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Phase Equilibrium Properties of Binary and Ternary Mixtures Containing 1,1-Dimethylethyl Methyl Ether, 1-Propanol, and Hexane at $T = 313.15$ K

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Experimental isothermal $P-x-y$ data for the ternary system 1,1-dimethylethyl methyl ether (MTBE) + 1-propanol + hexane and for the binary system 1,1-dimethylethyl methyl ether (MTBE) + 1-propanol at 313.15 K are reported. Data reduction by Barker's method provides correlations for g^E, using the Margules equation for the binary system and the Wohl expansion for the ternary system. Wilson, NRTL, and UNIQUAC models have been applied successfully to both the binary and the ternary systems presented here.

Introduction

Formulation of new gasolines, according to the environmental restrictions, means the use of ethers and alcohols as blending agents for enhancing the octane number and a modification of the refinery planning. Simulation of the processes is the first step in the design or optimization of any stage of the plant. The accuracy of a process simulation depends strongly on the thermodynamic models used to describe the physical behavior of the involved components. Highest quality vapor−liquid equilibrium (VLE) data are required to improve the interaction parameters of the predictive models that are used in process simulation packages. Our group has undertaken a research program on the thermodynamic characterization of ternary mixtures as the simplest multicomponent system, containing oxygenated additives (ethers and alcohols) and different types of hydrocarbons (paraffins, cycloparaffins, aromatics, and olefins) in order to better understand and model these reformulated gasolines. 1,1-Dimethylethyl methyl ether (MTBE), 1,1-dimethylpropyl methyl ether (TAME), diisopropyl ether (DIPE), and dibutyl ether (DBE) were chosen as representative ethers; methanol, 2-propanol, 1-propanol, and *tert*-amyl alcohol were chosen as alcohol additives.

In this work, experimental isothermal $P-x-y$ data are reported for the ternary system MTBE + 1-propanol + hexane and for the binary system MTBE +1-propanol. Results of the remaining binary systems involved, MTBE + hexane and 1-propanol + hexane, have been previously published.[1,2]

Experimental Section

Materials. MTBE, 1-propanol, and hexane were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (of the series puriss. p.a.) with a purity of >0.995 (by gas chromatography, GC) All liquids were thoroughly degassed before measurements by a modified distillation method based on the one suggested by Van Ness and Abbott.[3] The purity of the products after degassing was checked by GC, and the values obtained were found to be >0.998 for all the components. Water content in 1-propanol has been estimated by the Karl Fisher method to be less than 0.01 % in mass. 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.

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

	MTBE ($i = 1$)	1-propanol ($i = 2$)	hexane ($i = 3$)
P_i^{sat}/kPa	59.912	7.000	37.276
P_i^{sat}(lit.)/kPa	59.708[a]	6.988[b]	37.283[a]
	59.912[c]	7.008[d]	37.239[b]
	59.904[e]	6.987[f]	37.267[c]
			37.270[g]
V_i^L/(cm^3·mol^{-1})[h]	123	76	134
B_{i1}/(cm^3·mol^{-1})[i]	−1331	−1289	−1436
B_{i2}/(cm^3·mol^{-1})[i]	−1289	−1988	−999
B_{i3}/(cm^3·mol^{-1})[i]	−1436	−999	−1595
r_i[j]	3.6734	3.1277	3.795
q_i[j]	4.7846	3.3697	4.954

[a] Calculated from the Antoine equation using constants reported in ref 21. [b] Calculated from the Antoine equation using constants reported in ref 22. [c] Ref 6. [d] Ref 23. [e] Ref 24. [f] Ref 25. [g] Ref 26. [h] Ref 27. [i] Calculated by ref 13 from ref 14. [j] Ref 28.

Apparatus and Procedure. A static VLE apparatus, consisting of an isothermal total pressure cell, has been employed for measuring the VLE of binary and ternary mixtures. The apparatus and measuring technique are based on that by Van Ness and co-workers[4,5] and whose performance has been described in a previous paper.[6,7] The total uncertainties of the equilibrium properties directly measured are as follows: injected volume, ± 0.03 mL; temperature, ± 0.01 K; and total pressure, ± 5 Pa.

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 the addition of a pure species to a mixture

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Table 2. Total Pressure *P* for MTBE (1) + 1-Propanol (2) at $T = 313.15$ K and at Various Compositions of the Liquid Phase x_1 and the Calculated Composition of the Vapor Phase $y_{1,\mathrm{calc}}$ Using the Four-Parameter Margules Equation

x_1	$y_{1,\mathrm{calc}}$	P/kPa	x_1	$y_{1,\mathrm{calc}}$	P/kPa	x_1	$y_{1,\mathrm{calc}}$	P/kPa	x_1	$y_{1,\mathrm{calc}}$	P/kPa
0.0000	0.0000	6.999	0.2549	0.8123	29.171	0.4992	0.8984	41.771	0.7985	0.9533	52.491
0.0123	0.1683	8.338	0.2998	0.8361	31.976	0.5486	0.9088	43.706	0.8476	0.9625	54.189
0.0303	0.3338	10.221	0.3480	0.8561	34.700	0.5496	0.9090	43.770	0.8730	0.9676	55.073
0.0549	0.4777	12.722	0.3978	0.8725	37.182	0.5974	0.9181	45.548	0.8957	0.9724	55.901
0.1015	0.6304	17.175	0.3979	0.8726	37.243	0.5978	0.9182	45.576	0.9477	0.9848	57.853
0.1278	0.6831	19.563	0.4470	0.8861	39.487	0.6490	0.9274	47.391	0.9770	0.9929	59.008
0.1519	0.7196	21.603	0.4495	0.8867	39.650	0.6977	0.9358	49.087	0.9849	0.9953	59.292
0.1945	0.7671	24.936	0.4989	0.8984	41.722	0.7500	0.9448	50.861	1.0000	1.0000	59.924

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

x_1	x_2	$y_{1,\mathrm{calc}}$	$y_{2,\mathrm{calc}}$	P/kPa	x_1	x_2	$y_{1,\mathrm{calc}}$	$y_{2,\mathrm{calc}}$	P/kPa	x_1	x_2	$y_{1,\mathrm{calc}}$	$y_{2,\mathrm{calc}}$	P/kPa
1.00000	0.00000	1.00000	0.00000	59.910	1.00000	0.00000	1.00000	0.00000	59.915	0.00000	1.00000	0.00000	1.00000	7.000
0.30661	0.69339	0.83920	0.16080	32.358	0.29473	0.00000	0.42086	0.00000	46.475	0.00000	0.30162	0.00000	0.12547	39.425
0.29708	0.67167	0.74420	0.15059	34.243	0.28783	0.02351	0.39682	0.02539	46.385	0.03106	0.29226	0.04526	0.12006	40.003
0.29048	0.65670	0.68858	0.14472	35.315	0.27981	0.05081	0.37613	0.04464	46.111	0.04966	0.28666	0.07211	0.11695	40.346
0.27771	0.62751	0.59931	0.13558	37.032	0.26524	0.10041	0.34988	0.06529	45.487	0.10284	0.27060	0.14717	0.10852	41.382
0.26160	0.59076	0.51327	0.12742	38.609	0.25018	0.15159	0.33092	0.07773	44.842	0.15351	0.25529	0.21563	0.10099	42.376
0.24675	0.55697	0.45175	0.12219	39.642	0.23538	0.20185	0.31622	0.08632	44.204	0.20461	0.23986	0.28138	0.09377	43.387
0.23086	0.52086	0.39840	0.11821	40.430	0.22127	0.24979	0.30399	0.09301	43.589	0.25233	0.22545	0.33987	0.08728	44.333
0.21485	0.48455	0.35350	0.11533	40.979	0.20737	0.29697	0.29274	0.09892	42.984	0.30343	0.21003	0.39957	0.08049	45.362
0.20085	0.45283	0.31933	0.11343	41.309	0.19152	0.35076	0.28030	0.10530	42.253	0.40269	0.18005	0.50789	0.06764	47.361
0.18517	0.41732	0.28517	0.11174	41.566	0.17661	0.40134	0.26868	0.11124	41.525	0.44064	0.16860	0.54690	0.06282	48.135
0.16955	0.38200	0.25442	0.11034	41.720	0.16202	0.45081	0.25726	0.11723	40.750	0.47415	0.15850	0.58032	0.05861	48.811
0.15492	0.34894	0.22791	0.10916	41.798	0.14748	0.50014	0.24577	0.12361	39.888	0.00000	0.00000	0.00000	0.00000	37.252
0.00000	1.00000	0.00000	1.00000	7.007	0.00000	0.00000	0.00000	0.00000	37.302	0.00000	0.70116	0.00000	0.16586	34.772
0.69218	0.30782	0.93482	0.06518	48.886	0.69707	0.00000	0.77015	0.00000	55.276	0.03319	0.67785	0.06703	0.15935	35.395
0.67187	0.29877	0.89499	0.06485	48.982	0.67538	0.03116	0.75153	0.01427	54.257	0.05747	0.66081	0.11512	0.15441	35.905
0.65543	0.29146	0.86436	0.06468	49.030	0.65907	0.05457	0.73928	0.02316	53.520	0.10745	0.62568	0.20952	0.14415	37.028
0.62273	0.27684	0.80723	0.06456	49.044	0.62228	0.10740	0.71560	0.03914	51.971	0.15314	0.59358	0.28916	0.13505	38.096
0.58572	0.26030	0.74808	0.06471	48.953	0.59068	0.15276	0.69835	0.04979	50.753	0.20159	0.55956	0.36614	0.12590	39.243
0.55108	0.24484	0.69709	0.06506	48.769	0.55542	0.20337	0.68127	0.05962	49.488	0.25105	0.52483	0.43713	0.11715	40.423
0.51846	0.23029	0.65210	0.06550	48.552	0.51974	0.25457	0.66550	0.06824	48.225	0.30339	0.48809	0.50465	0.10851	41.689
0.48341	0.21467	0.60634	0.06605	48.238	0.48739	0.30100	0.65200	0.07544	47.087	0.35082	0.45481	0.55986	0.10115	42.792
0.44824	0.19900	0.56242	0.06665	47.886	0.45239	0.35121	0.63785	0.08299	45.825	0.40219	0.41877	0.61408	0.09357	44.006
0.41414	0.18381	0.52124	0.06725	47.495	0.41769	0.40100	0.62394	0.09058	44.525	0.44858	0.38624	0.65866	0.08698	45.108
0.38156	0.16932	0.48280	0.06781	47.091	0.38157	0.45281	0.60926	0.09892	43.089	0.49980	0.35033	0.70366	0.07988	46.325
0.34592	0.15346	0.44141	0.06840	46.609	0.34880	0.49981	0.59550	0.10720	41.678					

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".[8,9] Data reduction for the binary and ternary mixtures was done by Barker's method[10] according to well-established procedures.[11,12] 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[13] using the parameters given by Dymond and Smith,[14] which appear in Table 1.

Experimental data of the total vapor pressure and the corresponding composition of the liquid and vapor phases for the binary system MTBE + 1-propanol are presented in Table 2. The remaining binary systems involved in the ternary system, MTBE + hexane and 1-propanol + hexane, have been published previously.[1,2]

Table 3 shows the VLE data of the ternary system MTBE + 1-propanol + hexane at $T = 313.15$ K. They are adequately correlated by the Wohl equation:[15]

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

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[16] for MTBE + hexane; the four-parameter Margules equation for MTBE + 1-propanol; and the six-parameter Margules equation for 1-propanol + hexane:

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

Binary and ternary systems have been correlated using the Wilson,[17] NRTL,[18] and UNIQUAC[19] models. Results of data correlation for binary systems are summarized in Table 4. For the ternary system, the results of the correlation are given in Table 5. 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 4. These tables contain the root mean square (rms) of the differences between experimental and calculated pressures (rms ΔP) and

Table 4. Summary of the Data Reduction Results for Binary Systems MTBE (1) + 1-Propanol (2), MTBE (1) + Hexane (3), and 1-Propanol (2) + Hexane (3) at T = 313.15 K

	Margules	Wilson	NRTL	NRTL(3p)	UNIQUAC
			MTBE (1) + 1-Propanol (2)		
A_{12}	0.6809	0.8679	1.0210	0.8212	0.4193
A_{21}	1.0040	0.4210	−0.0456	0.1815	1.6684
λ_{12}	−0.0448				
λ_{21}	0.2393				
α_{12}			0.3	0.52	
rms ΔP/kPa	0.018	0.049	0.056	0.049	0.052
max$\|\Delta P\|$/kPa	0.039	0.120	0.100	0.099	0.116
			MTBE (1) + Hexane (3)[a]		
A_{13}	0.2102	0.9614	0.2365		0.9436
A_{31}	0.2262	0.8273	−0.0085		1.0123
$\lambda_{13} = \lambda_{31}$	−0.0058				
α_{13}			0.3		
rms ΔP/kPa	0.016	0.018	0.018		0.016
max $\|\Delta P\|$/kPa	0.030	0.031	0.031		0.033
			1-Propanol (2) + Hexane (3)[b]		
A_{23}	3.1274	0.0858	0.9115	1.1759	1.5212
A_{32}	1.8551	0.3778	1.9507	2.2003	0.3170
λ_{23}	5.1523				
λ_{32}	1.0589				
η_{23}	6.6359				
η_{32}	1.3453				
α_{23}			0.4	0.49	
rms P/kPa	0.038	0.126	0.494	0.204	0.750
max $\|\Delta P\|$/kPa	0.080	0.323	1.001	0.472	1.298
$x_{2(\text{azeotrope})}$	0.1089	0.1096	0.1150	0.1150	0.1141
$p_{(\text{azeotrope})}$	40.027	39.816	39.220	39.220	38.909

[a] Experimental data published in ref 1. [b] Experimental data published in ref 2.

Table 5. Summary of the Data Reduction Results Obtained for the Ternary System MTBE (1) + 1-Propanol (2) + Hexane (3) at T = 313.5 K

Correlation

	Wohl	Wilson	NRTL(3p.)	UNIQUAC
C_0	2.7176			
C_1	0.8403			
C_2	−0.3257			
A_{12}		0.8626	0.8352	0.4094
A_{21}		0.4197	0.1796	1.6808
A_{13}		0.8104	0.0251	1.2947
A_{31}		0.9712	0.2149	0.6997
A_{23}		0.0841	1.2017	1.6520
A_{32}		0.3945	2.1762	0.2642
α_{12}			0.52	
α_{13}			0.30	
α_{23}			0.49	
rms ΔP/kPa	0.057	0.058	0.059	0.165
max $\|\Delta P\|$/kPa	0.168	0.161	0.208	0.470

Prediction

	Wilson	NRTL(3p.)	UNIQUAC
rms ΔP/kPa	0.119	0.099	0.388
max $\|\Delta P\|$/kPa	0.313	0.208	0.906
% max $\|\Delta P\|/P_{\text{EXP}}$	0.85	0.60	2.54

the maximum value of these pressures residuals (max $|\Delta P|$), both indicators of the quality of the agreement with data.

Figure 1 shows a plot of ($P - P_{\text{EXP}}$) 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

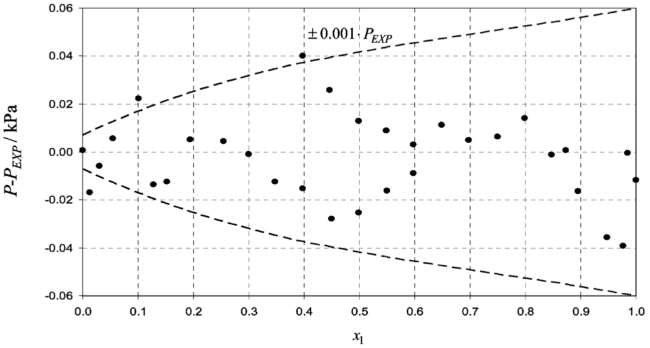

Figure 1. Pressure residuals ($P - P_{\text{EXP}}$) defined as differences between calculated and experimental pressures as a function of the liquid composition x_1 for the binary system MTBE (1) + 1-propanol (2).

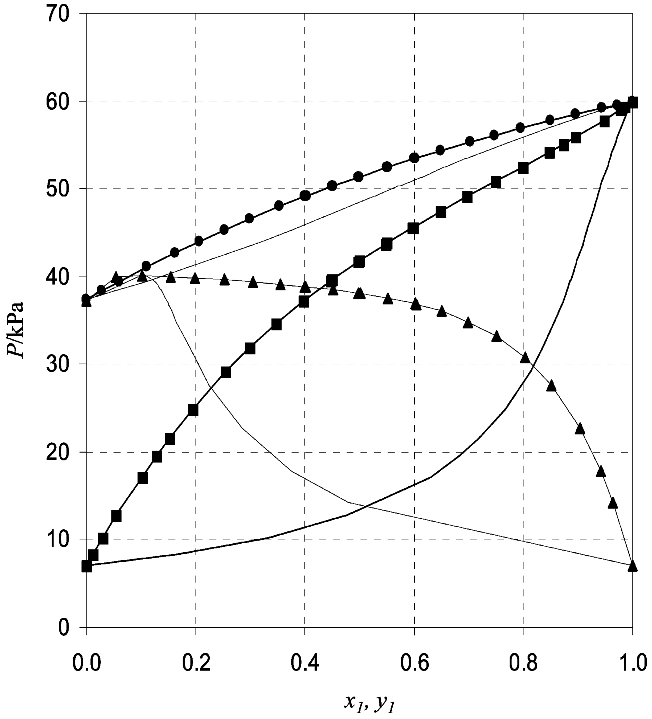

Figure 2. Total pressure P at T = 313.15 K of the binary systems as a function of the liquid x_1 and vapor composition y_1: ■, MTBE (1) + 1-propanol (2); ●, MTBE (1) + hexane 2; and ▲, 1-propanol (2) + hexane (3). Symbols represent the experimental points; lines are the calculations from the Margules equation.

The three binary systems involved in this work exhibit a positive deviation from ideality. This effect is stronger for 1-propanol + hexane, which present an azeotrope in the alcohol-rich region. The most ideal system is MTBE + hexane. These data agree with the literature data available for these binary systems,[20,6] as was commented on in previous papers.[2,1]

We have not found literature data available for the third binary system MTBE + 1-propanol. The four-parameter Margules equation leads to the best correlation results for this binary system. The rms deviation of the pressure is 18 Pa, and the maximum deviation is 39 Pa. The other models give higher values of the rms deviations. Figure 2 is a $P-x-y$ plot where the three binary subsystems involved in the ternary mixture are shown.

We have determined by the Margules equation the excess molar Gibbs energy, g^E, for the three binary systems as shown in Figure 3. It may be seen that the system 1-propanol + hexane gives the maximum value of 1286 J·mol^{-1} for g^E at a composition around $x_{\text{alcohol}} = 0.45$. This value is 535 J·mol^{-1} at $x_{\text{ether}} = 0.55$ for the binary system MTBE + 1-propanol and 143 J·mol^{-1} at $x_{\text{ether}} = 0.5$ for MTBE + hexane.

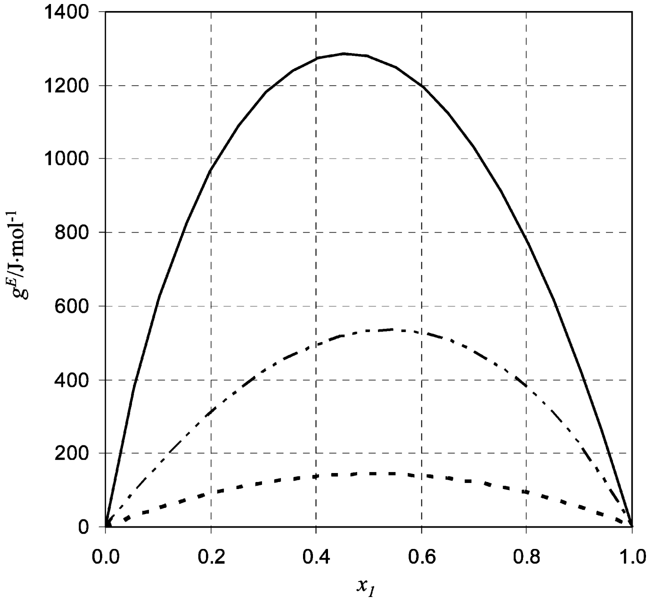

Figure 3. Excess Gibbs energy, calculated by the Margules equation, for the three binary systems as a function of the liquid mole fraction x_1: – · · –, MTBE (1) + 1-propanol (2); - -, MTBE (1) + hexane (3); and —, 1-propanol (2) + hexane (3).

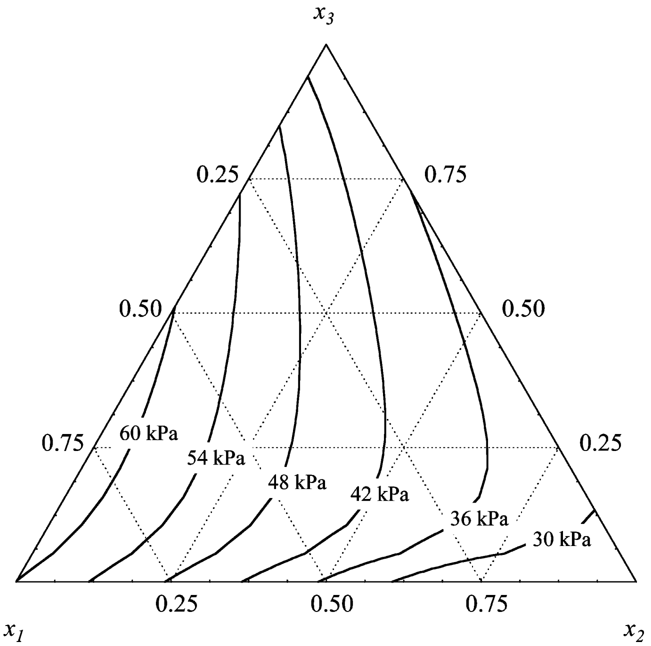

Figure 4. Isobar lines as a function of the ternary liquid composition, x_i, for the VLE at $T = 313.15$ K of the ternary system MTBE (1) + 1-propanol (2) + hexane (3), reduced by the Wohl equation.

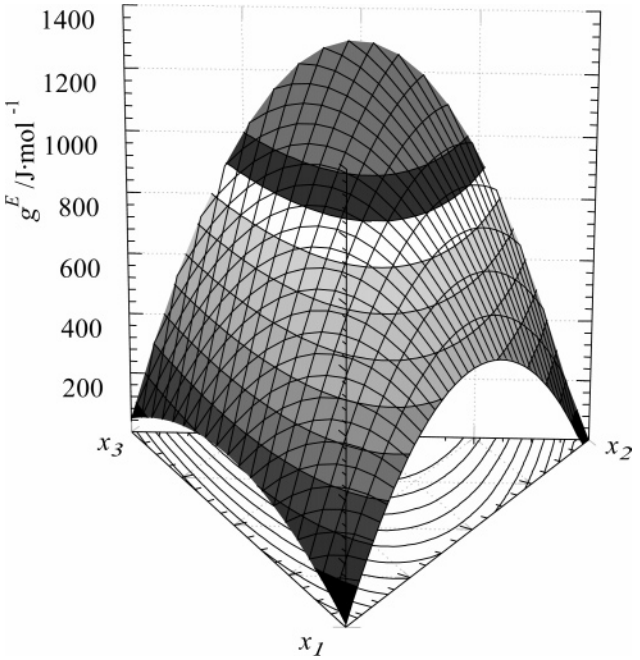

Figure 5. Molar excess Gibbs energy surface, reduced by the Wohl equation, for the ternary system MTBE (1) + 1-propanol (2) + hexane (3) at $T = 313.15$ K.

The measurements for the ternary system MTBE (1) + 1-propanol (2) + hexane (3) have been correlated by all models. The rms pressure deviation varies from 57 Pa using the Wohl model to 165 Pa for the UNIQUAC model, with a maximum value of absolute deviation in pressure of 161 Pa for the Wilson model to 470 Pa for the UNIQUAC model, within a maximum range of pressure close to 55 kPa.

Prediction of the ternary system from the Wilson, NRTL (three parameters), and UNIQUAC models presents very good results with a maximum deviation in pressure lower than 2 % from every model. Graphical results for the ternary system are in Figures 4 and 5. They show the isobar lines and an oblique view of the molar excess Gibbs energy surface, reduced by the Wohl equation. The ternary system also shows a positive deviation from ideality, and the molar excess Gibbs energy increases up to a maximum value, which corresponds to the less ideal binary system.

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