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Thermodynamics of Octane-Enhancing Additives in Gasolines: Vapor−Liquid Equilibrium of the Ternary Mixtures Methyl *tert*-Butyl Ether + Heptane + Benzene and Methyl *tert*-Butyl Ether + Benzene + 1-Hexene at 313.15 K†

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Experimental isothermal $P-x-y$ data for the ternary systems methyl *tert*-butyl ether (MTBE) + heptane + benzene and methyl *tert*-butyl ether (MTBE) + benzene + 1-hexene and for the binaries heptane + benzene and benzene + 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 systems and the Wohl expansion for the ternaries. Wilson, NRTL, and UNIQUAC models have been applied successfully to both the binary and the ternary systems presented here.

Introduction

Methyl *tert*-butyl ether (MTBE) is being used presently as a blending agent in the formulation of the new gasolines for enhancing the octane number in substitution of traditional leaded products. To better understand and model the new formulated gasolines, we started four years ago 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, olefins); MTBE was chosen as an additive.

In previous papers (Segovia et al., 1997, 1998; Segovia, 1997), we published the study of the ternary systems MTBE + benzene + cyclohexane and MTBE + heptane + 1-hexene and their corresponding binary mixtures at 313.15 K.

In this paper, two new ternary systems MTBE + heptane + benzene and MTBE + benzene + 1-hexene and the binaries heptane + benzene and benzene + 1-hexene at 313.15 K are presented.

Experimental Section

Materials. All 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% (GC) for MTBE, benzene, and heptane and >98% (GC) for 1-hexene, having checked in our laboratory the indicated assesments by gas chromatography and obtaining the following values: >99.9% (GC) for MTBE and benzene and >99.8% (GC) for 1-hexene and *n*-heptane. All liquids were thoroughly degassed previous to measurements using a modified distillation method based on the one suggested by Van Ness and Abbott (1978) and kept in glass balloons with leakproof 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 (Gibbs and Van Ness, 1972; Dielsi et al., 1978) and whose performance has been described in a previous paper (Lozano et al., 1995).

Table 1. Total-Pressure Data for Heptane (1) + Benzene (2) at 313.15 K

x_1	y_1(calcd)	P/kPa	x_1	y_1(calcd)	P/kPa
0.0000	0.0000	24.380	0.5004	0.3247	21.031
0.0520	0.0466	24.305	0.5494	0.3590	20.433
0.1020	0.0842	24.145	0.5508	0.3600	20.421
0.1486	0.1151	23.934	0.6009	0.3985	19.763
0.1989	0.1458	23.655	0.6501	0.4401	19.068
0.2485	0.1746	23.337	0.7008	0.4884	18.284
0.2982	0.2028	22.970	0.7500	0.5417	17.468
0.3490	0.2316	22.550	0.8005	0.6048	16.581
0.3993	0.2610	22.094	0.8472	0.6728	15.671
0.4009	0.2620	22.084	0.9128	0.7895	14.305
0.4490	0.2913	21.596	0.9469	0.8626	13.561
0.4505	0.2923	21.586	1.0000	1.0000	12.331
0.4989	0.3237	21.035			

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

x_1	y_1(calcd)	P/kPa	x_1	y_1(calcd)	P/kPa
0.0000	0.0000	44.973	0.5008	0.3619	37.762
0.0384	0.0285	44.524	0.5506	0.4006	36.860
0.0963	0.0707	43.803	0.5510	0.4009	36.845
0.1492	0.1088	43.125	0.6011	0.4417	35.883
0.2010	0.1457	42.427	0.6516	0.4853	34.852
0.2507	0.1809	41.732	0.7018	0.5320	33.754
0.3007	0.2164	41.000	0.7506	0.5821	32.583
0.3501	0.2515	40.251	0.8005	0.6392	31.284
0.4008	0.2879	39.454	0.8554	0.7122	29.709
0.4503	0.3240	38.642	0.8870	0.7606	28.700
0.4507	0.3243	38.634	0.9476	0.8727	26.541
0.5007	0.3619	37.767	1.0000	1.0000	24.381

The piston injectors are three 100 mL positive displacement pumps (Ruska, model 2200-801) with a resolution of 0.01 mL and an estimated total uncertainty of ±0.03 mL, allowing the injection of known volumes of the pure com-

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Table 3. Total-Pressure Data for MTBE (1) + Heptane (2) + Benzene (3) at 313.15 K

x_1	x_2	y_1(calcd)	y_2(calcd)	P/kPa	x_1	x_2	y_1(calcd)	y_2(calcd)	P/kPa
1.0000	0.0000	1.0000	0.0000	59.906	0.0000	0.0000	0.0000	0.0000	24.391
0.7044	0.0000	0.8425	0.0000	50.227	0.2925	0.0000	0.5122	0.0000	36.259
0.6869	0.0249	0.8345	0.0086	49.346	0.2855	0.0241	0.5024	0.0131	35.755
0.6702	0.0486	0.8269	0.0168	48.490	0.2784	0.0483	0.4930	0.0258	35.253
0.6339	0.1001	0.8105	0.0346	46.704	0.2635	0.0993	0.4745	0.0515	34.228
0.5984	0.1506	0.7943	0.0523	45.022	0.2489	0.1493	0.4577	0.0757	33.253
0.5632	0.2006	0.7781	0.0702	43.352	0.2345	0.1989	0.4420	0.0992	32.298
0.5279	0.2508	0.7615	0.0888	41.674	0.2199	0.2489	0.4267	0.1228	31.321
0.4931	0.3001	0.7445	0.1080	40.030	0.2049	0.3002	0.4114	0.1475	30.312
0.4579	0.3502	0.7265	0.1287	38.345	0.1905	0.3494	0.3968	0.1721	29.340
0.4234	0.3992	0.7077	0.1504	36.687	0.1760	0.3991	0.3819	0.1981	28.329
0.3872	0.4506	0.6865	0.1751	34.929	0.1614	0.4488	0.3665	0.2259	27.305
0.3517	0.5009	0.6638	0.2018	33.170	0.1467	0.4991	0.3503	0.2562	26.229
0.0000	0.0000	0.0000	0.0000	24.381	1.0000	0.0000	1.0000	0.0000	59.917
0.0000	0.3004	0.0000	0.2040	22.960	0.7039	0.2961	0.9101	0.0899	47.098
0.0268	0.2924	0.0694	0.1897	24.076	0.6911	0.2908	0.8993	0.0893	46.740
0.0507	0.2852	0.1261	0.1781	25.029	0.6694	0.2816	0.8809	0.0880	46.092
0.1019	0.2698	0.2328	0.1561	27.020	0.6328	0.2662	0.8492	0.0859	45.018
0.1499	0.2554	0.3187	0.1384	28.840	0.5992	0.2521	0.8195	0.0839	44.048
0.1994	0.2405	0.3959	0.1226	30.717	0.5647	0.2375	0.7884	0.0818	43.051
0.2496	0.2254	0.4649	0.1084	32.592	0.5277	0.2219	0.7543	0.0794	41.996
0.2992	0.2105	0.5255	0.0960	34.440	0.4933	0.2074	0.7217	0.0771	40.989
0.3563	0.1934	0.5876	0.0833	36.558	0.4579	0.1925	0.6874	0.0745	39.960
0.3992	0.1805	0.6299	0.0747	38.140	0.4230	0.1778	0.6526	0.0719	38.947
0.4487	0.1656	0.6745	0.0656	39.957	0.3875	0.1629	0.6158	0.0690	37.893
0.4987	0.1506	0.7158	0.0572	41.786	0.3522	0.1480	0.5779	0.0659	36.844
0.0000	1.0000	0.0000	1.0000	12.337	0.0000	1.0000	0.0000	1.0000	12.342
0.0000	0.6973	0.0000	0.4849	18.387	0.3004	0.6996	0.6892	0.3108	28.777
0.0315	0.6753	0.1044	0.4364	19.889	0.2931	0.6826	0.6689	0.3040	28.779
0.0545	0.6593	0.1707	0.4056	20.922	0.2867	0.6677	0.6513	0.2980	28.777
0.0978	0.6291	0.2770	0.3561	22.869	0.2708	0.6305	0.6084	0.2833	28.762
0.1500	0.5927	0.3814	0.3072	25.223	0.2554	0.5947	0.5688	0.2696	28.727
0.1977	0.5594	0.4602	0.2702	27.309	0.2407	0.5603	0.5320	0.2567	28.675
0.2475	0.5246	0.5298	0.2373	29.474	0.2253	0.5243	0.4948	0.2435	28.600
0.2995	0.4884	0.5917	0.2078	31.633	0.2105	0.4898	0.4603	0.2312	28.508
0.3487	0.4541	0.6426	0.1834	33.677	0.1953	0.4545	0.4262	0.2187	28.397
0.3987	0.4192	0.6882	0.1614	35.753	0.1803	0.4195	0.3932	0.2064	28.280
0.4486	0.3845	0.7284	0.1417	37.783	0.1653	0.3846	0.3612	0.1942	28.122
0.4986	0.3496	0.7647	0.1238	39.808	0.1504	0.3498	0.3299	0.1819	27.957

ponents, previously degassed, into the cell immersed in a high-precision water bath (Hart Scientific model 6020) ensuring a stability of 0.5 mK and thermostated at 313.15 K.

The cell is a cylindrical stainless steel piece with a capacity of about 180 mL and a magnetic stirrer externally operated. An initial amount of about 50 mL of one component is injected into the evacuated cell, the vapor pressure is recorded, and successive increases in composition of a second or a third component are generated until we nearly fill the cell completing a desired composition range. The total amount of mass injected is accurately determined from the volume differences read between two stop-points of the piston, the temperature of the injector and the value of the density for that pure component allowing us to ensure four digits in the value of the mole fraction. The stop-point for advancing the piston is in all cases determined by an accurate break-point torque wrench, set to overbalance the frictional effect of the packing around the piston.

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 done starting with 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 a calibrated standard PRT-100 (SDL model 5385/100) using as indicator an a/c resistance bridge (ASL model F250) resolving 1 mK in the reading of temperature and estimating an overall uncertainty of ±10 mK. The measurement of the pressure was done indirectly through a differential pressure cell and indicator (Ruska models 2413-705 and 2416-711, respectively). Once air balances the vapor pressure of the cell, a Bourdon fused quartz precision pressure gauge (Texas Instruments model 801) provided with a capsule reads the pressure with an estimated uncertainty of ±5 Pa for the 125 kPa range.

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; the mass of vapor in the cell is very small, yet 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, in fact, 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 for analysis, and the data are thermodynamically consistent "per se" (Van Ness and Abbott, 1982; Van Ness, 1995).

Data reduction for the binary and ternary mixtures was done by Barker's method (1953) according to well-established procedures (Abbott and Van Ness, 1975; Abbott et al., 1975), developing a computer program described in detail earlier (Lozano et al., 1995).

Table 4. Total-Pressure Data for MTBE (1) + Benzene (2) + 1-Hexene at 313.15 K

x_1	x_2	y_1(calcd)	y_2(calcd)	P/kPa	x_1	x_2	y_1(calcd)	y_2(calcd)	P/kPa
1.0000	0.0000	1.0000	0.0000	59.925	0.7005	0.2995	0.8401	0.1599	50.115
0.7004	0.0000	0.7481	0.0000	56.463	0.6802	0.2909	0.8143	0.1559	50.120
0.6884	0.0173	0.7408	0.0090	55.972	0.6652	0.2845	0.7954	0.1530	50.120
0.6660	0.0492	0.7272	0.0260	55.081	0.6306	0.2696	0.7529	0.1462	50.094
0.6298	0.1009	0.7046	0.0540	53.588	0.5948	0.2543	0.7102	0.1392	50.044
0.5954	0.1500	0.6827	0.0815	52.203	0.5608	0.2397	0.6705	0.1326	49.964
0.5597	0.2010	0.6593	0.1109	50.759	0.5260	0.2248	0.6306	0.1258	49.849
0.5254	0.2499	0.6362	0.1401	49.378	0.4913	0.2100	0.5914	0.1190	49.717
0.4907	0.2995	0.6120	0.1708	47.950	0.4559	0.1948	0.5518	0.1120	49.553
0.4554	0.3499	0.5866	0.2033	46.514	0.4213	0.1800	0.5133	0.1050	49.375
0.4201	0.4003	0.5601	0.2373	45.053	0.3863	0.1650	0.4744	0.0978	49.164
0.3853	0.4499	0.5329	0.2725	43.594	0.3513	0.1500	0.4354	0.0904	48.927
0.3502	0.5000	0.5039	0.3101	42.102	0.0000	1.0000	0.0000	1.0000	24.383
0.0000	1.0000	0.0000	1.0000	24.382	0.0000	0.6929	0.0000	0.5235	33.984
0.2931	0.7069	0.5129	0.4871	36.267	0.0257	0.6751	0.0457	0.5007	34.661
0.2853	0.6881	0.4888	0.4695	36.793	0.0493	0.6587	0.0861	0.4806	35.303
0.2769	0.6679	0.4647	0.4516	37.291	0.1002	0.6234	0.1675	0.4397	36.653
0.2643	0.6372	0.4309	0.4259	38.015	0.1491	0.5895	0.2397	0.4033	37.956
0.2489	0.6001	0.3938	0.3970	38.782	0.1998	0.5544	0.3089	0.3682	39.280
0.2352	0.5669	0.3636	0.3727	39.409	0.2498	0.5198	0.3725	0.3357	40.586
0.2204	0.5312	0.3337	0.3479	40.049	0.2991	0.4856	0.4312	0.3055	41.874
0.1909	0.4598	0.2798	0.3009	41.138	0.3500	0.4503	0.4879	0.2761	43.191
0.1766	0.4255	0.2559	0.2792	41.607	0.3995	0.4160	0.5398	0.2490	44.479
0.1619	0.3899	0.2323	0.2570	42.058	0.4540	0.3782	0.5937	0.2208	45.894
0.1471	0.3541	0.2095	0.2348	42.475	0.4998	0.3465	0.6364	0.1982	47.073
0.0000	0.0000	0.0000	0.0000	44.993	0.0000	0.0000	0.0000	0.0000	44.975
0.3231	0.0000	0.3952	0.0000	50.967	0.0000	0.2942	0.0000	0.2118	41.137
0.3164	0.0206	0.3891	0.0127	50.574	0.0249	0.2869	0.0368	0.2036	41.655
0.3076	0.0477	0.3810	0.0296	49.992	0.0493	0.2797	0.0719	0.1958	42.170
0.2916	0.0976	0.3663	0.0608	48.939	0.0992	0.2651	0.1406	0.1805	43.215
0.2750	0.1488	0.3513	0.0930	47.847	0.1509	0.2498	0.2081	0.1656	44.275
0.2593	0.1976	0.3369	0.1242	46.781	0.1990	0.2357	0.2677	0.1524	45.248
0.2426	0.2491	0.3216	0.1576	45.659	0.2585	0.2182	0.3377	0.1370	46.441
0.2272	0.2970	0.3074	0.1891	44.598	0.2993	0.2062	0.3836	0.1270	47.233
0.2107	0.3479	0.2920	0.2236	43.473	0.3495	0.1914	0.4379	0.1152	48.215
0.1949	0.3970	0.2770	0.2577	42.368	0.3993	0.1767	0.4897	0.1041	49.169
0.1786	0.4473	0.2613	0.2939	41.205	0.4494	0.1620	0.5397	0.0933	50.123
1.0000	0.0000	1.0000	0.0000	59.903	0.5005	0.1469	0.5890	0.0829	51.079

The nonideality of the vapor phase was taken into account with the virial equation of state, truncated in the second term. The second virial coefficients were calculated by the Hayden and O'Connell method (1975) using the parameters given by Dymond and Smith (1980).

The ternary systems methyl *tert*-butyl ether + heptane + benzene and methyl *tert*-butyl ether + benzene + 1-hexene and the binaries heptane + benzene and benzene + 1-hexene were measured at 313.15 K. Data for these ternary systems were adequately correlated by the three-parameter Wohl equation (Wohl, 1953), which also includes the parameters of the corresponding binaries.

$$g_{123} = \frac{G^{E}}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1 x_1 + C_2 x_2) x_1 x_2 x_3 \quad (1)$$

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 equation

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

which is the Margules equation up to four parameters (Margules, 1895). It was chosen for fitting the binary mixtures.

Binary and ternary systems were correlated using Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) models, whose expressions for the excess Gibbs energy are indicated by

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

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

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

where $G_{ji} = \exp(-\alpha_{ji} A_{ji})$; $\alpha_{ji} = 0.3$; $\vartheta_i = \dfrac{q_i x_i}{\sum_j q_j x_j}$;

$\varphi_i = \dfrac{r_i x_i}{\sum_j r_j x_j}$ and $z = 10$

Tables 1 and 2 give experimental values of total pressure and the corresponding compositions of the liquid and vapor phases for the binary systems. Tables 3 and 4 give the same information for the ternary systems. In these tables the compositions of the vapor phases were reduced by the

Table 5. Average Values of Experimental Vapor Pressures (P_i^{sat}) for the Pure Compounds, 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

	MTBE (1)	heptane (2)	benzene (3)	1-hexene (4)
P_i^{sat}/kPa	59.907	12.331	24.381	44.979
V_i^{L}/cm^3·mol^{-1}	122	150	91	129
B_{ii}/cm^3·mol^{-1}	−1426	−2520	−1310	−1510
B_{12}/cm^3·mol^{-1}	−1857	−1857		
B_{13}/cm^3·mol^{-1}	−1559		−1559	
B_{14}/cm^3·mol^{-1}	−1450			−1450
B_{23}/cm^3·mol^{-1}		−1813	−1813	
B_{24}/cm^3·mol^{-1}		−1919		−1919
B_{34}/cm^3·mol^{-1}			−1482	−1482

Table 6. Summary of Results of the Correlation for the Two Binary Systems at 313.15 K

Heptane (1) + Benzene (2)

	Margules (4 p.)	Wilson	NRTL	UNIQUAC
A_{12}	0.665 98	0.420 34	−0.408 85	0.800 22
A_{21}	0.392 52	1.196 77	1.116 06	1.053 92
λ_{12}	0.180 91			
λ_{21}	0.078 57			
rms ΔP/kPa	0.005	0.006	0.010	0.006
max $\lvert\Delta P\rvert$/kPa	0.014	0.015	0.025	0.018

Benzene (1) + 1-Hexene (2)

	Margules (3 p.)	Wilson	NRTL	UNIQUAC
A_{12}	0.307 86	1.131 46	0.744 00	1.046 17
A_{21}	0.429 23	0.568 22	−0.289 35	0.861 21
λ_{12}	0.037 06			
λ_{21}	0.037 06			
rms ΔP/kPa	0.004	0.005	0.005	0.004
max $\lvert\Delta P\rvert$/kPa	0.007	0.013	0.010	0.009

Table 7. Summary of Results of the Correlation for the Binary Systems Containing MTBE at 313.15 K

	Margules	Wilson	NRTL	UNIQUAC
MTBE (1) + Heptane (2)^a				
A_{12}	0.239 92	0.981 06	0.298 70	1.059 33
A_{21}	0.258 71	0.792 15	−0.046 52	0.884 23
$\lambda_{12} = \lambda_{21}$	0.040 26			
rms ΔP/kPa	0.022	0.029	0.030	0.030
max $\lvert\Delta P\rvert$/kPa	0.045	0.054	0.055	0.055
MTBE (1) + Benzene (2)^b				
A_{12}	0.171 25	0.643 06	−0.384 80	0.849 75
A_{21}	0.118 43	1.264 63	0.606 80	1.176 82
rms ΔP/kPa	0.015	0.019	0.017	0.022
max $\lvert\Delta P\rvert$/kPa	0.023	0.038	0.033	0.048
MTBE (1) + 1-Hexene (2)^a				
A_{12}	0.084 45	1.041 20	0.198 28	0.899 05
A_{21}	0.094 37	0.869 29	−0.096 57	1.084 13
$\lambda_{12} = \lambda_{21}$	−0.022 52			
rms ΔP/kPa	0.013	0.017	0.016	0.016
max $\lvert\Delta P\rvert$/kPa	0.031	0.045	0.045	0.045

[a] Segovia et al., 1998. [b] Segovia et al., 1997.

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

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.844 16			
C_1	0.035 97			
C_2	−0.026 13			
A_{12}		1.046 13	0.423 14	1.002 73
A_{21}		0.737 78	−0.157 50	0.938 33
A_{13}		0.575 26	−0.459 97	0.844 62
A_{31}		1.361 21	0.713 46	1.182 82
A_{23}		0.440 77	−0.374 42	0.787 30
A_{32}		1.151 66	1.077 80	1.064 16
rms ΔP/kPa	0.032	0.030	0.029	0.033
max $\lvert\Delta P\rvert$/kPa	0.083	0.090	0.089	0.088

Table 9. Summary of the Results Obtained for the Ternary System MTBE (1) + Benzene (2) + 1-Hexene (3) at 313.15 K

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.595 67			
C_1	−0.032 01			
C_2	−0.064 99			
A_{12}		0.593 12	−0.432 63	0.866 07
A_{21}		1.331 01	0.677 62	1.156 73
A_{13}		0.962 94	0.058 75	1.007 31
A_{31}		0.941 93	0.038 36	0.971 31
A_{23}		1.122 99	0.714 80	1.047 09
A_{32}		0.572 31	−0.266 27	0.858 98
rms ΔP/kPa	0.019	0.014	0.014	0.017
max $\lvert\Delta P\rvert$/kPa	0.053	0.029	0.028	0.042

Table 10. Results of the Prediction for the Ternary Systems at 313.15 K

	Wilson	NRTL	UNIQUAC
MTBE (1) + Heptane (2) + Benzene (3)			
rms ΔP/kPa	0.036	0.037	0.057
max $\lvert\Delta P\rvert$/kPa	0.071	0.085	0.134
MTBE (1) + Benzene (2) + 1-Hexene (3)			
rms ΔP/kPa	0.024	0.026	0.023
max $\lvert\Delta P\rvert$/kPa	0.058	0.059	0.056

Margules equation for the binary systems and the Wohl expansion for the ternary systems.

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}, B_{ij}) are indicated in Table 5.

Results of data correlation for the binary systems are summarized in Table 6. The results of the correlation of the binaries containing MTBE have been published previously (Segovia et al., 1997, 1998), and these are summarized in Table 7. For the ternary systems, the results of the correlation are given in Tables 8 and 9. All 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 $|\Delta P|$).

The expressions of the excess Gibbs energy for multicomponent systems using the Wilson, NRTL, and UNIQUAC models only depend on the binary interaction parameters that can be adjusted directly from the multicomponent data or can be obtained from the binary systems and used for predicting the behavior of the ternary mixture. In Table 10 are summarized the results of the prediction for the ternary systems using the correlation parameters of the binaries.

Discussion

We have not found any literature data available for comparison concerning both ternary systems at 313.15 K. Heptane + benzene at 313.15 K has been measured previously by our research group, and it was published (Lozano et al., 1997) and also by Góral et al. (1994). We have measured it again obtaining a better result for the correlation; in Table 11 the results obtained using the Margules equation for the three determinations are compared. The value of the root-mean-square pressure residuals for the new set of data was 5 Pa with a maximum of 14 Pa, and the literature data give slightly higher values for both statistical parameters.

Table 11. Comparison of the Data Reduction of This Work and Two Literature Data for the Binary System Heptane (1) + Benzene (2) at 313.15 K, Using the Margules Equation

	this work	Góral (1994)	Lozano et al. (1997)
P_1^{sat} (kPa)	12.331	12.334	12.338
P_2^{sat} (kPa)	24.381	24.366	24.376
A_{12}	0.665 98	0.655 47	0.661 00
A_{21}	0.392 52	0.456 89	0.406 30
λ_{12}	0.180 91	0.086 70	0.139 10
λ_{21}	0.078 57	0.257 18	0.139 10
rms ΔP/kPa	0.005	0.012	0.011
max $\lvert\Delta P\rvert$/kPa	0.014	0.024	0.022

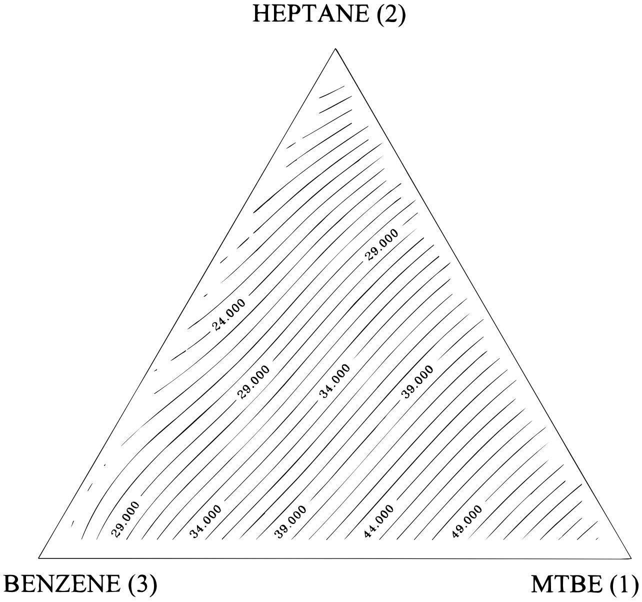

Figure 1. Lines of constant pressure, P/kPa, for the MTBE (1) + heptane (2) + benzene (3) system at 313.15 K.

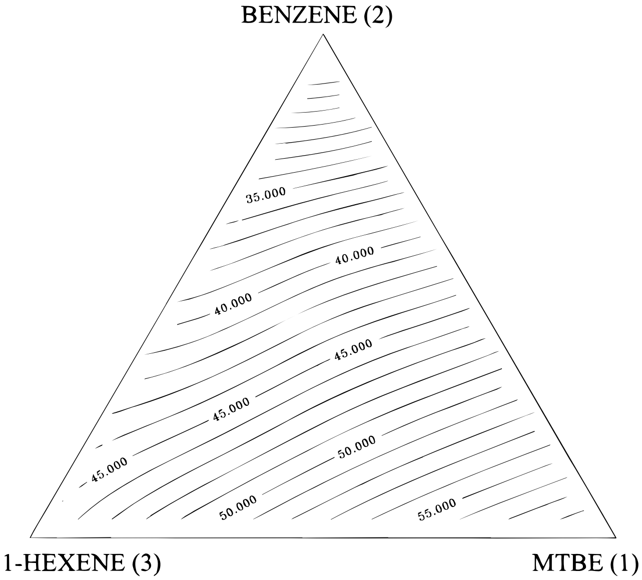

Figure 2. Lines of constant pressure, P/kPa, for the MTBE (1) + benzene (2) + 1-hexene (3) system at 313.15 K.

The two binary systems studied present a slight positive deviation from ideality, and the results of the correlation gave a root-mean-square pressure residuals between 4 Pa for the system benzene + 1-hexene and 5 Pa for the other binary using the Margules equation of three and four parameters, respectively. The other models, Wilson, NRTL, and UNIQUAC, gave almost the same values.

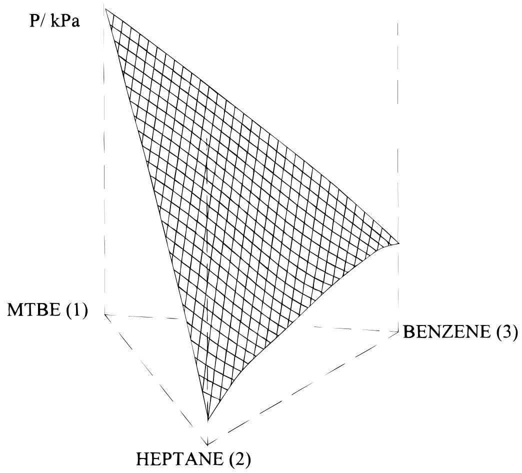

Figure 3. Oblique view of the constant pressure, P/kPa, for the MTBE (1) + heptane (2) + benzene (3) system at 313.15 K.

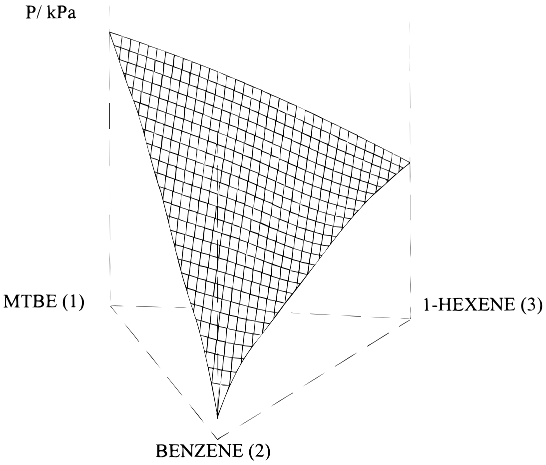

Figure 4. Oblique view of the constant pressure, P/kPa, for the MTBE (1) + benzene (2) + 1-hexene (3) system at 313.15 K.

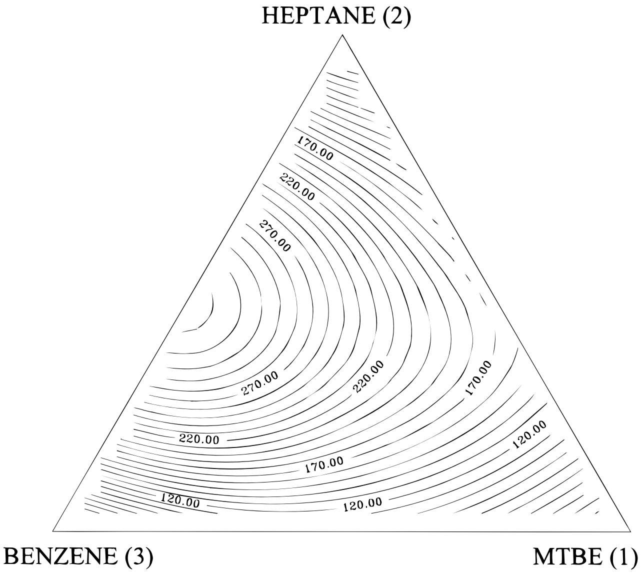

Figure 5. Lines of constant excess Gibbs energy, G^E/J mol^{-1}, for the MTBE (1) + heptane (2) + benzene (3) system at 313.15 K.

The results for the ternary MTBE + heptane + benzene were well correlated by all the models, showing a root-mean-square pressure residual of 32 Pa, with a maximum value of the absolute deviation in pressure of 83 Pa for the

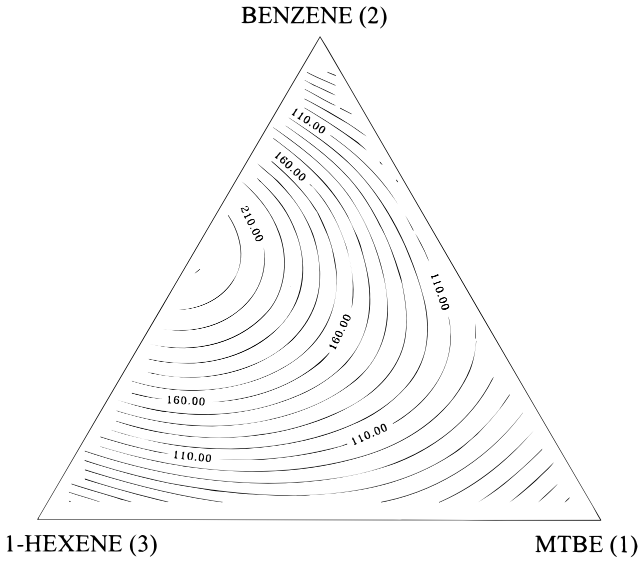

Figure 6. Lines of constant excess Gibbs energy, G^E/J mol^{-1}, for the MTBE (1) + benzene (2) + 1-hexene (3) system at 313.15 K.

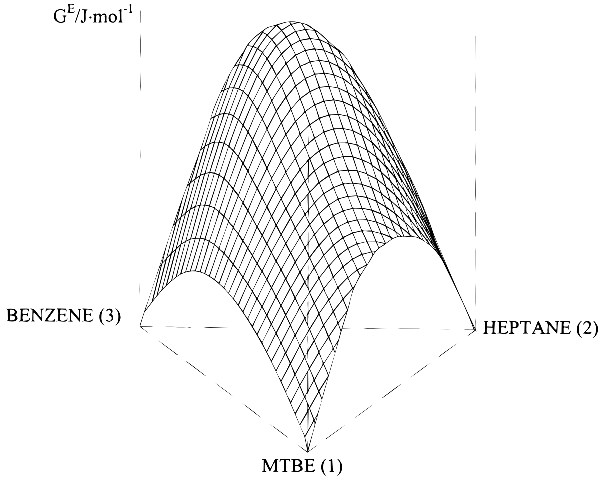

Figure 7. Oblique view of the constant excess Gibbs energy, G^E/J mol^{-1}, for the MTBE (1) + heptane (2) + benzene (3) system at 313.15 K.

Wohl equation and up to 90 Pa for the other equations, within a maximum range of pressure close to 60 kPa.

For the system MTBE + benzene+ 1-hexene, all the models correlated well the experimental values but the best results were obtained with NRTL and Wilson models. The value of the root-mean-square pressure residuals was 14 Pa for both, with a maximum value of the absolute deviation in pressure of 28 and 29 Pa, respectively; for the other models the maximum value of root-mean-square pressure residuals was 19 Pa for the Wohl equation, and the highest value of the maximum absolute deviation in pressure was 53 Pa for the same model.

Graphical results for the ternary systems are shown by the contour diagrams of Figures 1−8. Lines of constant pressure are shown in Figures 1 and 2; lines of constant excess Gibbs energy, G^E, are shown in Figures 3 and 4, and the oblique view of the pressure and of the excess Gibbs energy surface for the ternary systems is shown in Figures 5−8.

The total equilibrium pressure is always increasing 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 a positive deviation from ideality; the behavior of the molar excess Gibbs energy is also increasing up to a maximum value, which corresponds to the less ideal binary system. The ternary system MTBE + heptane + benzene is the least ideal ternary system because the binary heptane + benzene is also the least ideal binary system, with a maximum value of G^E of 328 J·mol^{-1}. On the other hand, the highest value of G^E for the ternary system MTBE + benzene + 1-hexene is 235 J·mol^{-1}, which corresponds to the binary benzene + 1-hexene.

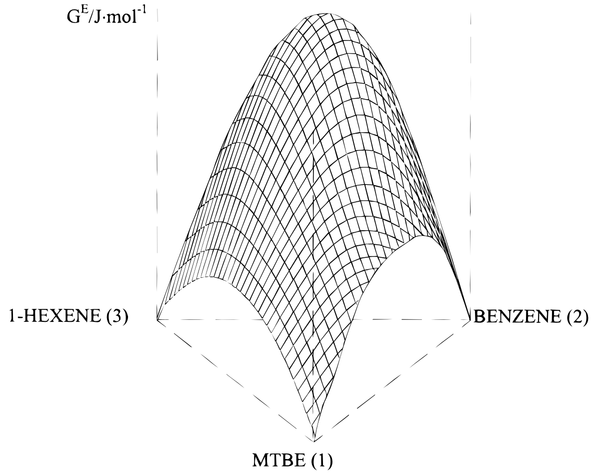

Figure 8. Oblique view of the constant excess Gibbs energy, G^E/J mol^{-1}, for the MTBE (1) + benzene (2) + 1-hexene (3) system at 313.15 K.

Finally the results of the prediction for the ternary system using the Wilson equation are only slightly bigger than those obtained directly from the ternary experimental data.

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