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Phase Equilibrium Properties of Binary and Ternary Mixtures Containing Dibutyl Ether, Cyclohexane, and Heptane or 1-Hexene at $T = 313.15$ K

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New experimental isothermal P, x, y data for the ternary systems dibutyl ether + cyclohexane + heptane and dibutyl ether + cyclohexane + 1-hexene and for the binary systems dibutyl ether + 1-hexene and dibutyl ether + heptane 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 ternary systems. Wilson, NRTL, and UNIQUAC models have been applied successfully to both of the binary and ternary mixtures presented here.

Introduction

Due to the environmental regulations placed by the Clean Air Act of 1990 on automobile emissions, refineries worldwide have increased continuously their use of alcohol- and ether-based oxygenates in gasoline blending. IUPAC has sponsored three international workshops on vapor–liquid equilibria and related properties in binary and ternary mixtures of ethers, alkanes, and alkanols with the objective of developing a set of recommended values. A comprehensive review of the thermophysical property measurements of these mixtures is presented by Marsh et al. in ref 1. Our group has contributed to this research program on the thermodynamic characterization of ternary mixtures as the simplest multicomponent system, containing oxygenated additives (ethers and alcohols) and different type of hydrocarbons (paraffins, cycloparaffins, aromatics, olefins) to better understand and model these reformulated gasolines.[2–6] Methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), and dibutyl ether (DBE) have been chosen as representative ethers, and some of them have been used widely as commercial fuel additives.

An appropriate gasoline blending requires finding a balance between the combustion performance and the volatility of the involved fuel mixtures. Key parameters in the formulation and storage of commercial gasoline are the distillation curve, which affects the evolution of fuel's combustion, together with Reid's vapor pressure (RVP) which is widely used as a volatility indicator. Both the distillation curve and RVP depend directly on the vapor–liquid equilibrium (VLE) behavior of fuel mixtures.

In this work, experimental isothermal P, x, y data are reported for the ternary systems dibutyl ether + cyclohexane + heptane and dibutyl ether + cyclohexane + 1-hexene and for the binary systems dibutyl ether + 1-hexene and dibutyl ether + heptane at 313.15 K. Results of the remaining binary systems involved, dibutyl ether + cyclohexane,[6] cyclohexane + heptane,[7] and cyclohexane + 1-hexene,[7] have been previously published.

Table 1. 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, Second Virial Coefficients, B_{ii}, B_{ij}, and van der Waals Molecular Volumes, r_i, and Surfaces, q_i, at $T = 313.15$ K Used for the Reduction of the Systems

	dibutyl ether ($i = 1$)	cyclohexane ($i = 2$)	heptane ($i = 3$)	1-hexene ($i = 4$)
P_i^{sat}/kPa	2.068	24.623	12.337	>44.964
P_i^{sat}(lit.)/kPa	2.163[a]	24.643[a]	12.336[a]	45.055[a]
		24.634[b]	12.335[b]	45.050[b]
		24.630[c]	12.348[c]	44.989[c]
		24.635[d]	12.331[d]	44.979[d]
		24.650[e]	12.351[e]	44.932[e]
$V_i^L/(cm^3\cdot mol^{-1})$[f]	173	134	150	129
$B_{i1}/(cm^3\cdot mol^{-1})$[g]	−4372	−2537	−3263	−2455
$B_{i2}/(cm^3\cdot mol^{-1})$[g]	−2537	−1565	−1982	−1525
$B_{i3}/(cm^3\cdot mol^{-1})$[g]	−3263	−1982	−2521	
$B_{i4}/(cm^3\cdot mol^{-1})$[g]	−2455	−1525		−1522
r_i[h]	5.5709	4.2816	4.4275	3.8132
q_i[h]	6.9116	5.181	5.6621	4.7867

[a] Calculated from the Antoine equation using constants reported in ref 25. [b] Calculated from the Antoine equation using constants reported in ref 26. [c] Ref 27. [d] Ref 28. [e] Ref 3. [f] Ref 29. [g] Calculated by Hayden et al.[16] from Dymond et al.[17] [h] Ref 30.

Experimental Section

Materials. All the chemicals used were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (of the series puriss. p.a.) with a stated purity >99.5 % (GC) for dibutyl ether, cyclohexane, and heptane and >98 % (GC) for 1-hexene. Only dibutyl ether was additionally distilled in a packed column. The first and last portions of the distillate were discarded, and the intermediate fraction distilling at constant temperature was collected. The purity was improved up to 99.7 % (GC). All reagents were thoroughly degassed. The purity of the products after degassing was checked by gas chromatography, and the values were >99.8 % (GC) for all the compounds.

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Table 2. Total Pressure, P, for Dibutyl Ether (1) + Heptane (2) and Dibutyl Ether (1) + 1-Hexene (2) at T = 313.15 K and at Various Compositions of the Liquid Phase, x_1, and the Calculated Composition of the Vapor Phase, $y_{1,\mathrm{calcd}}$, Using the Three-Parameter Margules Equation

dibutyl ether (1) + heptane (2)						dibutyl ether (1) + 1-hexene (2)					
x_1	$y_{1,\mathrm{calcd}}$	P/kPa	x_1	$y_{1,\mathrm{calcd}}$	P/kPa	x_1	$y_{1,\mathrm{calcd}}$	P/kPa	x_1	$y_{1,\mathrm{calcd}}$	P/kPa
0.000	0.000	0.000	0.448	0.122	7.891	0.0000	0.0000	44.955	0.5070	0.0468	22.864
0.000	0.000	0.000	0.498	0.143	7.3880	0.0494	0.0025	42.795	0.5513	0.0555	20.969
0.000	0.000	12.331	0.500	0.144	7.361	0.1032	0.0055	40.440	0.5556	0.0564	20.780
0.053	0.010	11.806	0.550	0.170	6.851	0.1597	0.0090	37.984	0.5997	0.0669	18.862
0.099	0.020	11.350	0.596	0.197	6.386	0.2103	0.0126	35.776	0.6055	0.0680	18.632
0.149	0.031	10.830	0.645	0.231	5.862	0.2566	0.0162	33.764	0.6519	0.0824	16.624
0.203	0.044	10.314	0.693	0.270	5.367	0.3096	0.0209	31.452	0.6968	0.0994	14.713
0.252	0.057	9.830	0.748	0.325	4.798	0.3584	0.0259	29.330	0.7431	0.1221	12.750
0.298	0.070	9.374	0.794	0.383	4.313	0.4012	0.0310	27.472	0.7939	0.1566	10.603
0.350	0.085	8.865	0.845	0.465	3.779	0.4076	0.0318	27.202	0.8462	0.2099	8.410
0.396	0.101	8.407	0.905	0.601	3.128	0.4513	0.0378	25.298	0.8900	0.2812	6.585
0.399	0.103	8.381	0.943	0.721	2.723	0.4572	0.0386	25.022	0.9416	0.4384	4.446
0.445	0.120	7.914	1.000	1.000	2.080	0.5010	0.0457	23.140	1.0000	1.0000	2.066

In Table 1, the vapor pressures of the pure constituents measured in this work are compared with those reported in the literature as a check for complete degassing.

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 co-workers,[8,9] and whose performance has been described detailed in previous papers.[10,11]

The total uncertainties of the equilibrium properties directly measured are: injected volume ± 0.03 mL, temperature ± 0.01 K, total pressure ± 5 Pa, and liquid phase mole fraction ± 0.001.

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 mixture, 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.

Experimental Results and Correlations

The use of the static VLE measurement allows a condition of true thermodynamic equilibrium to be established. As a consequence of Duhem's theorem, sampling of the phases is not necessary. Given a set of isothermal pressure and total composition data, thermodynamics allows calculation of the coexisting liquid and vapor phases. Thus, the equilibrium vapor does not need to be sampled for analysis, and the data are thermodynamically consistent "per se".[12] Data reduction for the binary and ternary mixtures was done by Barker's[13] method according to well-established procedures.[14,15] 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[16] using the parameters given by Dymond and Smith,[17] and they appear in Table 1.

Experimental data of the total vapor pressure and the corresponding composition of the liquid and vapor phases for the binary systems dibutyl ether + heptane and dibutyl ether + 1-hexene at 313.15 K are presented in Table 2. The remaining binary systems involved in the ternaries, dibutyl ether + cyclohexane,[6] cyclohexane + heptane,[7] and cyclohexane + 1-hexene,[7] have been previously published.

Table 3 and Table 4 show VLE data of the ternary system dibutyl ether + cyclohexane + heptane and dibutyl ether + cyclohexane + 1-hexene at T = 313.15 K. They are adequately correlated by the Wohl equation.[18]

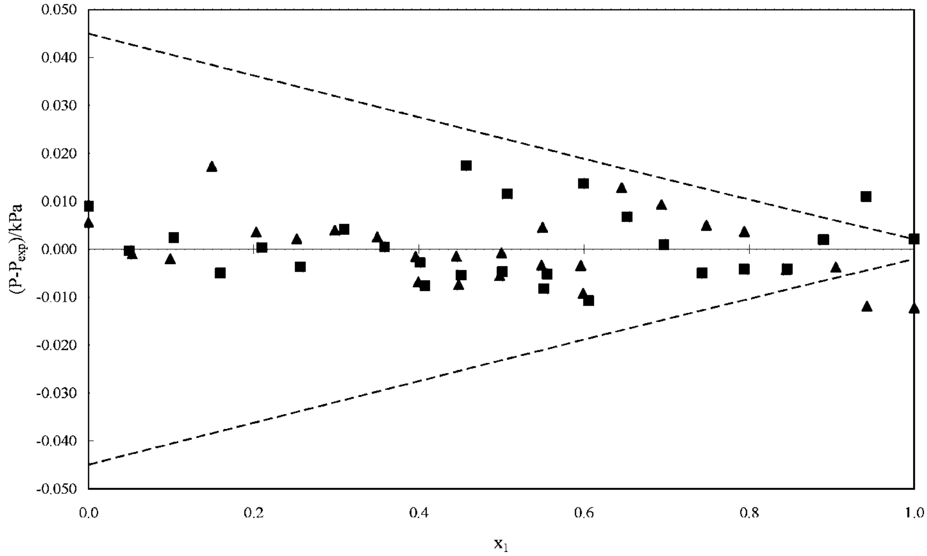

Figure 1. Pressure residuals, ($P - P_{\mathrm{expt}}$), defined as differences between calculated and experimental pressures as a function of the liquid composition, x_1, for the binary systems: ■, dibutyl ether (1) + heptane (2); ▲, dibutyl ether (1) + 1-hexene (2); - - -, ± 0.1 % P_{expt}.

Table 3. Total Pressure, *P*, for the Ternary System Dibutyl Ether (1) + Cyclohexane (2) + Heptane (3) at $T = 313.15$ K and at Various Compositions of the Liquid, x_1, x_2, and the Vapor Phases, $y_{1,\mathrm{calcd}}$, $y_{2,\mathrm{calcd}}$, Calculated Using the Wohl Expansion

x_1	x_2	$y_{1,\mathrm{calcd}}$	$y_{2,\mathrm{calcd}}$	P/kPa
1.0000	0.0000	1.0000	0.0000	2.045
0.6902	0.0000	0.2668	0.0000	5.352
0.6663	0.0346	0.2313	0.1354	6.016
0.6477	0.0615	0.2080	0.2237	6.546
0.6172	0.1057	0.1761	0.3442	7.410
0.5852	0.1522	0.1492	0.4455	8.313
0.5533	0.1983	0.1274	0.5272	9.214
0.5137	0.2556	0.1055	0.6090	10.341
0.4824	0.3011	0.0912	0.6622	11.226
0.4508	0.3468	0.0789	0.7077	12.115
0.4153	0.3983	0.0672	0.7513	13.118
0.3808	0.4482	0.0574	0.7874	14.086
0.3465	0.4980	0.0489	0.8187	15.055
1.0000	0.0000	1.0000	0.0000	2.062
0.3064	0.0000	0.0720	0.0000	9.249
0.2940	0.0403	0.0647	0.0973	9.893
0.2882	0.0595	0.0615	0.1400	10.197
0.2725	0.1106	0.0538	0.2440	11.018
0.2583	0.1571	0.0477	0.3275	11.759
0.2450	0.2006	0.0426	0.3971	12.457
0.2294	0.2512	0.0374	0.4692	13.253
0.2134	0.3035	0.0326	0.5351	14.083
0.1990	0.3504	0.0289	0.5878	14.818
0.1842	0.3987	0.0254	0.6367	15.597
0.1680	0.4517	0.0220	0.6849	16.387
0.1522	0.5033	0.0190	0.7272	17.184
1.0000	0.0000	1.0000	0.0000	2.035
0.2975	0.7025	0.0355	0.9645	17.902
0.2899	0.6847	0.0348	0.9466	17.786
0.2809	0.6634	0.0339	0.9251	17.639
0.2662	0.6287	0.0325	0.8896	17.390
0.2525	0.5963	0.0312	0.8558	17.166
0.2374	0.5607	0.0298	0.8179	16.907
0.2221	0.5246	0.0284	0.7785	16.645
0.2064	0.4877	0.0268	0.7368	16.364
0.1920	0.4535	0.0254	0.6970	16.107
0.1773	0.4190	0.0239	0.6554	15.837
0.1624	0.3839	0.0224	0.6118	15.565
0.1475	0.3486	0.0208	0.5662	15.290
0.0000	1.0000	0.0000	1.0000	24.621
0.6878	0.3122	0.1578	0.8422	9.095
0.6700	0.3041	0.1523	0.8118	9.122
0.6465	0.2935	0.1452	0.7725	9.241
0.6077	0.2758	0.1339	0.7100	9.456
0.5799	0.2633	0.1261	0.6671	9.599
0.5408	0.2455	0.1155	0.6087	9.809
0.5044	0.2290	0.1061	0.5567	9.998
0.4718	0.2143	0.0979	0.5119	10.161
0.4348	0.1975	0.0889	0.4628	10.467
0.4001	0.1817	0.0808	0.4187	10.508
0.3656	0.1661	0.0730	0.3764	10.672
0.3326	0.1511	0.0657	0.3373	10.831
0.0000	0.0000	0.0000	0.0000	12.326
0.0000	0.6836	0.0000	0.8078	20.986
0.0271	0.6651	0.0029	0.8055	20.449
0.0489	0.6501	0.0053	0.8036	20.041
0.1016	0.6141	0.0115	0.7986	19.017
0.1482	0.5823	0.0175	0.7937	18.128
0.1991	0.5475	0.0247	0.7878	17.152
0.2506	0.5123	0.0329	0.7812	16.166
0.2968	0.4808	0.0411	0.7744	15.281
0.3476	0.4460	0.0512	0.7660	14.310
0.3960	0.4129	0.0623	0.7570	13.392
0.4468	0.3782	0.0756	0.7460	12.429
0.4967	0.3441	0.0907	0.7335	11.483
0.0000	1.0000	0.0000	1.0000	24.615
0.0000	0.2808	0.0000	0.4420	16.040
0.0258	0.2736	0.0036	0.4394	15.652
0.0473	0.2675	0.0068	0.4373	15.341
0.0867	0.2565	0.0128	0.4333	14.763
0.1335	0.2434	0.0206	0.4283	14.089
0.1743	0.2319	0.0279	0.4237	13.506
0.2228	0.2183	0.0374	0.4180	12.812
0.2685	0.2055	0.0473	0.4123	12.164
0.3158	0.1922	0.0586	0.4061	11.493
0.3611	0.1795	0.0706	0.3996	10.863
0.4103	0.1657	0.0853	0.3920	10.180
0.4634	0.1507	0.1035	0.3829	9.444

Table 4. Total Pressure, *P*, for the Ternary System Dibutyl Ether (1) + Cyclohexane (2) + 1-Hexene (3) at $T = 313.15$ K and at Various Compositions of the Liquid, x_1, x_2, and the Vapor Phases, $y_{1,\mathrm{calcd}}$, $y_{2,\mathrm{calcd}}$, Calculated Using the Wohl Expansion

x_1	x_2	$y_{1,\mathrm{calcd}}$	$y_{2,\mathrm{calcd}}$	P/kPa
0.0000	1.0000	0.0000	1.0000	24.613
0.3153	0.6847	0.0380	0.9620	17.552
0.3074	0.6677	0.0354	0.8998	18.293
0.2981	0.6474	0.0326	0.8330	19.170
0.2848	0.6186	0.0291	0.7492	20.469
0.2687	0.5836	0.0255	0.6612	21.983
0.2517	0.5467	0.0223	0.5815	23.545
0.2360	0.5126	0.0197	0.5168	24.963
0.2233	0.4852	0.0178	0.4699	26.101
0.2052	0.4458	0.0154	0.4094	27.712
0.1888	0.4102	0.0135	0.3601	29.142
0.1739	0.3780	0.0119	0.3195	30.428
0.1568	0.3407	0.0102	0.2763	31.901
0.0000	0.0000	0.0000	0.0000	44.949
0.3044	0.0000	0.0204	0.0000	31.725
0.2951	0.0306	0.0199	0.0255	31.585
0.2877	0.0550	0.0194	0.0460	31.480
0.2760	0.0934	0.0187	0.0784	31.291
0.2593	0.1481	0.0176	0.1249	31.016
0.2451	0.1948	0.0167	0.1650	30.791
0.2288	0.2483	0.0157	0.2115	30.503
0.2131	0.2997	0.0147	0.2566	30.223
0.2001	0.3425	0.0139	0.2945	29.986
0.1850	0.3919	0.0130	0.3388	29.695
0.1681	0.4475	0.0119	0.3894	29.354
0.1521	0.5000	0.0109	0.4381	29.006
0.0000	0.0000	0.0000	0.0000	44.951
0.0000	0.2893	0.0000	0.1927	39.776
0.0271	0.2815	0.0015	0.1922	38.715
0.0466	0.2758	0.0026	0.1917	37.963
0.1015	0.2600	0.0059	0.1905	35.827
0.1653	0.2415	0.0104	0.1891	33.361
0.2108	0.2283	0.0140	0.1880	31.593
0.2664	0.2122	0.0190	0.1867	29.434
0.3140	0.1984	0.0238	0.1854	27.602
0.3639	0.1840	0.0297	0.1840	25.680
0.4165	0.1687	0.0369	0.1823	23.659
0.4640	0.1550	0.0445	0.1806	21.834
0.5138	0.1406	0.0539	0.1786	19.936
1.0000	0.0000	1.0000	0.0000	2.055
0.6865	0.0000	0.0951	0.0000	15.144
0.6707	0.0231	0.0914	0.0377	15.402
0.6481	0.0560	0.0862	0.0894	15.785
0.6220	0.0941	0.0806	0.1463	16.183
0.5830	0.1509	0.0727	0.2259	16.805
0.5506	0.1980	0.0665	0.2876	17.310
0.5168	0.2472	0.0606	0.3482	17.838
0.4816	0.2985	0.0547	0.4076	18.373
0.4463	0.3499	0.0493	0.4638	18.905
0.4124	0.3992	0.0443	0.5148	19.412
0.3786	0.4484	0.0397	0.5630	19.903
0.3413	0.5028	0.0348	0.6137	20.438
1.0000	0.0000	1.0000	0.0000	2.050
0.7139	0.2861	0.1758	0.8242	8.512
0.6903	0.2766	0.1484	0.6989	9.716
0.6690	0.2681	0.1293	0.6108	10.794
0.6398	0.2564	0.1085	0.5150	12.308
0.6067	0.2431	0.0905	0.4316	14.020
0.5686	0.2279	0.0745	0.3573	15.945
0.5332	0.2137	0.0628	0.3026	17.776
0.4983	0.1997	0.0534	0.2584	19.566
0.4644	0.1862	0.0457	0.2224	21.294
0.4207	0.1687	0.0375	0.1836	23.541
0.3925	0.1574	0.0330	0.1620	24.926
0.3610	0.1448	0.0286	0.1407	26.600
0.0000	0.0000	0.0000	0.0000	44.955
0.0000	0.7058	0.0000	0.5606	31.628
0.0222	0.6901	0.0015	0.5603	31.011
0.0588	0.6642	0.0041	0.5597	29.807
0.0996	0.6354	0.0072	0.5589	28.576
0.1506	0.5994	0.0116	0.5575	27.046
0.2001	0.5644	0.0163	0.5557	25.519
0.2440	0.5335	0.0210	0.5538	24.164
0.3042	0.4910	0.0284	0.5506	22.373
0.3502	0.4585	0.0348	0.5476	20.991
0.3997	0.4236	0.0428	0.5437	19.469
0.4468	0.3903	0.0516	0.5392	18.107
0.4971	0.3548	0.0626	0.5335	16.599
1.0000	0.0000	1.0000	0.0000	2.055

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

Here, G^{E} is the excess molar Gibbs energy, and the parameters C_0, C_1, and C_2 were found by regression of the ternary data. The parameters g_{ij} of the constituent binary systems were represented by the three-parameter Margules equation[19]

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

Binary and ternary systems have been correlated using the Wilson,[20] NRTL,[21] and UNIQUAC[22] models. Results of data correlation for binary systems are summarized in Table 5. For the ternary systems, the results of the correlation are given in Tables 6 and 7. We have made also the prediction of the fluid phase equilibrium behavior of the ternary system using the correlation parameters of the binary systems included in Table 5. These tables contain the root-mean-square of the differences between experimental and calculated pressures, rms ΔP, and the maximum value of these pressures residuals, max $|\Delta P|$, both indicators of the quality of the agreement with data.

Table 5. Summary of the Data Reduction Results for Binary Systems Dibutyl Ether (1) + Cyclohexane (2), Dibutyl Ether (1) + Heptane (3), Dibutyl Ether (1) + 1-Hexene (3), Cyclohexane (2) + Heptane (3), and Cyclohexane (2) + 1-Hexene (3) at T = 313.15 K

	Margules	Wilson	NRTL	UNIQUAC
dibutyl ether (1) + cyclohexane (2)[a]				
A_{12}	0.0223	0.5078	−0.6506	1.2931
A_{21}	−0.0104	1.6517	0.8126	0.7403
$\lambda_{12} = \lambda_{21}$	0.0218			
α_{12}			0.3	
rms ΔP/kPa	0.007	0.006	0.007	0.006
max $\|\Delta P\|$/kPa	0.014	0.014	0.010	0.014
dibutyl ether (1) + heptane (3)				
A_{13}	0.1129	0.7047	−0.3452	1.0770
A_{31}	0.0889	1.2426	0.4895	0.9100
$\lambda_{13} = \lambda_{31}$	0.0372			
α_{13}			0.3	
rms ΔP/kPa	0.007	0.008	0.008	0.008
max $\|\Delta P\|$/kPa	0.017	0.017	0.017	0.017
dibutyl ether (1) + 1-hexene (3)				
A_{13}	−0.0032	0.5056	−0.6537	1.2272
A_{31}	−0.0250	1.6829	0.7904	0.7878
$\lambda_{13} = \lambda_{31}$	0.0222			
α_{13}		0.3		
rms ΔP/kPa	0.008	0.007	0.008	0.007
max $\|\Delta P\|$/kPa	0.018	0.015	0.018	0.015
cyclohexane (2) + heptane (3)[b]				
A_{23}	0.0480	1.3540	0.5794	0.8642
A_{32}	0.0745	0.6528	−0.4439	1.1304
$\lambda_{23} = \lambda_{32}$	0.0236			
α_{23}			0.3	
rms ΔP/kPa	0.009	0.009	0.009	0.009
max $\|\Delta P\|$/kPa	0.017	0.017	0.018	0.017
cyclohexane (2) + 1-hexene (3)[b]				
A_{23}	0.1055	1.3048	0.6202	0.7273
A_{32}	0.1568	0.6316	−0.4135	1.2853
$\lambda_{23} = \lambda_{32}$	0.0315			
α_{23}			0.3	
rms ΔP/kPa	0.014	0.014	0.015	0.014
max $\|\Delta P\|$/kPa	0.032	0.033	0.033	0.033

[a] Experimental data published in ref 6. [b] Experimental data published in ref 7.

Table 6. Summary of the Data Reduction Results Obtained for the Ternary System Dibutyl Ether (1) + Cyclohexane (2) + Heptane (3) at T = 313.5 K

correlation	Wohl	Wilson	NRTL	UNIQUAC
C_0	−0.0715			
C_1	−0.0347			
C_2	−0.2282			
A_{12}		−0.7079	0.4728	1.3167
A_{21}		0.9223	1.6971	0.7203
A_{13}		0.1857	1.0646	0.8538
A_{31}		−0.1117	0.8783	1.1452
A_{23}		0.7042	1.4498	0.6961
A_{32}		−0.5202	0.5772	1.3519
α_{12}				
α_{13}				
α_{23}				
rms ΔP/kPa	0.044	0.042	0.043	0.043
max $\|\Delta P\|$/kPa	0.094	0.082	0.080	0.080

prediction	Wilson	NRTL	UNIQUAC
rms ΔP/kPa	0.059	0.060	0.053
max $\|\Delta P\|$/kPa	0.122	0.127	0.100
max $\|\Delta P\|/P_{\mathrm{exptl}}$	0.016	0.016	0.016

Table 7. Summary of the Data Reduction Results Obtained for the Ternary System Dibutyl Ether (1) + Cyclohexane (2) + 1-Hexene (3) at T = 313.5 K

correlation	Wohl	Wilson	NRTL	UNIQUAC
C_0	−0.0090			
C_1	0.0860			
C_2	0.0410			
A_{12}		0.5257	−0.6734	1.3446
A_{21}		1.6018	0.8723	0.6998
A_{13}		1.0981	−0.6564	1.1583
A_{31}		0.9209	0.7954	0.8444
A_{23}		1.2814	0.6144	0.7178
A_{32}		0.6457	−0.4072	1.3016
α_{12}			0.3	
α_{13}			0.3	
α_{23}			0.3	
rms ΔP/kPa	0.028	0.034	0.029	0.030
max $\|\Delta P\|$/kPa	0.065	0.103	0.063	0.062

prediction	Wilson	NRTL	UNIQUAC
rms ΔP/kPa	0.048	0.046	0.072
max $\|\Delta P\|$/kPa	0.116	0.111	0.165
max $\|\Delta P\|/P_{\mathrm{exptl}}$	0.009	0.009	0.009

Figure 1 shows a plot of $(P - P_{\mathrm{expt}})$ versus x_1 for the binary systems presented here, where the pressure was calculated by the Margules equation. 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 less than 0.1 % of the total pressure.

Discussion

The binary systems presented in this work, dibutyl ether + heptane and dibutyl ether + 1-hexene, show rather ideal behavior with respect to Raoult's law. For the binary system dibutyl ether + heptane, we have found literature data at 363.15 K,[23] far away from the temperature of this work. For the binary system dibutyl ether + cyclohexane, we have found literature data at 298.15 K.[24] We have not found literature data for the remaining binary and ternary systems involved in this work. All models used to fit the experimental data show very similar results for the binaries. The root-mean-square deviation of the pressure is 8 Pa, and the maximum deviation is 17 Pa. Figure 2 is a P, x, y plot, where both binary subsystems are shown.

We have determined by the Margules equation the excess molar Gibbs energy, G^{E}, for the five binary systems involved in the ternaries measured, as Figure 3 shows. We can see a

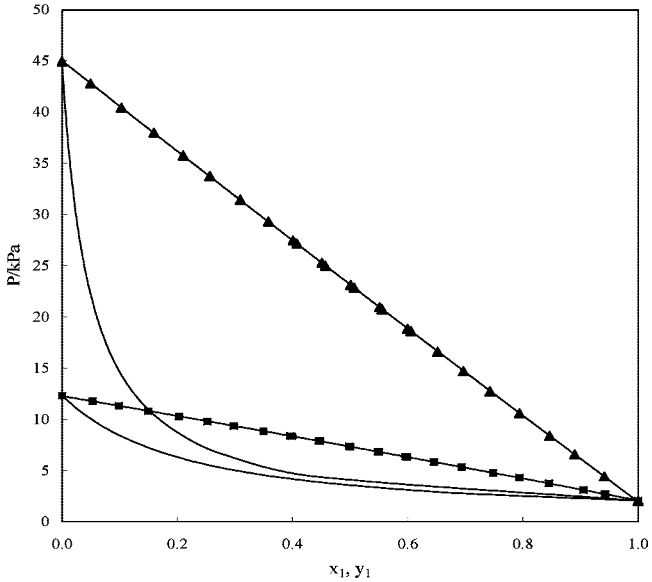

Figure 2. Total pressure, P, at $T = 313.15$ K of the binary systems as a function of the liquid, x_1, and vapor composition, y_1: ■, dibutyl ether (1) + heptane (2); ▲, dibutyl ether (1) + 1-hexene (2). Symbols represent the experimental points; lines are calculated from the Margules equation.

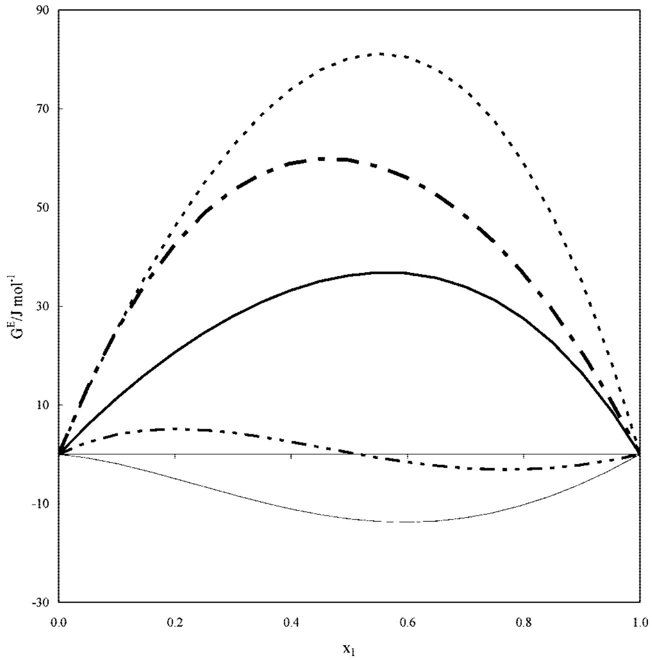

Figure 3. Excess Gibbs energy, calculated by the Margules equation, for the five binary systems involved in the work, as a function of the liquid mole fraction, x_1: ___, dibutyl ether (1) + 1-hexene (2); – – –, dibutyl ether (1) + cyclohexane (2); —, cyclohexane (1) + heptane (2); -•-, dibutyl ether (1) + heptane (2); •••, cyclohexane (1) + 1-hexene (2).

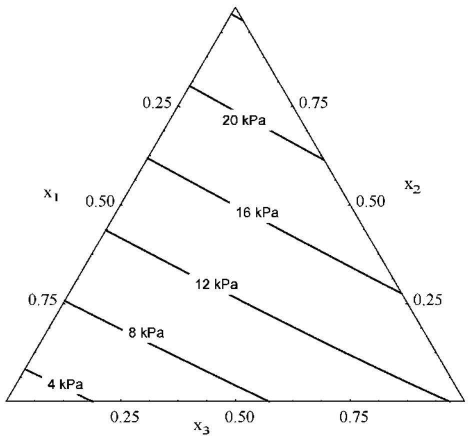

Figure 4. Isobar lines, P/kPa, as a function of the ternary liquid composition, x_i, for the VLE at $T = 313.15$ K of the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3), reduced by the Wilson equation.

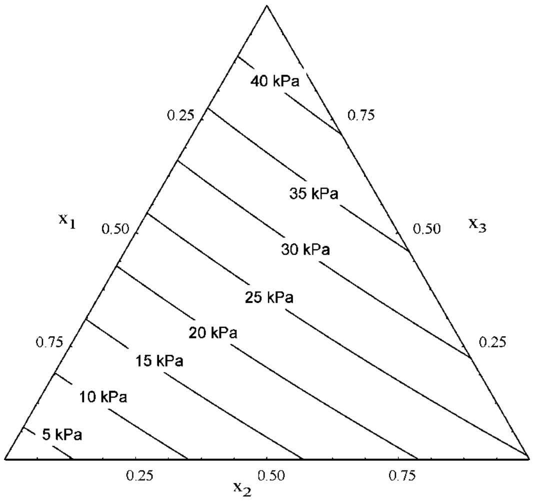

Figure 5. Isobar lines, P/kPa, as a function of the ternary liquid composition, x_i, for the VLE at $T = 313.15$ K of the ternary system dibutyl ether (1) + cyclohexane (2) + 1-hexene (3), reduced by the Wilson equation.

varied behavior of the mixtures: from a positive deviation from ideality in the mixtures of two hydrocarbons or dibutyl ether + heptane to a negative deviation with negative values of G^E in the binary system dibutyl ether +1-hexene, going through an alternative behavior in function of the composition on the mixture dibutyl ether + cyclohexane. Maximum positive values of the excess Gibbs energy are for cyclohexane + 1-hexene, 81 J·mol^{-1} for dibutyl ether (1) + heptane (2) in $x_1 = 0.44$, and 36.8 J·mol^{-1} in $x_1 = 0.55$ in the binary system cyclohexane (1) + heptane (2). The remaining binary systems, dibutyl ether + 1-hexene and dibutyl ether + cyclohexane, show very small values of G^E, −13.8 J·mol^{-1} and 5.1 J·mol^{-1}, respectively.

Concerning the ternary systems, all models employed to correlate the data give very similar values. For the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3), root-mean-square pressure residuals are 43 Pa for the NRTL model with a maximum deviation of 80 Pa. For dibutyl ether (1) + cyclohexane (2) + 1-hexene (3), root-mean-square pressure residuals are 30 Pa for the UNIQUAC model with a maximum deviation of 62 Pa.

Prediction of the ternary systems from the Wilson, NRTL, and UNIQUAC models presents very good results. The maximum deviation in pressure is 127 Pa from the NRTL model in the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3) and 165 Pa from the UNIQUAC model for the ternary system dibutyl ether (1) + cyclohexane (2) + 1-hexene (3).

Graphical results for the ternary systems are in Figures 4 to 7. They show the isobar lines and an oblique view of the excess molar Gibbs energy surface, reduced by the Wilson equation. The total equilibrium pressure is always increasing from the value of the vapor pressure of the less volatile compound (dibutyl ether) to the vapor pressure of the more volatile compound (cyclohexane in the first ternary system or 1-hexene

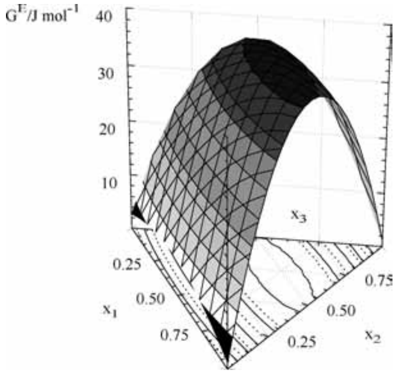

Figure 6. Excess molar Gibbs energy surface, reduced by the Wilson equation, for the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3) at T = 313.15 K.

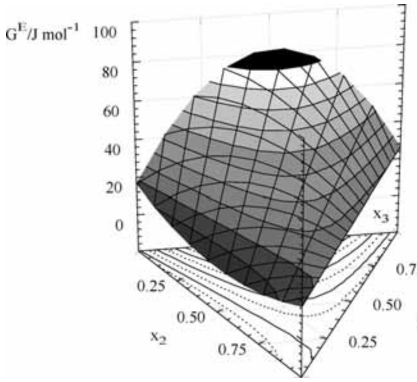

Figure 7. Excess molar Gibbs energy surface, reduced by the Wilson equation, for the ternary system dibutyl ether (1) + cyclohexane (2) + 1-hexene (3) at T = 313.15 K.

in the second one). The behavior of the excess molar Gibbs energy is also increasing up to a maximum value which corresponds to the less ideal binary system (dibutyl ether + heptane in the first ternary system and cyclohexane + 1-hexene in the second one).

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