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Vapor−Liquid Equilibrium of Ternary Mixtures Containing Methyl *tert*-Butyl Ether and/or Substitution Hydrocarbons. Methyl *tert*-Butyl Ether + Heptane + Cyclohexane and Methyl *tert*-Butyl Ether + Cyclohexane + 1-Hexene at 313.15 K[†]

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Experimental isothermal $P-x-y$ data for the ternary systems methyl *tert*-butyl ether + heptane + cyclohexane and methyl *tert*-butyl ether + cyclohexane + 1-hexene at 313.15 K and for the binaries cyclohexane + heptane and cyclohexane + 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

For the purpose of studying the thermodynamic characterization of unleaded gasolines, methyl *tert*-butyl ether (MTBE) was chosen as an additive, and we are measuring the vapor−liquid equilibrium of ternary mixtures containing MTBE and hydrocarbons (paraffins, cycloparaffins, aromatics, olefins) that are components of gasolines.

In previous papers, the vapor−liquid equilibrium data of other ternary systems containing MTBE and their corresponding binaries, all of them measured at 313.15 K, were published (Segovia et al., 1997, 1998a,b; Segovia (1997)).

Vapor−liquid equilibrium measurements are reported for two new ternary systems MTBE + heptane + cyclohexane and MTBE + cyclohexane + 1-hexene and the binaries cyclohexane + heptane and cyclohexane + 1-hexene at 313.15 K.

Experimental Section

Materials. All the chemicals used 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, cyclohexane, and heptane and >98% (GC) for 1-hexene, checked by gas chromatography in our laboratory, and the values obtained were >99.9% (GC) for MTBE and cyclohexane and >99.8% (GC) for 1-hexene and *n*-heptane. All sustances were thoroughly degassed using a modified distillation method based on the one suggested by Van Ness and Abbott (1978).

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 Cyclohexane (1) + Heptane (2) at 313.15 K

x_1	y_1(calcd)	P/kPa	x_1	y_1(calcd)	P/kPa
0.0000	0.0000	12.329	0.5443	0.7030	19.308
0.0539	0.1054	13.062	0.5501	0.7078	19.357
0.1009	0.1878	13.670	0.5990	0.7463	19.976
0.1465	0.2605	14.283	0.6002	0.7472	19.970
0.1985	0.3361	14.940	0.6501	0.7842	20.567
0.2482	0.4020	15.584	0.7001	0.8193	21.174
0.2980	0.4625	16.223	0.7500	0.8526	21.753
0.3483	0.5190	16.866	0.7994	0.8840	22.334
0.3980	0.5707	17.491	0.8498	0.9147	22.912
0.4489	0.6198	18.131	0.9015	0.9449	23.499
0.4501	0.6209	18.121	0.9529	0.9740	24.096
0.4984	0.6643	18.740	1.0000	1.0000	24.635
0.5005	0.6661	18.749			

Table 2. Total-Pressure Data for Cyclohexane (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	44.992	0.5009	0.3606	35.784
0.0416	0.0258	44.241	0.5504	0.4046	34.786
0.0989	0.0624	43.210	0.5509	0.4051	34.799
0.1509	0.0965	42.285	0.6018	0.4530	33.785
0.2001	0.1297	41.384	0.6502	0.5013	32.798
0.2510	0.1652	40.458	0.7017	0.5560	31.727
0.2997	0.2004	39.555	0.7514	0.6130	30.657
0.3493	0.2374	38.634	0.8020	0.6760	29.545
0.3995	0.2765	37.688	0.8523	0.7447	28.381
0.4010	0.2776	37.708	0.8951	0.8092	27.367
0.4504	0.3177	36.725	0.9677	0.9353	25.537
0.4508	0.3180	36.758	1.0000	1.0000	24.644
0.5006	0.3602	35.759			

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 components, previously degassed, into the cell immersed in a high-precision water bath (Hart Scientific model 6020) ensuring an 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

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Table 3. Total-Pressure Data for MTBE (1) + Heptane (2) + Cyclohexane (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
0.0000	1.0000	0.0000	1.0000	12.331	1.0000	0.0000	1.0000	0.0000	59.919
0.0000	0.6983	0.0000	0.5331	16.255	0.7042	0.0000	0.8313	0.0000	51.650
0.0346	0.6742	0.1393	0.4586	18.371	0.6827	0.0305	0.8257	0.0087	50.553
0.0623	0.6548	0.2284	0.4109	19.936	0.6690	0.0498	0.8220	0.0142	49.875
0.0960	0.6313	0.3172	0.3634	21.728	0.6335	0.1004	0.8118	0.0293	48.056
0.1496	0.5939	0.4281	0.3041	24.550	0.5982	0.1505	0.8009	0.0451	46.282
0.1996	0.5589	0.5084	0.2611	27.071	0.5630	0.2005	0.7891	0.0618	44.501
0.2504	0.5235	0.5744	0.2259	29.497	0.5278	0.2504	0.7763	0.0795	42.716
0.2976	0.4905	0.6256	0.1986	31.701	0.4930	0.2999	0.7623	0.0983	40.890
0.3492	0.4545	0.6734	0.1731	33.989	0.4577	0.3500	0.7468	0.1190	39.065
0.3987	0.4199	0.7130	0.1520	36.140	0.4225	0.4002	0.7295	0.1415	37.210
0.4535	0.3816	0.7515	0.1315	38.482	0.3878	0.4495	0.7105	0.1658	35.359
0.4977	0.3508	0.7793	0.1167	40.305	0.3522	0.4999	0.6886	0.1935	33.447
0.0000	1.0000	0.0000	1.0000	12.329	1.0000	0.0000	1.0000	0.0000	59.908
0.0000	0.2972	0.0000	0.1788	21.203	0.2989	0.7011	0.6877	0.3123	28.718
0.0279	0.2889	0.0942	0.1614	22.797	0.2909	0.6825	0.6716	0.3037	28.705
0.0560	0.2806	0.1740	0.1467	24.311	0.2839	0.6662	0.6577	0.2963	28.685
0.1008	0.2672	0.2790	0.1275	26.694	0.2690	0.6311	0.6277	0.2804	28.646
0.1516	0.2521	0.3739	0.1102	29.213	0.2547	0.5975	0.5992	0.2655	28.593
0.1999	0.2378	0.4477	0.0968	31.436	0.2393	0.5615	0.5686	0.2497	28.527
0.2478	0.2236	0.5095	0.0857	33.568	0.2246	0.5268	0.5390	0.2347	28.445
0.3007	0.2078	0.5680	0.0752	35.780	0.2096	0.4915	0.5087	0.2196	28.348
0.3455	0.1945	0.6113	0.0675	37.602	0.1945	0.4561	0.4781	0.2045	28.234
0.3983	0.1788	0.6567	0.0594	39.642	0.1796	0.4210	0.4473	0.1897	28.101
0.4447	0.1650	0.6927	0.0531	41.397	0.1646	0.3858	0.4160	0.1748	27.953
0.4983	0.1491	0.7306	0.0464	43.346	0.1497	0.3507	0.3844	0.1600	27.785
0.0000	0.0000	0.0000	0.0000	24.628	1.0000	0.0000	1.0000	0.0000	59.925
0.3074	0.0000	0.5415	0.0000	38.932	0.7017	0.2983	0.9093	0.0907	47.002
0.2993	0.0263	0.5370	0.0090	38.273	0.6857	0.2916	0.8968	0.0889	46.671
0.2915	0.0516	0.5326	0.0179	37.583	0.6691	0.2845	0.8838	0.0869	46.288
0.2764	0.1007	0.5236	0.0360	36.324	0.6329	0.2691	0.8552	0.0827	45.492
0.2609	0.1512	0.5136	0.0558	35.042	0.5972	0.2539	0.8266	0.0786	44.708
0.2460	0.1999	0.5034	0.0762	33.769	0.5624	0.2391	0.7984	0.0746	43.888
0.2303	0.2509	0.4918	0.0990	32.459	0.5260	0.2236	0.7683	0.0704	43.033
0.2152	0.3003	0.4796	0.1229	31.159	0.4912	0.2088	0.7388	0.0665	42.188
0.1999	0.3499	0.4663	0.1489	29.861	0.4559	0.1938	0.7079	0.0625	41.285
0.1846	0.4000	0.4515	0.1773	28.564	0.4209	0.1789	0.6761	0.0586	40.358
0.1696	0.4488	0.4357	0.2076	27.288	0.3859	0.1640	0.6429	0.0547	39.396
0.1540	0.4995	0.4175	0.2422	25.947	0.3510	0.1491	0.6080	0.0508	38.388

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).

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 MTBE + heptane + cyclohexane and MTBE + cyclohexane + 1-hexene and the binaries cyclohexane + heptane and cyclohexane + 1-hexene were

Table 4. Total-Pressure Data for MTBE (1) + Cyclohexane (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	59.908	0.2983	0.7017	0.5324	0.4676	38.630
0.7023	0.0000	0.7497	0.0000	56.482	0.2918	0.6864	0.5174	0.4561	38.782
0.6882	0.0201	0.7421	0.0112	56.032	0.2835	0.6670	0.4988	0.4419	38.962
0.6697	0.0464	0.7322	0.0259	55.315	0.2687	0.6321	0.4663	0.4165	39.299
0.6311	0.1014	0.7110	0.0569	53.891	0.2538	0.5968	0.4345	0.3912	39.624
0.5971	0.1497	0.6921	0.0845	52.655	0.2387	0.5613	0.4037	0.3663	39.948
0.5617	0.2002	0.6718	0.1139	51.336	0.2241	0.5268	0.3745	0.3423	40.268
0.5266	0.2501	0.6513	0.1435	50.023	0.2093	0.4920	0.3459	0.3184	40.588
0.4922	0.2992	0.6303	0.1735	48.701	0.1941	0.4562	0.3172	0.2941	40.911
0.4569	0.3495	0.6078	0.2052	47.352	0.1794	0.4216	0.2902	0.2708	41.230
0.4212	0.4002	0.5840	0.2384	45.923	0.1644	0.3863	0.2631	0.2472	41.546
0.3863	0.4500	0.5592	0.2727	44.540	0.1494	0.3509	0.2366	0.2237	41.866
0.0000	0.0000	0.0000	0.0000	45.007	1.0000	0.0000	1.0000	0.0000	59.916
0.0000	0.2930	0.0000	0.1954	39.689	0.7015	0.2985	0.8297	0.1703	51.675
0.0247	0.2858	0.0410	0.1881	40.334	0.6835	0.2908	0.8107	0.1659	51.559
0.0524	0.2777	0.0849	0.1802	41.093	0.6667	0.2837	0.7931	0.1618	51.458
0.1003	0.2636	0.1561	0.1673	42.357	0.6317	0.2688	0.7561	0.1533	51.226
0.1498	0.2491	0.2242	0.1548	43.595	0.5964	0.2538	0.7189	0.1448	50.979
0.1998	0.2344	0.2883	0.1430	44.824	0.5548	0.2360	0.6746	0.1349	50.680
0.2497	0.2198	0.3477	0.1319	45.994	0.5269	0.2242	0.6448	0.1282	50.466
0.2991	0.2053	0.4031	0.1214	47.122	0.4911	0.2089	0.6062	0.1197	50.186
0.3488	0.1908	0.4555	0.1114	48.209	0.4562	0.1940	0.5681	0.1115	49.898
0.3995	0.1759	0.5064	0.1016	49.290	0.4210	0.1790	0.5291	0.1031	49.598
0.4500	0.1611	0.5545	0.0922	50.326	0.3858	0.1640	0.4896	0.0948	49.289
0.4994	0.1466	0.5996	0.0834	51.309	0.3504	0.1490	0.4493	0.0864	48.966
0.0000	0.0000	0.0000	0.0000	44.986	0.0000	1.0000	0.0000	1.0000	24.650
0.2998	0.0000	0.3706	0.0000	50.587	0.0000	0.6981	0.0000	0.5521	31.800
0.2893	0.0351	0.3643	0.0202	49.824	0.0270	0.6793	0.0600	0.5211	32.909
0.2806	0.0642	0.3590	0.0372	49.186	0.0489	0.6640	0.1048	0.4978	33.791
0.2657	0.1139	0.3497	0.0668	48.076	0.0987	0.6292	0.1959	0.4501	35.677
0.2508	0.1636	0.3401	0.0971	46.991	0.1484	0.5945	0.2748	0.4085	37.464
0.2362	0.2123	0.3302	0.1276	45.903	0.1994	0.5589	0.3463	0.3705	39.186
0.2218	0.2602	0.3200	0.1586	44.821	0.2490	0.5243	0.4084	0.3372	40.803
0.2074	0.3085	0.3093	0.1908	43.713	0.2983	0.4898	0.4644	0.3069	42.330
0.1927	0.3573	0.2978	0.2246	42.582	0.3493	0.4542	0.5173	0.2781	43.847
0.1782	0.4058	0.2857	0.2597	41.455	0.3992	0.4194	0.5651	0.2519	45.285
0.1632	0.4557	0.2725	0.2974	40.272	0.4478	0.3854	0.6084	0.2279	46.643
0.1485	0.5050	0.2585	0.3367	39.075	0.4995	0.3493	0.6518	0.2037	48.046
0.0000	1.0000	0.0000	1.0000	24.656					

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)	cyclohexane (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}	−1469		−1469	
B_{14}/cm^3·mol^{-1}	−1450			−1450
B_{23}/cm^3·mol^{-1}		−1973	−1973	
B_{24}/cm^3·mol^{-1}		−1919		−1919
B_{34}/cm^3·mol^{-1}			−1519	−1519

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.

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

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 equation

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

which is the Margules equation (Margules, 1895) up to four parameters (three parameters when $\lambda_{ij} = \lambda_{ji} = \lambda$). 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

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

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

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

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

$$\vartheta_i = \frac{q_ix_i}{\sum_j q_jx_j}; \quad \varphi_i = \frac{r_ix_i}{\sum_j r_jx_j} \quad \text{and} \quad z = 10$$

Tables 1 and 2 show experimental values of total pressure and the corresponding compositions of the liquid

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

Cyclohexane (1) + Heptane (2)

	Margules (3 p.)	Wilson	NRTL	UNIQUAC
A_{12}	0.047 96	1.353 89	0.579 37	0.864 18
A_{21}	0.074 85	0.652 78	−0.443 93	1.130 37
λ	0.023 55			
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

Cyclohexane (1) + 1-Hexene (2)

	Margules (3 p.)	Wilson	NRTL	UNIQUAC
A_{12}	0.105 54	1.304 77	0.620 19	0.727 25
A_{21}	0.156 76	0.631 62	−0.413 47	1.285 29
λ	0.031 51			
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

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

	Margules	Wilson	NRTL	UNIQUAC
MTBE (1) + *n*-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
λ	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) + Cyclohexane (2)[b]				
A_{12}	0.368 77	0.691 97	−0.119 91	1.100 92
A_{21}	0.281 64	1.014 08	0.476 59	0.843 86
λ_{12}	0.085 55			
λ_{21}	−0.049 03			
rms ΔP/kPa	0.014	0.022	0.022	0.022
max $\lvert\Delta P\rvert$/kPa	0.027	0.048	0.053	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
λ	−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., 1998b. [b] Segovia et al., 1997.

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

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.513 05			
C_1	0.080 12			
C_2	0.078 39			
A_{12}		1.019 26	0.363 29	1.031 05
A_{21}		0.759 42	−0.104 62	0.910 80
A_{13}		0.691 44	−0.118 13	1.090 26
A_{31}		1.016 74	0.472 12	0.853 93
A_{23}		0.875 67	−0.211 39	1.129 86
A_{32}		1.064 27	0.296 31	0.863 19
rms ΔP/kPa	0.024	0.025	0.025	0.026
max $\lvert\Delta P\rvert$/kPa	0.077	0.069	0.068	0.075

and vapor phases, reduced by Margules equation for the binary systems cyclohexane + heptane and cyclohexane + 1-hexene, respectively. The same information for the ternary systems MTBE + heptane + cyclohexane and MTBE + cyclohexane + 1-hexene is given in Tables 3 and 4, where the composition of the vapor phase was calculated by the Wohl expansion.

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.

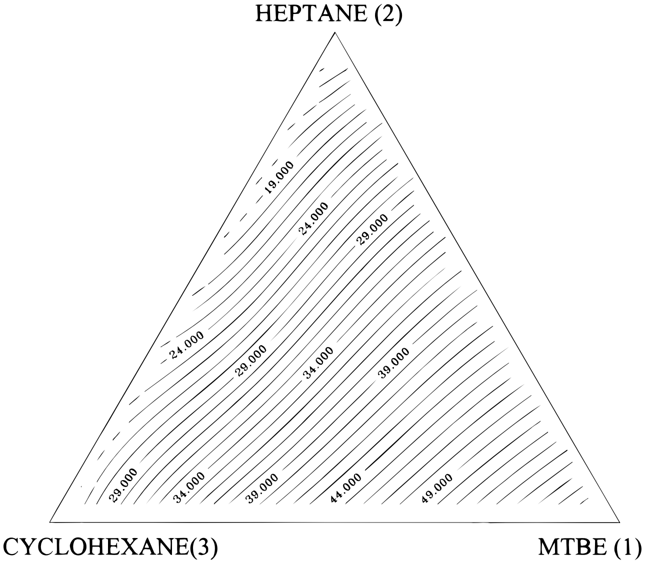

Figure 1. Lines of constant pressure, P/kPa, for the MTBE (1) + heptane (2) + cyclohexane (3) system at 313.15 K.

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

	Wohl	Wilson	NRTL	UNIQUAC
C_0	0.500 49			
C_1	0.064 97			
C_2	0.056 96			
A_{12}		0.711 60	−0.074 92	1.075 31
A_{21}		0.988 66	0.425 25	0.866 06
A_{13}		1.022 73	0.167 13	0.892 99
A_{31}		0.884 37	−0.065 71	1.090 29
A_{23}		1.303 71	0.633 66	0.726 87
A_{32}		0.631 46	−0.422 16	1.285 43
rms ΔP/kPa	0.022	0.017	0.016	0.017
max $\lvert\Delta P\rvert$/kPa	0.069	0.043	0.044	0.044

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

	Wilson	NRTL	UNIQUAC
MTBE (1) + heptane (2) + cyclohexane (3)			
rms ΔP/kPa	0.036	0.036	0.029
max $\lvert\Delta P\rvert$/kPa	0.080	0.080	0.085
MTBE (1) + cyclohexane (2) + 1-hexene (3)			
rms ΔP/kPa	0.033	0.030	0.029
max $\lvert\Delta P\rvert$/kPa	0.061	0.062	0.060

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

	this work	Lozano et al. (1995)
P_1^{sat} (kPa)	24.635	24.631
P_2^{sat} (kPa)	12.331	12.351
A_{12}	0.047 96	0.054 79
A_{21}	0.074 85	0.071 79
λ	0.023 55	0.0
rms ΔP/kPa	0.009	0.014
max $\lvert\Delta P\rvert$/kPa	0.017	0.028

Results of data correlation for the binary systems reported here are summarized in Table 6. The results of correlation of the binaries containing MTBE have been published previously (Segovia et al., 1997, Segovia et al., 1998b), and these are summarized in Table 7. For the ternary systems, the results of correlation are given in Tables 8 and 9. These tables contain values of the adjustable parameters of the different models, which lead

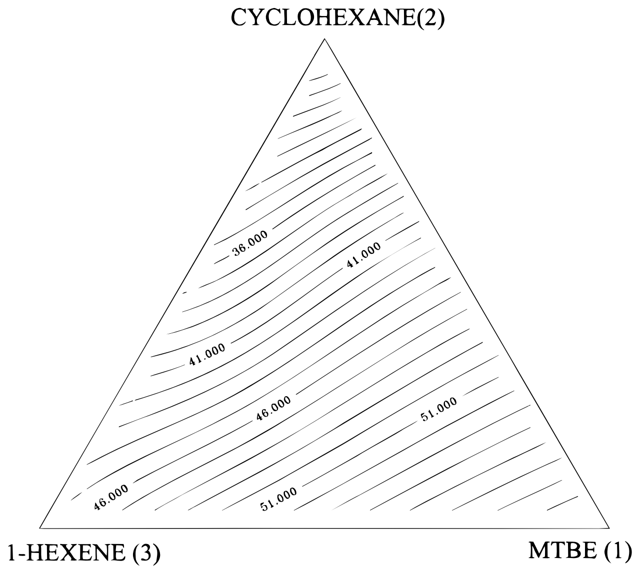

Figure 2. Lines of constant pressure, *P*/kPa, for the MTBE (1) + cyclohexane (2) + 1-hexene (3) system at 313.15 K.

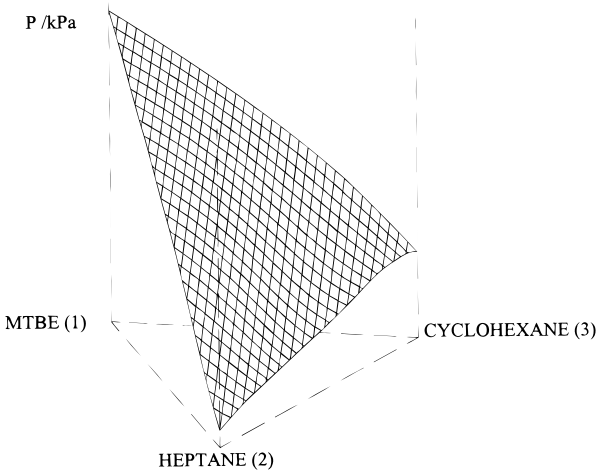

Figure 3. Oblique view of the constant pressure, *P*/kPa, for the MTBE (1) + heptane (2) + cyclohexane (3) system at 313.15 K.

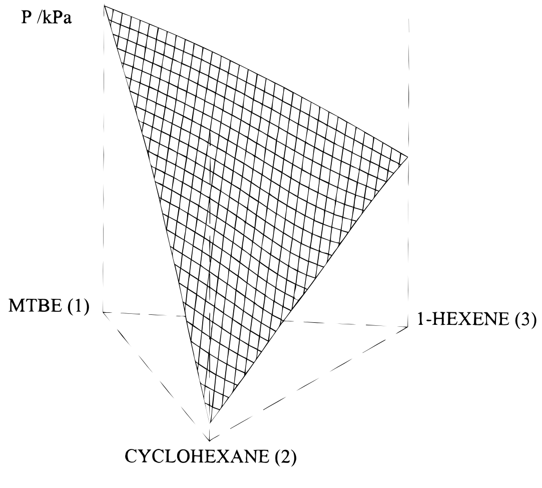

Figure 4. Oblique view of the constant pressure, *P*/kPa, for the MTBE (1) + cyclohexane (2) + 1-hexene (3) system at 313.15 K.

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 $|\Delta P|$).

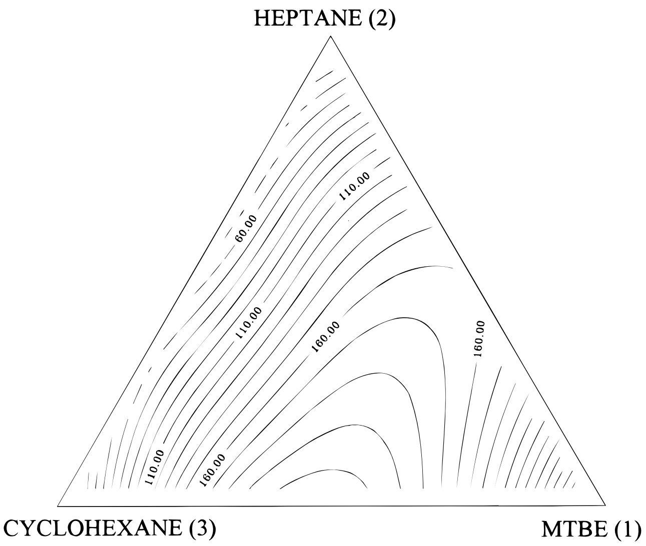

Figure 5. Lines of constant excess Gibbs energy, G^E/J·mol^{-1}, for the MTBE (1) + heptane(2) + cyclohexane (3) system at 313.15 K.

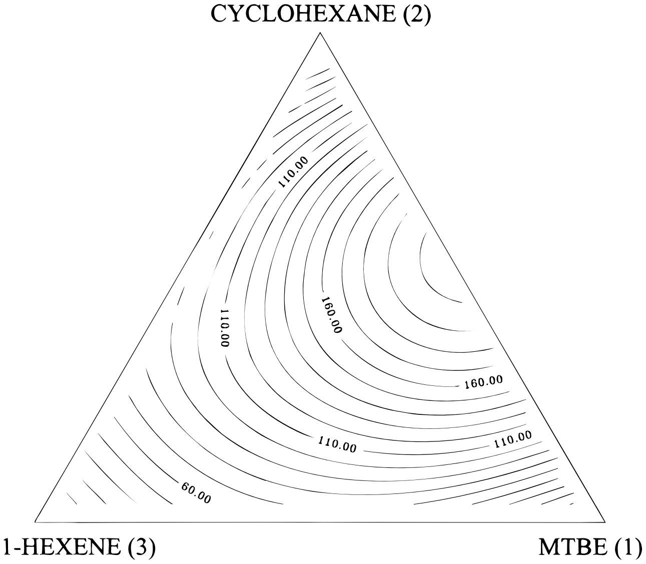

Figure 6. Lines of constant excess Gibbs energy, G^E/J·mol^{-1}, for the MTBE (1) + cyclohexane (2) + 1-hexene (3) system at 313.15 K.

Through the expressions of the excess Gibbs energy for multicomponent systems of Wilson, NRTL and UNIQUAC models, we have predicted the behavior of the ternary mixture using the parameters obtained from the correlation of the binary systems; the results of prediction are summarized in Table 10.

Discussion

We have compared the binary system cyclohexane + heptane with one reported in the literature also measured in our laboratory (Lozano et al., 1995). As it is shown in Table 11, the agreement is excellent.

The two binary systems studied present a slight positive deviation from ideality, and the results of the correlation gave a root-mean-square pressure residual between 9 Pa for the system cyclohexane + heptane and 14 Pa for the binary cyclohexane + 1-hexene using the Margules equation of three parameters. Nearly the same values were obtained with Wilson, NRTL, and UNIQUAC models.

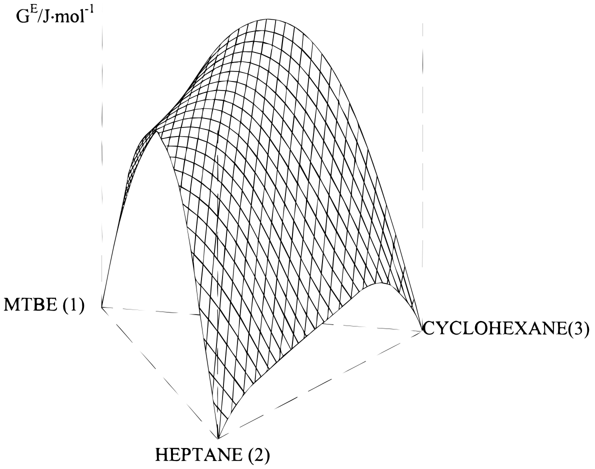

Figure 7. Oblique view of the constant excess Gibbs energy, G^E/J·mol^{-1}, for the MTBE (1) + heptane (2) + cyclohexane (3) system at 313.15 K.

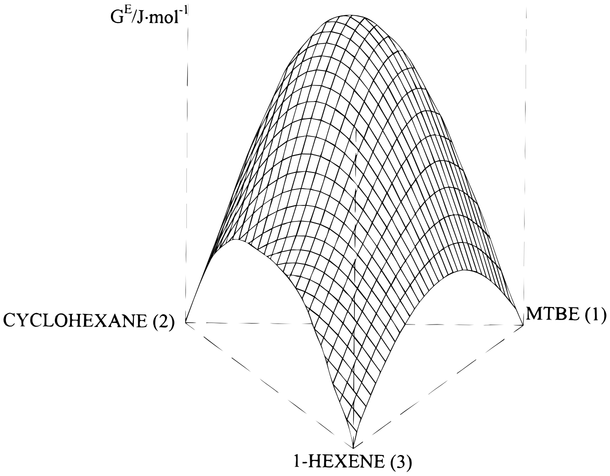

Figure 8. Oblique view of the constant excess Gibbs energy, G^E/J·mol^{-1}, for the MTBE (1) + cyclohexane (2) + 1-hexene (3) system at 313.15 K.

The results for both ternary systems were correlated by all the models used, showing a root-mean-square pressure residual less than 26 Pa, with a maximum value of the absolute deviation in pressure under 77 Pa for the ternary MTBE + heptane + cyclohexane whereas for the system MTBE + cyclohexane + 1-hexene, the root-mean-square pressure residuals were less than 22 Pa, and the maximum value of the absolute deviation in pressure was under 69 Pa; the values of the latter system were obtained with Wohl equation.

Results for the ternary systems are also shown graphically by contour lines of Figures 1−8. Lines of constant pressure are shown in Figures 1 and 2, lines of constant excess Gibbs energy, G^E, in are shown Figures 5 and 6, and the oblique view of the pressure and of the excess Gibbs energy surface for the ternary systems is shown in Figures 3, 4, 7, and 8.

Although the two ternary systems show differences in detail, their general behavior is similar. 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.

According with Table 10 the results of the prediction for the ternary systems using Wilson, NRTL, or UNIQUAC models were only slightly bigger than those obtained directly from the ternary experimental data.

Literature Cited

Abbott, M. M.; Van Ness, H. C. Vapor−Liquid Equilibrium: Part III. Data Reduction with Precise Expressions for G^E. *AIChE J.* **1975**, *21*, 62−71.

Abbott, M. M.; Floess, J. K.; Walsh, G. E., Jr.; Van Ness, H. C. Vapor−Liquid Equilibrium: Part IV. Reduction of P−x Data for Ternary Systems. *AIChE J.* **1975**, *21*, 72−76.

Abrams, D. S.; Prausnitz, J. M Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

Barker, J. A. Determination of Activity Coefficients from Total Pressure Measurements. *Aust. J. Chem.* **1953**, *6*, 207−210.

Dielsi, D. P.; Patel, R. B.; Abbott, M. M.; Van Ness, H. C. Excess Thermodynamic Functions for Ternary Systems: 3. Total Pressure Data and G^E for Acetone−Acetonitrile-Methyl Acetate at 50 °C. *J. Chem. Eng. Data* **1978**, *23*, 242−245.

Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures—A Critical Compilation*; Clarendon Press: Oxford, 1980.

Gibbs, R. E.; Van Ness, H. C. Vapor−Liquid Equilibria from Total-Pressure Measurements. A New Apparatus. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410−413.

Hayden, J. G.; O'Connell, J. P. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

Lozano, L. M.; Montero, E. A.; Martín, M. C.; Villamañán, M. A. Vapor−Liquid Equilibria of Binary Mixtures Containing Methyl *tert*-Butyl Ether (MTBE) and/or Substitution Hydrocarbons at 298.15 K and 313.15 K. *Fluid Phase Equilib.* **1995**, *110*, 219−230.

Margules, M.. *Akad. Wiss. Wien, Math. Naturw.* **1895**, *104*, 1243.

Renon, H, Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

Segovia, J. J. Thermodynamic Research about the Fluid Phases Equilibrium of Ternary Mixtures Constituited by the Oxygenated Additives MTBE and Methanol and the Substitution Hydrocarbons for the Development of New Unleaded Gasolines. Ph.D. Thesis, University of Valladolid, Spain, 1997.

Segovia, J. J.; Martín, M. C.; Chamorro, C. R.; Villamañán, M. A. Excess Thermodynamics Functions for Ternary Systems Containing Fuel Oxygenates and Substitution Hydrocarbons. 1. Total-Pressure Data and G^E for Methyl *tert*-Butyl Ether−Benzene−Cyclohexane. *Fluid Phase Equilib.* **1997**, *133*, 163−172.

Segovia, J. J.; Martín, M. C.; Chamorro, C. R.; Villamañán, M. A. 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. *J. Chem. Eng. Data* **1998a**, *43*, 1014−1020.

Segovia, J. J.; Martín, M. C.; Chamorro, C. R.; Montero, E. A.; Villamañán, M. A. Excess Thermodynamics Functions for Ternary Systems Containing Fuel Oxygenates and Substitution Hydrocarbons. 2. Total-Pressure Data and G^E for Methyl *tert*-Butyl Ether/*n*-Heptane/1-Hexene at 313.15 K. *Fluid Phase Equilib.* **1998b**, in press.

Van Ness, H. C. Thermodynamics in the Treatment of (Vapor + Liquid) Equilibria. *J. Chem. Thermodyn.* **1995**, *27*, 113−134.

Van Ness, H. C.; Abbott, M. M. A Procedure for Rapid Degassing of Liquids. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 66−67.

Van Ness, H. C.; Abbott M. M. *Classical Thermodynamics of Nonelectrolyte Solutions with Applications to Phase Equilibria;* McGraw-Hill: New York, 1982.

Wilson, G. M. Vapor-Liquid Equilibrium. XI: A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

Wohl, K. Thermodynamic Evaluation of Binary and Ternary Liquid Mixtures. *Chem. Eng. Prog.* **1953**, *49*, 218.

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