2308	0.6060	40.029
20.74	22.6	0.2083	0.4921	0.2083	0.4917	0.1964	0.5846	39.175	28.30	22.3	0.2997	0.4921	0.3000	0.4916	0.2789	0.5685	39.828
26.13	22.4	0.1932	0.4566	0.1932	0.4561	0.1855	0.5581	38.465	35.52	22.3	0.3495	0.4572	0.3498	0.4567	0.3269	0.5310	39.634
32.30	22.5	0.1785	0.4217	0.1784	0.4212	0.1748	0.5316	37.743	44.02	22.3	0.3997	0.4219	0.4001	0.4214	0.3758	0.4927	39.437
39.68	22.7	0.1635	0.3864	0.1635	0.3859	0.1640	0.5041	36.978	53.97	22.3	0.4494	0.3869	0.4499	0.3864	0.4249	0.4543	39.242
48.46	22.6	0.1487	0.3514	0.1486	0.3509	0.1532	0.4760	36.193	65.96	22.1	0.4994	0.3518	0.4999	0.3513	0.4746	0.4152	39.045
		Dilution Line $V_1 = 47.26$ cm^3 + $V_3 = 12.58$ cm^3									Dilution Line $V_2 = 17.59$ cm^3 + $V_3 = 37.80$ cm^3						
0.00	22.1	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	37.129	0.00	22.4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.397
0.00	22.2	0.7027	0.0000	0.7024	0.0000	0.7674	0.0000	34.213	0.00	22.2	0.0000	0.3016	0.0000	0.3010	0.0000	0.4702	33.839
1.60	22.0	0.6843	0.0262	0.6841	0.0261	0.7381	0.0367	34.590	1.71	22.5	0.0237	0.2944	0.0237	0.2939	0.0269	0.4556	33.892
3.17	22.0	0.6672	0.0505	0.6670	0.0505	0.7117	0.0698	34.923	3.93	22.4	0.0528	0.2856	0.0528	0.2851	0.0597	0.4381	33.981
6.56	22.2	0.6330	0.0992	0.6328	0.0991	0.6612	0.1336	35.587	7.69	22.3	0.0984	0.2719	0.0984	0.2714	0.1101	0.4114	34.113
10.55	22.2	0.5970	0.1505	0.5968	0.1504	0.6109	0.1973	36.267	12.40	22.4	0.1496	0.2564	0.1497	0.2560	0.1658	0.3824	34.263
14.89	22.3	0.5622	0.2000	0.5620	0.1999	0.5647	0.2560	36.899	17.61	22.4	0.1999	0.2413	0.2000	0.2409	0.2196	0.3549	34.411
19.88	22.4	0.5269	0.2502	0.5267	0.2502	0.5200	0.3131	37.521	23.49	22.4	0.2500	0.2262	0.2501	0.2258	0.2724	0.3284	34.565
25.53	22.4	0.4919	0.3000	0.4917	0.3000	0.4777	0.3674	38.122	30.23	22.3	0.3002	0.2110	0.3003	0.2107	0.3246	0.3026	34.720
32.08	22.3	0.4568	0.3500	0.4566	0.3501	0.4369	0.4199	38.701	37.96	22.4	0.3501	0.1960	0.3503	0.1957	0.3759	0.2777	34.877
39.81	22.5	0.4212	0.4006	0.4210	0.4007	0.3973	0.4712	39.279	47.04	22.5	0.4003	0.1808	0.4005	0.1806	0.4269	0.2533	35.038
48.43	22.4	0.3876	0.4484	0.3874	0.4486	0.3611	0.5183	39.802	57.62	22.5	0.4498	0.1659	0.4501	0.1657	0.4768	0.2298	35.200
59.54	22.4	0.3515	0.4999	0.3512	0.5001	0.3234	0.5675	40.357	70.41	22.6	0.4998	0.1508	0.5001	0.1506	0.5265	0.2066	35.366

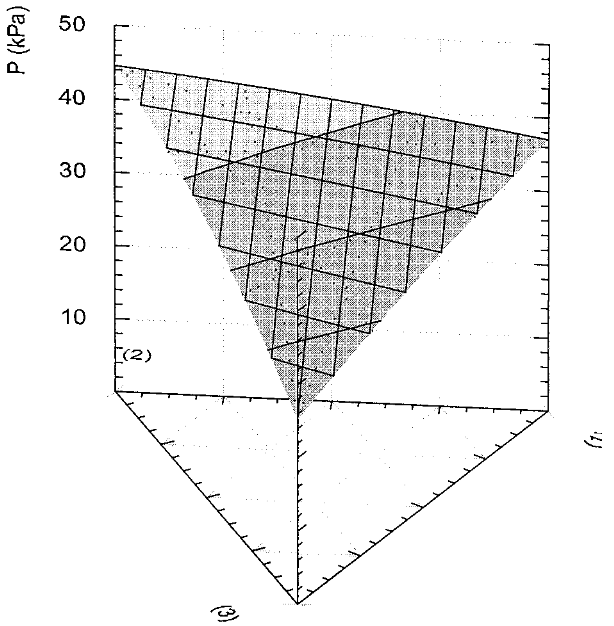

Figure 1. Oblique view of the constant pressure, *P* (kPa), for the DIPE (1) + 1-hexene (2) + benzene (3) system at 313.15 K.

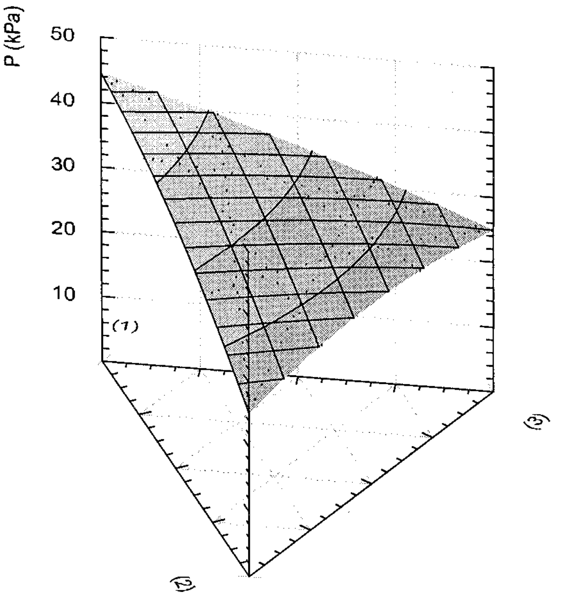

Figure 2. Oblique view of the constant pressure, *P* (kPa), for the 1-hexene (1) + benzene (2) + cyclohexane (3) system at 313.15 K.

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

Table 2. Total Pressure Data for 1-Hexene (1) + Benzene (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(calc.)	y_2(calc.)	kPa	cm^3	°C	z_1	z_2	x_1	x_2	y_1(calc.)	y_2(calc.)	kPa
Dilution Line $V_1 = 47.25$ cm^3 + $V_2 = 14.34$ cm^3									Dilution Line $V_1 = 22.91$ cm^3 + $V_3 = 44.99$ cm^3								
0.00	23.0	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	44.978	0.00	23.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.655
0.00	23.0	0.7007	0.2993	0.7003	0.2997	0.7842	0.2158	41.005	0.00	23.0	0.3056	0.0000	0.3053	0.0000	0.4513	0.0000	31.862
1.46	22.9	0.6836	0.2920	0.6832	0.2923	0.7701	0.2129	40.697	1.36	23.0	0.2980	0.0249	0.2977	0.0249	0.4382	0.0269	31.926
3.22	23.0	0.6640	0.2836	0.6636	0.2840	0.7540	0.2094	40.317	2.81	23.0	0.2903	0.0501	0.2900	0.0501	0.4253	0.0534	31.976
6.58	22.9	0.6296	0.2689	0.6292	0.2692	0.7255	0.2032	39.644	5.96	23.0	0.2748	0.1006	0.2745	0.1007	0.4009	0.1041	32.033
10.32	23.0	0.5953	0.2543	0.5948	0.2545	0.6969	0.1968	38.968	9.45	23.0	0.2595	0.1507	0.2593	0.1507	0.3781	0.1517	32.041
14.66	23.0	0.5598	0.2392	0.5594	0.2393	0.6671	0.1899	38.261	12.36	23.0	0.2480	0.1883	0.2478	0.1884	0.3618	0.1860	32.018
19.43	23.0	0.5255	0.2245	0.5250	0.2246	0.6377	0.1828	37.565	17.77	23.0	0.2291	0.2502	0.2289	0.2503	0.3363	0.2401	31.926
25.03	23.1	0.4901	0.2094	0.4897	0.2095	0.6069	0.1753	36.843	22.85	23.0	0.2138	0.3002	0.2136	0.3004	0.3166	0.2821	31.809
31.41	23.0	0.4553	0.1945	0.4548	0.1945	0.5758	0.1675	36.104	28.73	23.0	0.1985	0.3504	0.1983	0.3506	0.2976	0.3232	31.649
39.11	23.1	0.4193	0.1791	0.4188	0.1791	0.5429	0.1590	35.367	35.55	23.0	0.1833	0.4003	0.1830	0.4005	0.2791	0.3632	31.450
47.69	23.0	0.3853	0.1646	0.3849	0.1646	0.5110	0.1506	34.642	43.56	23.0	0.1681	0.4499	0.1679	0.4501	0.2611	0.4026	31.211
58.20	23.1	0.3506	0.1498	0.3501	0.1497	0.4772	0.1415	33.873	53.22	23.0	0.1529	0.4998	0.1527	0.5001	0.2431	0.4422	30.932
Dilution Line $V_1 = 22.29$ cm^3 + $V_2 = 36.15$ cm^3									Dilution Line $V_2 = 34.26$ cm^3 + $V_3 = 17.76$ cm^3								
0.00	23.1	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	24.398	0.00	23.3	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	24.411
0.00	23.1	0.3046	0.6954	0.3042	0.6958	0.4734	0.5266	33.922	0.00	23.3	0.0000	0.7012	0.0000	0.7012	0.0000	0.6613	27.151
1.66	23.2	0.2968	0.6776	0.2964	0.6780	0.4587	0.5171	33.786	2.52	23.2	0.0353	0.6764	0.0353	0.6765	0.0672	0.6207	28.085
3.47	23.1	0.2888	0.6592	0.2884	0.6596	0.4440	0.5074	33.657	4.23	23.2	0.0579	0.6605	0.0578	0.6607	0.1068	0.5966	28.664
7.09	23.1	0.2739	0.6253	0.2735	0.6256	0.4180	0.4895	33.393	7.94	23.2	0.1035	0.6286	0.1034	0.6287	0.1802	0.5517	29.759
11.10	23.0	0.2591	0.5915	0.2588	0.5918	0.3933	0.4717	33.118	12.52	23.2	0.1540	0.5932	0.1538	0.5933	0.2529	0.5067	30.917
16.04	23.1	0.2430	0.5547	0.2427	0.5549	0.3676	0.4522	32.801	17.25	23.2	0.2005	0.5606	0.2004	0.5607	0.3136	0.4687	31.922
21.11	23.1	0.2284	0.5213	0.2281	0.5215	0.3452	0.4342	32.501	23.11	23.2	0.2515	0.5248	0.2514	0.5249	0.3746	0.4301	32.980
27.14	23.1	0.2131	0.4865	0.2129	0.4866	0.3225	0.4151	32.174	29.52	23.1	0.3003	0.4906	0.3002	0.4907	0.4286	0.3956	33.933
34.01	23.0	0.1981	0.4522	0.1978	0.4522	0.3007	0.3957	31.831	37.06	23.1	0.3502	0.4556	0.3501	0.4557	0.4800	0.3622	34.881
42.17	23.0	0.1827	0.4172	0.1825	0.4171	0.2790	0.3752	31.468	46.00	23.0	0.4008	0.4201	0.4008	0.4202	0.5292	0.3299	35.806
51.76	23.0	0.1675	0.3824	0.1673	0.3823	0.2578	0.3541	31.087	56.27	23.1	0.4500	0.3856	0.4500	0.3856	0.5746	0.2998	36.682
63.19	23.1	0.1524	0.3478	0.1522	0.3477	0.2370	0.3322	30.688	68.89	23.1	0.5004	0.3503	0.5005	0.3502	0.6191	0.2699	37.547
Dilution Line $V_1 = 49.20$ cm^3 + $V_3 = 17.00$ cm^3									Dilution Line $V_2 = 14.08$ cm^3 + $V_3 = 39.90$ cm^3								
0.00	21.7	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	37.129	0.00	23.1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.654
0.00	21.5	0.7144	0.0000	0.7024	0.0000	0.7674	0.0000	34.213	0.00	23.1	0.0000	0.3003	0.0000	0.3003	0.0000	0.3384	27.135
1.07	21.4	0.6991	0.0214	0.6841	0.0261	0.7381	0.0367	34.590	2.01	23.1	0.0296	0.2914	0.0295	0.2914	0.0517	0.3210	27.786
2.61	21.3	0.6782	0.0507	0.6670	0.0505	0.7117	0.0698	34.923	3.65	23.2	0.0524	0.2846	0.0523	0.2845	0.0896	0.3082	28.269
5.52	21.2	0.6419	0.1014	0.6328	0.0991	0.6612	0.1336	35.587	7.58	23.2	0.1030	0.2694	0.1029	0.2694	0.1680	0.2818	29.327
8.69	21.1	0.6066	0.1508	0.5968	0.1504	0.6109	0.1973	36.267	11.83	23.2	0.1520	0.2547	0.1519	0.2547	0.2377	0.2583	30.321
12.27	21.1	0.5711	0.2005	0.5620	0.1999	0.5647	0.2560	36.899	16.60	23.1	0.2010	0.2400	0.2008	0.2400	0.3021	0.2366	31.283
16.38	21.1	0.5352	0.2508	0.5267	0.2502	0.5200	0.3131	37.521	22.07	23.1	0.2506	0.2251	0.2505	0.2251	0.3629	0.2162	32.232
21.02	21.1	0.4997	0.3005	0.4917	0.3000	0.4777	0.3674	38.122	28.47	23.2	0.3014	0.2098	0.3013	0.2098	0.4211	0.1966	33.198
26.32	21.1	0.4645	0.3498	0.4566	0.3501	0.4369	0.4199	38.701	35.59	23.2	0.3503	0.1951	0.3503	0.1951	0.4740	0.1787	34.097
32.61	21.5	0.4286	0.4000	0.4281	0.4004	0.5547	0.3127	36.274	44.01	23.2	0.4000	0.1802	0.4000	0.1802	0.5248	0.1616	34.995
40.05	21.9	0.3928	0.4502	0.3923	0.4506	0.5239	0.3507	35.672	53.97	23.2	0.4499	0.1652	0.4499	0.1652	0.5731	0.1453	35.879
48.87	22.0	0.3574	0.4998	0.3569	0.5002	0.4929	0.3889	35.048	65.99	23.2	0.5000	0.1502	0.5000	0.1501	0.6195	0.1296	36.761

constant T, thermodynamics allows calculation of the y values. Thus, the equilibrium vapor need not be sampled for analysis and the data are thermodynamically consistent "per se".[21,22] Data reduction for the ternary mixtures was done by Barker's method[23] according to well-established procedures.[24,25]

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 by the Hayden and O'Connell method[26] using the parameters given by Dymond and Smith.[27]

The ternary systems di-isopropyl ether (DIPE) + 1-hexene + benzene and 1-hexene + benzene + cyclohexane were measured at 313.15 K. Data for these ternary systems were adequately correlated by the three-parameter Wohl equation,[28] which also includes the parameters of the corresponding binaries,

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

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

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

which is the Margules equation with up to four parameters.[29] It was chosen for fitting the binary mixtures.

The ternary systems were correlated using Wilson,[30] NRTL,[31] and UNIQUAC[32] models, whose expressions for the excess Gibbs energy are given by

$$\frac{G^{\mathrm{E}}}{RT} = -\sum_i x_i \ln\left(\sum_j x_jA_{ij}\right) \tag{3}$$

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

$$\frac{G^{\mathrm{E}}}{RT} = \sum_i x_i \ln\frac{\varphi_i}{x_i} + \frac{z}{2}\sum_i q_ix_i \ln\frac{\vartheta_i}{q_i} - \sum_i q_ix_i \ln\left(\sum_j \vartheta_jA_{ji}\right) \tag{5}$$

where

$$G_{ji} = \exp(-\alpha_{ji}A_{ji}), \quad \alpha_{ji} = 0.3, \quad \vartheta_i = \frac{q_ix_i}{\sum_j q_jx_j}, \quad \varphi_i = \frac{r_ix_i}{\sum_j r_jx_j},$$

and $z = 10$

Tables 1 and 2 give the original injected volumes, the temperature during the injection, the total cell composition (z_i), and the experimental values of total pressure with the

Table 3. Average Values of Experimental Vapor Pressures (P_i^{sat}) for the Pure Compounds Measured in This Work and Literature Values (P_i^{sat}) (lit.), 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**)	cyclohexane (**2**)	1-hexene (**3**)	benzene (**4**)
P_i^{sat} (kPa)	37.125	24.653	44.959	24.402
P_i^{sat} (lit.) (kPa)	37.081[a]	24.635[c]	44.979[c]	24.381[c]
	37.090[b]	24.630[d]	44.989[d]	24.383[d]
		24.634[e]	45.050[e]	24.369[e]
		24.670[f]	45.030[f]	24.320[f]
V_i^L (cm^3·mol^{-1})	145.4	110.8	128.6	91.0
B_{ii} (cm^3·mol^{-1})	−1688	−1554	−1510	−1311
B_{13} (cm^3·mol^{-1})	−1581			
B_{14} (cm^3·mol^{-1})	−1701			
B_{23} (cm^3·mol^{-1})		−1521		
B_{24} (cm^3·mol^{-1})		−1427		
B_{34} (cm^3·mol^{-1})			−1483	

[a] Calculated from the Antoine equation using constants reported by Riddick et al.[33] [b] Reported by Ambrose et al.[34] [c] Reported by Segovia.[1] [d] Reported by Montero.[35] [e] Calculated from the Antoine equation using constants reported in TRC tables.[36] [f] Calculated from the Antoine equation using constants reported by Reid et al.[37]

Table 4. Summary of Results for the Other Binary Systems Involved in the Ternary Systems at 313.15 K

	Margules (3 p.)	Wilson	NRTL	UNIQUAC
DIPE (**1**) + Cyclohexane (**2**)[a]				
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**)[b]				
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**)[c]				
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**)[b]				
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] Chamorro et al.[11] [b] Segovia et al.[5] [c] Segovia et al.[3]

corresponding compositions of the liquid, x_i, and vapor, y_i, phases for the ternary systems (DIPE + 1-hexene + benzene) and (1-hexene + benzene + cyclohexane), respectively, where the Wohl expansion has been used in the data reduction.

The average values of the experimental vapor pressures (P_i^{sat}) for the pure compounds compared with literature values (P_i^{sat}, literature), molar volumes of pure liquids (V_i^L), and second virial coefficients (B_{ii}, B_{ij}) are indicated in Table 3.

Results of the data correlation for the ternary systems are summarized in Tables4 and 5. Both 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 $\lvert\Delta P\rvert$).

Table 5. Summary of the Results Obtained for the Ternary System DIPE (1) + 1-Hexene (2) + Benzene (3) at 313.15 K

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.4215			
C_1	0.0443			
C_2	0.0353			
A_{12}		0.8730	−0.1777	0.9826
A_{21}		1.0988	0.2250	1.0074
A_{13}		0.5305	−0.5154	0.9217
A_{31}		1.4056	0.8217	1.0470
A_{23}		0.5435	−0.3087	0.9011
A_{32}		1.1621	0.7740	1.0021
$\alpha_{12} = \alpha_{23} = \alpha_{13}$			0.3	
rms ΔP (kPa)	0.010	0.008	0.008	0.009
max $\lvert\Delta P\rvert$ (kPa)	0.032	0.018	0.019	0.019

Table 6. Summary of the Results Obtained for the Ternary System 1-Hexene (1) + Benzene (2) +Cyclohexane (3) at 313.15 K

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.7692			
C_1	0.0852			
C_2	0.0535			
A_{12}		0.5784	−0.2627	0.9769
A_{21}		1.1167	0.7080	1.0103
A_{13}		0.6331	−0.4034	0.8857
A_{31}		1.3059	0.6035	1.0202
A_{23}		0.9431	0.5435	0.8151
A_{32}		0.6401	−0.0431	1.0361
$\alpha_{12} = \alpha_{23} = \alpha_{13}$			0.3	
rms ΔP (kPa)	0.011	0.013	0.012	0.011
max $\lvert\Delta P\rvert$ (kPa)	0.022	0.046	0.038	0.034

Discussion

We have not found literature data available for comparison for any of the ternary systems presented in this paper.

The meaurements for the ternary di-isopropyl ether (DIPE) + 1-hexene + benzene were well-correlated by all the models, showing root-mean-square pressure residuals of 8 Pa, with a maximum value of the absolute deviation at a pressure of 18 Pa for the Wilson equation which corresponds to the best fit.

For the system 1-hexene + benzene + cyclohexane again, all the models closely correlated the experimental values. The value of the root-mean-square pressure residuals was 11 Pa, with a maximum value of the absolute deviation at a pressure of 22 Pa, for the Wohl expansion. The binary system benzene + cyclohexane has an azeotrope; nevertheless, the addition of the third component 1-hexene destroys this azeotrope.

Graphical results for the ternary systems are in Figures 1−4. They show an 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 the less volatile compound to the saturation pressure of the more volatile compound. The two measured ternary systems show slight positive deviations from ideality; the molar excess Gibbs energy also increases up to a maximum value, which corresponds to a less ideal binary system. The ternary system di-isopropyl ether (DIPE) + 1-hexene + benzene + cyclohexane is the least ideal ternary system because the binary benzene + cyclohexane is also the least ideal binary

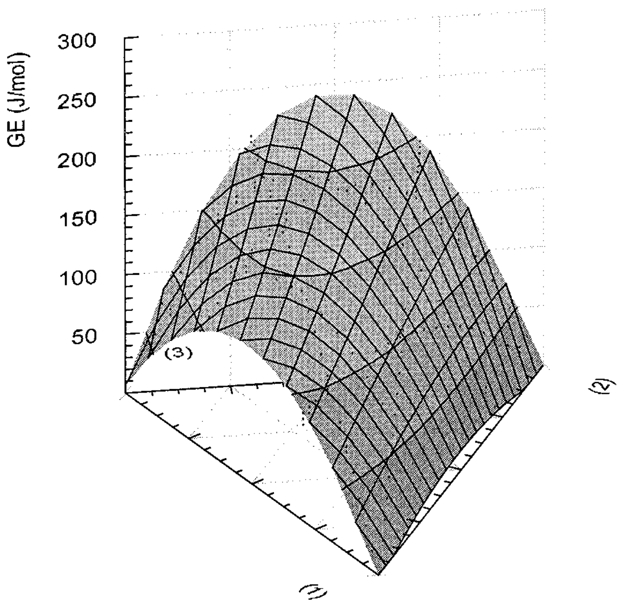

Figure 3. Oblique view of the constant excess Gibbs energy, G^E (J mol$^{-1)}$, for the DIPE (1) + 1-hexene (2) + benzene (3) system at 313.15 K.

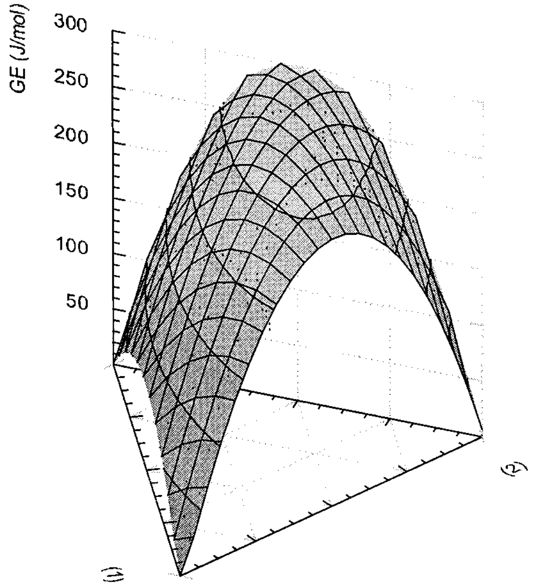

Figure 4. Oblique view of the constant excess Gibbs energy, G^E (J mol^{-1}), for the 1-hexene (1) + benzene (2) + cyclohexane (3) system at 313.15 K.

system, with a maximum value of G^E around 300 J·mol^{-1}. On the other hand, the highest value of G^E for the ternary system DIPE + 1-hexene + benzene is around 236 J·mol^{-1} which corresponds to the binary 1-hexene + benzene.

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