

P-x isothermal equilibrium data for two ternary systems containing long-chain bioalcohols: 1-butanol or 2-butanol + cyclohexane + methylbenzene at 313.15 K

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ABSTRACT

Butanols can be incorporated as biofuels in gasoline. As a consequence, the thermodynamic behavior in the blend of the different type of accompanying hydrocarbons (paraffins, cycloparaffins, olefins, aromatics) should be explored. Being a multicomponent mixture the best testing ground for checking prediction is the generation of the ternary systems made up of combinations of representatives of the indicated hydrocarbons two by two with alcohols. This paper reports the isothermal vapor–liquid equilibrium (VLE) at 313.15 K of the two remaining ternaries of an overall comprehensive study involving 1- or 2- butanol. A recognized accurate static technique consisting of an isothermal total pressure cell has been used for the measurements (Van Ness' apparatus). Data were reduced using Barker's method together with Wilson equation, as excess Gibbs energy model, enabling the determination of all phase equilibrium properties. Starting from our new data we complete the study by discussing the ternary prediction from four model equations by Wohl, Wilson, NRTL and UNIQUAC commonly used. Parameters fed by their constituent binaries reported in previous papers conclude that Wilson model provides the best result in both of our ternary systems.

Keywords: isothermal VLE measurements, excess Gibbs energy, ternary mixtures, 1-butanol, 2-butanol, cyclohexane, methylbenzene.

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1. INTRODUCTION

Alcohols and ethers are usually added to conventional gasoline blends to improve their anti-knocking combustion effect as well as to reduce pollution. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with different type of hydrocarbon mixtures. Experimental determination of vapor–liquid equilibrium (VLE) is indispensable for the design of separation processes such as distillation, extractive distillation and for the selection of solvents as well as operative factors such as vapor- lock, evaporation and cold start problems in vehicles. Although these data can be estimated from available predictive VLE models, experimental data are required to update and improve the data bank used to fit model parameters.

Higher- chain alcohols have energy densities close to gasoline, are not as volatile or corrosive as ethanol, and do not readily absorb water. Furthermore, branched- chain alcohols have higher-octane numbers resulting in less knocking in spark-ignition engines. They are produced naturally during the fermentation of sugars and other carbohydrates and it also may be a byproduct of the decay process of organic matter.

1- Butanol (n-butanol) has been proposed as a bio-component or as a replacement for gasoline and diesel fuel. The highest content of 1-butanol is limited in the EU to 10 v/v% in gasoline according to the European standard EN 228. Its longer hydrocarbon chain causes it to be fairly non-polar and more similar to gasoline than ethanol, surpassing it in energy density (29 MJ/L) similar to gasoline (32 MJ/L) and much higher than ethanol (16 MJ/L), what is translated into a fuel consumption more comparable to gasoline than ethanol. In addition, it is potentially less corrosive, has a lower vapor pressure, lower miscibility with water, a higher flash point and can be transported in existing pipelines.

As potential biofuel (butanol fuel) can be used without any change to the engine up to 85 percent strength in cars designed for gasoline (unlike 85% ethanol). Moreover, it can reduce hydrocarbon emissions by 95% and nitrogen oxides by 37%. Butanol can also be added to diesel fuel to reduce soot emissions. Its application will outpace ethanol, biodiesel and hydrogen because of its safety and simplicity of use. It can be produced from biomass (as “biobutanol”) as well as fossil fuels (as “petrobutanol”). As a second-generation biofuel is produced from waste biomass or non-food agricultural products by means of fermentation by bacteria.

2. OUR TERNARY SYSTEM APPROACH

This is the last paper of a systematic thermodynamic characterization program on ternary mixtures involving, 1-butanol or 2-butanol, with the last two remaining hydrocarbons of the undertaken research [1-5]. We have typified any fossil gasoline hydrocarbon blend considering four classes of essential hydrocarbons characterizing their specific functional groups. This way we have chosen as representative substitution hydrocarbons: iso-octane (standard reference material for measuring octane rating) for paraffins, 1-hexene for olefins, cyclohexane for cycloparaffins and methylbenzene for aromatics.

In the progression of VLE measurements from binary to ternary to multicomponent systems the required experimental effort increases substantially. Indeed, one cannot hope to have direct measurements for the multitude of complex systems of practical interest. This means that reliable prediction methods are indispensable, coming either from empirical correlations or from molecular theory. All predictive methods presume the availability of a large and accurate VLE data base for binary systems. However, such data are insufficient, since accurate data coming from measurements of more complex mixtures are required for comparison to prediction results.

Ternary mixtures are by far the easiest multicomponent systems to treat experimentally, and clearly represent the most appropriate testing ground for predictive models. This approach is proposed and followed by classical authors [6] and followed by our research program. Coming to our contribution we have generated a collection of ternary systems, containing the two alcohols, 1- or 2- butanol together with the mentioned substitution hydrocarbons taken two by two. Therefore six ternary systems result, four of them have already been published, as well as their ten corresponding constituent binaries mentioned before [1- 5] and [7].

This paper presents the completion of this program with isothermal VLE measurements of two ternaries, 1-butanol or 2-Butanol + cyclohexane + methylbenzene at temperature 313.15 K, suited for chemical engineering applications and for theory testing. No isothermal VLE measurements have been found in literature so far, only isobaric data at conditions of temperature and pressure far from our measurements as will be discussed in detail in the Discussion section of this paper later on.

3. EXPERIMENTAL SECTION

3.1. Materials:

Table 1 reports the suppliers, CAS#, formulas, and purities of the pure components used in this study, together with the densities (ρ) and the refractive indices (RI), of pure liquids at 293.15 K. The measured values are compared with those reported in the literature.

Table 1.

CAS#, formulas, supplier, purities, density (ρ), measured and from literature, and refractive indices (RI) measured and from literature.

Component	1-butanol	2-butanol	Cyclohexane	Methylbenzene
CAS#	71-36-3	78-92-2	110-82-7	108-88-3
Formula	C ₄ H ₁₀ O	C ₄ H ₁₀ O	C ₆ H ₁₂	C ₇ H ₈
Supplier	Fluka Chemie AG	Sigma –Aldrich	Fluka Chemie AG	Aldrich
Mass fraction purity ^a	> 0.998	> 0.999	> 0.999	> 0.999
$\rho_{meas}^b / \text{g cm}^{-3}(\text{293.15 K}^b)$	0.80965	0.80734	0.77848	0.86691
$\rho_{lit} / \text{g cm}^{-3} (\text{293.15 K})$	0.8095 ^d	0.8067 ^d	0.7784 ^e	0.8668 ^f
$RI_{meas}^b \text{ }^c(\text{293.15 K}^b)$	1.3993	1.3973	1.4265	1.4969
$RI_{lit} (\text{293.15 K})$	1.3992 ^d	1.3972 ^d	1.4264 ^e	1.4970 ^g

^a Checked by Gas Chromatography

^b Standard uncertainties ($k=1$): $u(\rho) = 0.00025 \text{ g}\cdot\text{cm}^{-3}$, $u(RI) = 0.00005$, $u(T) = 0.01 \text{ K}$.

^c $\lambda = 589 \text{ nm}$ at 293.15 K.

^d Reported by Rodriguez et al. [8]

^e Reported by Rodriguez et al. [9]

^f Reported by Zeberg-Mikkelsen et al. [10]

^g Reported by Al-Kandary et al. [11]

All chemicals were thoroughly degassed before measurements by a modified distillation method based on the one method suggested by Van Ness and Abbott [12] and kept in glass balloons equipped with leak-proof valves. Purities were specified by the supplier and double-checked by Gas Chromatography. No further purification methods were carried out. In Table 2, 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. Others sources of uncertainties (like

degasification) have been taken into account with non-repeatability of the pure constituents giving a maximum deviation of 40 Pa in the pure 1-butanol and cyclohexane. Uncertainties has been expressed in Table 2 between brackets at the side of the value of vapor pressure of pure components

Table 2

Average values of experimental vapour pressures (p_i^{sat})^a for the pure compounds measured in this work and literature values ($p_i^{sat}(\text{lit})$) at T = 313.15 K^a.

Compounds	1-butanol (i = 1)	2-butanol (i = 2)	Cyclohexane (i = 3)	Methylbenzene (i = 4)
P_i^{sat} (exp)/ kPa^a	2.496 (0.010) ^a	6.048 (0.010) ^a	24.596 (0.040) ^a	7.873 (0.020) ^a
P_i^{sat} (lit)/ kPa	2.502 ^b	6.058 ^g	24.629 ^g	7.877 ^g
	2.516 ^c	6.055 ^h	24.630 ^k	7.897 ^k
	2.464 ^d	6.048 ⁱ	24.625 ^l	7.875 ⁿ
	2.550 ^e	6.017 ^j	24.652 ^m	7.886 ^o
	2.496 ^f			7.880 ^p

^a Average of 2 runs (1-butanol and 2-butanol); Average of 4 runs (cyclohexane and methylbenzene). Expanded uncertainties ($k=2$): $U(P)/P=2 \cdot 10^{-4} + 4 \text{ Pa}$, $U(T)=0.02 \text{ K}$.

^b Reported by Belabbaci et al. [1]

^c Reported by Oracz et al. [13]

^d Calculated according to Brown et Smith. [14]

^e Calculated according to Geiseler et al. [15]

^f Calculated from Antoine equation using constants reported by Kemme et al. [16]

^g Reported by Belabbaci et al. [2]

^h Reported by Villamañan et al. [17]

ⁱ Reported by Garriga et al. [18]

^j Reported by Ambrose et al. [19]

^k Reported by Chamorro et al. [7]

^l Reported by Oracz et al. [20]

^m Calculated from the Antoine equation using constants reported by Negadi et al. [21]

ⁿ Reported by Villamañan et al. [22]

^o Calculated from the Antoine equation using constants reported in NIST (coefficients calculated by NIST from ref [23]).

^p Reported by Munday et al. [24]

3.2. Density and refractive index measurements:

Densities (ρ) of the pure components were measured at 293.15 K using a DSA 5000 densimeter (Anton Paar, Austria) with an expanded uncertainty ($k=2$) $U(\rho)=5\cdot 10^{-4}$ g·cm⁻³. The density determination is based on measuring the period of oscillation of a vibrating U-shaped tube filled with the liquid sample. During the operation, the temperature of the apparatus was maintained constant to within ± 0.01 K. The refractive indices (RI) of pure liquids were measured at 293.15 K using an Abbemat 300 refractometer (Anton Paar, Austria) with a wave length in standard conditions ($T=293.15$ K) of 589 nm. During the operation, the temperature of the apparatus was maintained constant to within ± 0.01 K. The estimated expanded uncertainties ($k=2$) in refractive index measurements is $U(RI) = 10^{-5}$.

3.3. VLE measurements:

A static VLE apparatus, consisting of an isothermal total pressure cell, was used to measure the vapor–liquid equilibrium of ternary mixtures. The apparatus and measuring technique are based on that suggested by Van Ness and co-workers [25, 26], the schema of the equipment is shown in Figure 1. Their performance has been described in a previous paper [27, 28]. Three positive displacement pumps, of 100 mL capacity (Ruska, model 2200-801), were used to inject known volumes of pure degassed components into the cell. This one was immersed in a high-precision water bath (Hart Scientific model 6020) assuring a temperature stability of ± 0.5 mK and thermostatted at $T=313.15$ K. The pump resolution was 0.01 mL, and the resulting expanded uncertainty ($k=2$) in the volume injected was 0.03 mL.

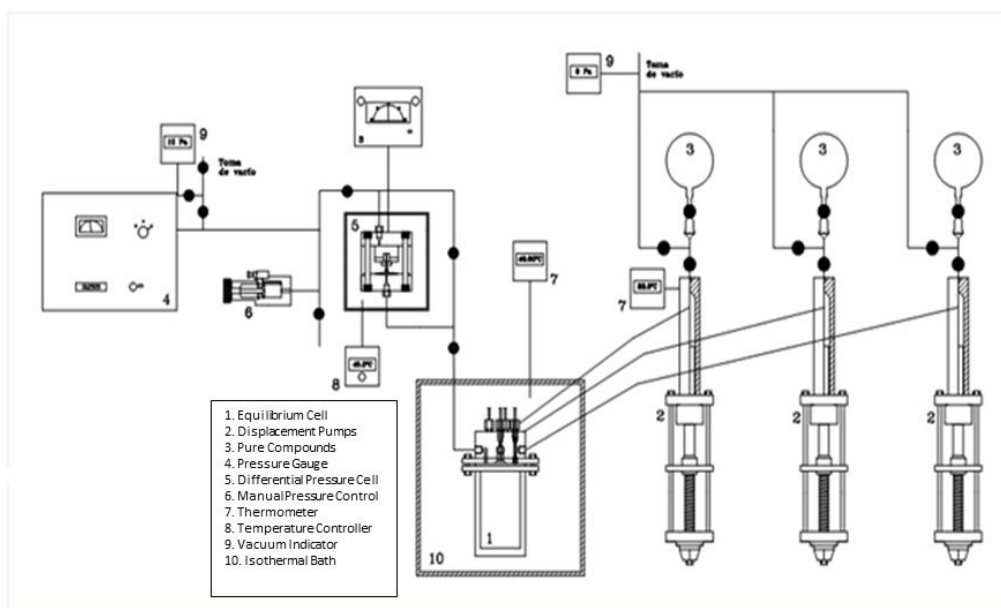


Figure 1. Schematic view of the VLE apparatus

The cell is a cylindrical stainless-steel piece with a volume of about 180 mL provided with an externally operated magnetic stirrer. Temperature was measured by a calibrated platinum resistance thermometer (SDL model 5385/100) connected to an A.C. resistance bridge (ASL model F250) with a temperature resolution of 1 mK. The estimated expanded uncertainty of the temperature ($k=2$) measurement was $U(T)=0.02$ K. The measurement of pressure was done using a differential pressure cell provided with a null indicator (Ruska models 2413-705 and 2416-711, respectively). The membrane of the null indicator is balanced by regulated atmospheric air pressure until it zeroes, then a quartz Bourdon tube precision pressure gauge (Texas Instruments, model 801) was used, which was provided with a capsule for the 125 kPa pressure range. Taking into account all the influence parameters we have calculated an expanded uncertainty ($k=2$) of $U(P)/P=2 \cdot 10^{-4} + 4$ Pa for the referred pressure range. Others sources of uncertainties (like degasification) have been taken into account with non-repeatability of the pure constituents as referred previously in table 1.

Once thermal equilibrium is reached in the bath, the evacuated cell is filled with one pure component (around 50 mL) from the corresponding injection pump. Then, successive volume injections of the second compound modify the composition and the corresponding vapor pressures are recorded until the cell is nearly full. Experimental values of total vapor pressure for the binary mixtures are obtained from two different runs, the first one adding the second component to the first one up to a concentration close to $x_1 = 0.4$, and the second run adding the

first component to the second one up to $x_1 = 0.6$, completing in this way the whole concentration range. From $x_1 = 0.4$ to $x_1 = 0.6$, the points are overlapped to check the good agreement of the vapor pressure. For the ternary mixtures, data are obtained by addition of a pure compound to a mixture of the other two: six runs (dilution lines) are 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.

The total mass injected was determined accurately from the volume differences corresponding to the initial and final positions of the pistons, the temperature of the injectors, and the densities for the injected components, allowing an estimated expanded uncertainty ($k=2$) in the mole fraction of $U(x_i)=0.0010$. The composition of the liquid phase was close to the overall composition but was corrected taking into account the vapor space of the cell and using the 2-term-virial equation, whereas the composition of the vapor phase was calculated by data reduction. Data reduction for the binary and ternary mixtures was done by Barker's method [29] according to well-established procedures. The use of a static technique for measuring the equilibrium means that the vapor phase need not be sampled for analysis and the data are thermodynamically consistent "per se" [30].

4. EXPERIMENTAL RESULTS AND CORRELATIONS

Data reduction was done by Barker's method [29] according to well established procedures [31, 32]. The objective function was the sum of the squared absolute deviations in pressure:

$$F.O = \sum (P_{calc} - P_{exp})^2 \quad (1)$$

The second virial coefficients, used to account of the non-ideality of the vapor phase, were calculated by the Hayden O'Connell method [33] using the coefficients given by Dymond et al. [34]. These values and other properties used in the data reduction are given in Table 3.

Table 3

Molar volumes of pure liquids (V_i^L), van der Waals molecular volumes (r_i), surfaces (q_i) and second virial coefficients (B_{ii} , B_{ij}) calculated by the method of Hayden et al. [33] at $T = 313.15$ K used for the calculations.

Compounds	1-butanol (i = 1)	2-butanol (i = 2)	Cyclohexane (i = 3)	Methylbenzene (i = 4)
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$V_i^L/(\text{cm}^3\text{mol}^{-1})^a$	93	94	111	109
$B_{i1}/(\text{cm}^3\text{mol}^{-1})$	-5179.5		-1163.7	-1336.5
$B_{i2}/(\text{cm}^3\text{mol}^{-1})$		-3241.8	-1143.7	-1311.8
$B_{i3}/(\text{cm}^3\text{mol}^{-1})$	-1163.7	-1143.7	-1554.6	-1793
$B_{i4}/(\text{cm}^3\text{mol}^{-1})$	-1336.5	-1311.8	-1793	-2105.7
r_i^b	3.9243	3.9235	4.0464	3.9228
q_i^b	3.668	3.664	3.240	2.968

^a Reported in TRC [35].

^b Calculated from Ref. [36]

Tables 4 and 5 show experimental values of total pressure, mole fractions of liquid phase and the calculated compositions of the Vapor Phase and activity coefficients using the Wilson equation for the two ternary systems studied, 1-butanol (1) or 2-butanol (1) + cyclohexane (2) + methylbenzene (3) at 313.15K.

Table 4

Experimental total pressure (P)^a for the ternary system **1-butanol (1) + cyclohexane (2) + methylbenzene (3)** at $T = 313.15 \text{ K}^b$, equilibrium compositions of the liquid (x_1, x_2)^c, calculated vapor (y_1, y_2)^c phases using Wilson equation and calculated activity coefficients ($\gamma_1, \gamma_2, \gamma_3$), with Wilson equation in Barker's method of data reduction.

x_1^c	x_2^c	y_1^c	y_2^c	P / kPa^a	γ_1	γ_2	γ_3
1.0000	0.0000	1.0000	0.0000	2.494	1.0000	3.9173	3.3933
0.7014	0.2986	0.1052	0.8948	18.219	1.1024	2.2703	2.3797
0.6839	0.2912	0.1049	0.8703	18.079	1.1111	2.2318	2.3001
0.6664	0.2837	0.1047	0.8464	18.291	1.1212	2.1946	2.2244
0.6312	0.2688	0.1045	0.8007	17.645	1.1455	2.1237	2.0844
0.5957	0.2537	0.1047	0.7568	16.992	1.1760	2.0576	1.9579
0.5608	0.2389	0.1050	0.7153	16.362	1.2125	1.9971	1.8459
0.5249	0.2237	0.1057	0.6738	15.733	1.2578	1.9392	1.7419
0.4898	0.2088	0.1065	0.6340	15.135	1.3110	1.8863	1.6498
0.4554	0.1941	0.1075	0.5954	14.573	1.3732	1.8378	1.5675
0.4202	0.1792	0.1087	0.5560	14.018	1.4493	1.7914	1.4909

0.3852	0.1643	0.1100	0.5167	13.485	1.5401	1.7483	1.4216
0.3501	0.1493	0.1113	0.4768	12.968	1.6506	1.7078	1.3579
0.0000	1.0000	0.0000	1.0000	24.570	20.4799	1.0000	1.6225
0.3008	0.6992	0.0627	0.9373	23.812	1.9823	1.3102	1.7354
0.2931	0.6813	0.0627	0.9228	23.797	2.0046	1.3046	1.6842
0.2857	0.6639	0.0627	0.9090	23.429	2.0291	1.2999	1.6376
0.2706	0.6290	0.0630	0.8821	22.692	2.0867	1.2923	1.5529
0.2555	0.5939	0.0634	0.8557	21.968	2.1563	1.2871	1.4782
0.2404	0.5589	0.0639	0.8297	21.244	2.2386	1.2842	1.4127
0.2253	0.5239	0.0647	0.8036	20.508	2.3354	1.2832	1.3546
0.2102	0.4888	0.0655	0.7770	19.789	2.4487	1.2842	1.3031
0.1952	0.4539	0.0665	0.7498	19.059	2.5801	1.2868	1.2577
0.1801	0.4190	0.0675	0.7214	18.308	2.7334	1.2911	1.2173
0.1650	0.3839	0.0687	0.6914	17.592	2.9132	1.2969	1.1813
0.1501	0.3491	0.0698	0.6597	16.853	3.1222	1.3041	1.1496
0.0000	0.0000	0.0000	0.0000	7.863	10.9611	1.4616	1.0000
0.2980	0.0000	0.1692	0.0000	8.293	1.8896	1.7859	1.2551
0.2893	0.0289	0.1500	0.1316	9.312	1.9241	1.7407	1.2462
0.2816	0.0548	0.1365	0.2240	10.149	1.9574	1.7018	1.2389
0.2683	0.0994	0.1189	0.3463	11.489	2.0205	1.6381	1.2279
0.2537	0.1484	0.1047	0.4452	12.819	2.0997	1.5725	1.2180
0.2386	0.1990	0.0938	0.5226	13.994	2.1936	1.5095	1.2103
0.2238	0.2487	0.0854	0.5823	15.137	2.3004	1.4519	1.2053
0.2085	0.3002	0.0786	0.6325	16.219	2.4288	1.3966	1.2027
0.1934	0.3507	0.0731	0.6733	17.162	2.5761	1.3463	1.2030
0.1789	0.3995	0.0686	0.7071	17.998	2.7433	1.3012	1.2060
0.1641	0.4492	0.0648	0.7371	18.786	2.9443	1.2586	1.2120
0.1491	0.4995	0.0613	0.7640	19.541	3.1881	1.2188	1.2212
1.0000	0.0000	1.0000	0.0000	2.498	1.0000	3.9173	3.3933
0.6998	0.0000	0.2807	0.0000	6.788	1.0924	2.6731	2.0849
0.6814	0.0264	0.2293	0.2003	8.274	1.1030	2.5730	2.0421
0.6647	0.0501	0.1980	0.3227	9.462	1.1137	2.4876	2.0055
0.6275	0.1032	0.1539	0.4961	11.452	1.1422	2.3113	1.9299

0.5924	0.1534	0.1289	0.5953	13.802	1.1752	2.1616	1.8661
0.5610	0.1983	0.1136	0.6567	15.214	1.2106	2.0400	1.8146
0.5252	0.2494	0.1010	0.7081	16.614	1.2586	1.9143	1.7619
0.4908	0.2985	0.0919	0.7458	17.759	1.3139	1.8048	1.7167
0.4554	0.3492	0.0847	0.7766	18.788	1.3821	1.7020	1.6752
0.4199	0.3998	0.0789	0.8017	19.677	1.4644	1.6086	1.6387
0.3851	0.4497	0.0742	0.8224	20.445	1.5624	1.5249	1.6072
0.3502	0.4995	0.0703	0.8402	21.065	1.6821	1.4484	1.5800
0.0000	1.0000	0.0000	1.0000	24.573	20.4799	1.0000	1.6225
0.0000	0.6988	0.0000	0.8599	20.815	15.1338	1.0489	1.2217
0.0253	0.6811	0.0288	0.8371	21.204	9.5673	1.0599	1.2143
0.0503	0.6636	0.0413	0.8277	21.255	6.8988	1.0774	1.2194
0.1000	0.6289	0.0525	0.8201	21.194	4.3982	1.1228	1.2477
0.1501	0.5939	0.0582	0.8168	21.064	3.2311	1.1781	1.2899
0.2002	0.5588	0.0622	0.8147	20.896	2.5727	1.2411	1.3410
0.2517	0.5229	0.0658	0.8129	20.685	2.1471	1.3131	1.4008
0.3000	0.4891	0.0691	0.8113	20.441	1.8740	1.3877	1.4631
0.3504	0.4539	0.0727	0.8094	20.181	1.6678	1.4730	1.5345
0.4004	0.4190	0.0768	0.8071	19.865	1.5148	1.5662	1.6119
0.4503	0.3841	0.0813	0.8044	19.495	1.3977	1.6684	1.6962
0.5001	0.3493	0.0866	0.8010	19.035	1.3061	1.7805	1.7879
0.0000	0.0000	0.0000	0.0000	7.871	10.9611	1.4616	1.0000
0.0000	0.3015	0.0000	0.6144	14.737	12.0308	1.2344	1.0315
0.0252	0.2939	0.0348	0.5949	15.043	8.2824	1.2470	1.0337
0.0499	0.2864	0.0519	0.5854	15.136	6.2665	1.2648	1.0433
0.1000	0.2713	0.0692	0.5758	15.130	4.1547	1.3112	1.0763
0.1501	0.2562	0.0783	0.5705	15.039	3.1136	1.3672	1.1207
0.2000	0.2412	0.0847	0.5664	14.907	2.5073	1.4307	1.1732
0.2499	0.2261	0.0902	0.5627	14.749	2.1159	1.5010	1.2328
0.3001	0.2110	0.0956	0.5589	14.561	1.8431	1.5789	1.2998
0.3499	0.1960	0.1011	0.5549	14.343	1.6473	1.6632	1.3730
0.4000	0.1809	0.1071	0.5506	14.084	1.4989	1.7561	1.4543
0.4500	0.1658	0.1139	0.5457	13.795	1.3850	1.8572	1.5432

0.5000	0.1507	0.1217	0.5402	13.447	1.2957	1.9676	1.6407
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^a Expanded uncertainties ($k=2$): $U(P)/P=2 \cdot 10^{-4} + 4 \text{ Pa}$, ^b $u(T) = 0.02 \text{ K}$, ^c $u(x_i) = 0.0010$, ^c

Table 5

Experimental total pressure (P)^a for the ternary system **2-butanol (1) + cyclohexane (2) + methylbenzene (3)** at $T = 313.15 \text{ K}$ ^b, equilibrium compositions of the liquid (x_1, x_2)^c and calculated vapor (y_1, y_2)^c phases using Wilson equation and calculated activity coefficients ($\gamma_1, \gamma_2, \gamma_3$), with Wilson equation in Barker's method of data reduction.

x_1^c	x_2^c	y_1^c	y_2^c	P / kPa^a	γ_1	γ_2	γ_3
1.0000	0.0000	1.0000	0.0000	6.048	1.0000	3.8265	4.0526
0.7006	0.2994	0.2246	0.7754	21.029	1.1029	2.2139	2.5746
0.6831	0.2919	0.2250	0.7514	20.706	1.1146	2.1647	2.4505
0.6655	0.2844	0.2255	0.7286	20.333	1.1278	2.1187	2.3366
0.6302	0.2694	0.2271	0.6859	19.611	1.1594	2.0353	2.1358
0.5948	0.2543	0.2293	0.6463	18.902	1.1979	1.9622	1.9654
0.5598	0.2394	0.2318	0.6093	18.240	1.2434	1.8986	1.8213
0.5248	0.2245	0.2347	0.5739	17.600	1.2970	1.8423	1.6973
0.4897	0.2095	0.2377	0.5396	16.988	1.3597	1.7924	1.5899
0.4546	0.1945	0.2409	0.5059	16.393	1.4330	1.7481	1.4965
0.4195	0.1795	0.2439	0.4727	15.818	1.5184	1.7087	1.4150
0.3845	0.1646	0.2467	0.4397	15.257	1.6178	1.6738	1.3440
0.3496	0.1497	0.2491	0.4067	14.716	1.7337	1.6429	1.2821
0.0000	1.0000	0.0000	1.0000	24.619	14.7766	1.0000	1.5859
0.2998	0.7002	0.1401	0.8599	25.664	1.9738	1.2842	1.6706
0.2923	0.6829	0.1408	0.8466	25.334	2.0029	1.2769	1.6209
0.2848	0.6652	0.1415	0.8333	24.947	2.0347	1.2704	1.5737
0.2695	0.6296	0.1430	0.8074	24.182	2.1048	1.2602	1.4888
0.2546	0.5949	0.1445	0.7829	23.443	2.1820	1.2536	1.4169
0.2396	0.5599	0.1460	0.7586	22.704	2.2687	1.2500	1.3538
0.2245	0.5247	0.1474	0.7343	21.952	2.3656	1.2493	1.2985
0.2095	0.4895	0.1487	0.7098	21.199	2.4729	1.2512	1.2504
0.1945	0.4545	0.1499	0.6850	20.448	2.5911	1.2556	1.2086

0.1795	0.4194	0.1507	0.6594	19.680	2.7217	1.2623	1.1721
0.1644	0.3842	0.1512	0.6327	18.907	2.8662	1.2713	1.1402
0.1495	0.3494	0.1512	0.6048	18.125	3.0236	1.2824	1.1128
0.0000	0.0000	0.0000	0.0000	7.876	5.8688	1.5004	1.0000
0.2994	0.0000	0.3541	0.0000	10.068	1.9766	1.7526	1.1842
0.2906	0.0296	0.3188	0.1111	11.077	2.0062	1.7050	1.1774
0.2835	0.0532	0.2959	0.1835	11.808	2.0319	1.6687	1.1726
0.2691	0.1013	0.2592	0.3004	13.174	2.0900	1.5992	1.1644
0.2540	0.1516	0.2303	0.3926	14.483	2.1605	1.5323	1.1582
0.2386	0.2032	0.2076	0.4663	15.656	2.2443	1.4693	1.1543
0.2243	0.2509	0.1907	0.5214	16.663	2.3340	1.4158	1.1530
0.2090	0.3021	0.1757	0.5708	17.659	2.4456	1.3629	1.1539
0.1950	0.3487	0.1641	0.6091	18.491	2.5632	1.3187	1.1570
0.1798	0.3996	0.1532	0.6456	19.331	2.7131	1.2741	1.1629
0.1646	0.4504	0.1437	0.6778	20.105	2.8893	1.2335	1.1714
0.1498	0.4997	0.1353	0.7060	20.802	3.0920	1.1974	1.1824
1.0000	0.0000	1.0000	0.0000	6.048	1.0000	3.8265	4.0526
0.7001	0.0000	0.4973	0.0000	9.514	1.1253	2.5109	2.0463
0.6805	0.0281	0.4290	0.1508	10.935	1.1369	2.4139	2.0019
0.6636	0.0522	0.3854	0.2473	12.003	1.1481	2.3354	1.9657
0.6298	0.1004	0.3231	0.3859	13.936	1.1743	2.1900	1.8981
0.5949	0.1502	0.2797	0.4832	15.646	1.2072	2.0547	1.8346
0.5606	0.1992	0.2490	0.5526	17.084	1.2460	1.9345	1.7780
0.5260	0.2487	0.2256	0.6060	18.328	1.2928	1.8246	1.7259
0.4903	0.2996	0.2069	0.6493	19.438	1.3502	1.7221	1.6774
0.4558	0.3489	0.1923	0.6834	20.374	1.4165	1.6319	1.6348
0.4208	0.3989	0.1801	0.7123	21.213	1.4967	1.5486	1.5957
0.3854	0.4495	0.1698	0.7371	21.956	1.5943	1.4718	1.5603
0.3504	0.4994	0.1610	0.7584	22.608	1.7114	1.4025	1.5291
0.0000	1.0000	0.0000	1.0000	24.620	14.7766	1.0000	1.5859
0.0000	0.7046	0.0000	0.8614	20.774	9.3550	1.0432	1.2341
0.0249	0.6871	0.0499	0.8213	21.759	7.1724	1.0544	1.2162
0.0501	0.6693	0.0793	0.7980	22.158	5.7506	1.0696	1.2097

0.1003	0.6340	0.1113	0.7730	22.410	4.0814	1.1085	1.2192
0.1505	0.5986	0.1289	0.7595	22.429	3.1537	1.1562	1.2483
0.2001	0.5636	0.1406	0.7505	22.343	2.5809	1.2108	1.2908
0.2504	0.5282	0.1500	0.7432	22.220	2.1892	1.2734	1.3452
0.3001	0.4931	0.1583	0.7365	22.024	1.9135	1.3426	1.4092
0.3502	0.4578	0.1664	0.7299	21.794	1.7076	1.4200	1.4836
0.4002	0.4226	0.1748	0.7228	21.502	1.5509	1.5058	1.5682
0.4502	0.3874	0.1839	0.7150	21.158	1.4285	1.6011	1.6641
0.5002	0.3521	0.1942	0.7061	20.746	1.3315	1.7068	1.7720
0.0000	0.0000	0.0000	0.0000	7.881	5.8688	1.5004	1.0000
0.0000	0.3032	0.0000	0.6154	14.714	6.6788	1.2348	1.0361
0.0248	0.2957	0.0543	0.5848	15.524	5.6033	1.2484	1.0344
0.0498	0.2881	0.0915	0.5639	15.922	4.7953	1.2645	1.0375
0.0998	0.2729	0.1381	0.5375	16.246	3.6964	1.3028	1.0552
0.1496	0.2578	0.1666	0.5210	16.342	2.9967	1.3482	1.0849
0.1999	0.2426	0.1868	0.5088	16.344	2.5157	1.4007	1.1251
0.2497	0.2275	0.2024	0.4987	16.281	2.1738	1.4593	1.1743
0.2997	0.2123	0.2158	0.4894	16.171	1.9186	1.5248	1.2329
0.3497	0.1972	0.2283	0.4804	16.018	1.7235	1.5974	1.3008
0.3996	0.1820	0.2405	0.4711	15.824	1.5708	1.6778	1.3790
0.4498	0.1668	0.2533	0.4612	15.592	1.4487	1.7670	1.4687
0.4997	0.1517	0.2671	0.4505	15.312	1.3507	1.8655	1.5708

^a Expanded uncertainties ($k=2$): $U(P)/P=2\cdot 10^{-4} + 4 \text{ Pa}$, ^b $u(T) = 0.02 \text{ K}$, ^c $u(x_i) = 0.0010$, ^c

The three-parameter Wohl equation [37] has been used for data reduction

$$g_{123} = \frac{G^E}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \quad (2)$$

Where C_0 , C_1 and C_2 are adjustable parameters found by regression of the ternary data, and, g_{ij} , are the parameters of the corresponding binary systems, determined by Margules equation [38]:

$$g_{ij} = \frac{g^E}{x_i x_j RT} = \left[A_{ji} x_i + A_{ij} x_j - (\lambda_{ji} x_i + \lambda_{ij} x_j) x_i x_j + (\eta_{ji} x_i + \eta_{ij} x_j) x_i^2 x_j^2 \right] \quad (3)$$

Where parameters A_{ij} , A_{ji} , λ_{ij} , λ_{ji} , η_{ij} and η_{ji} were obtained by regression of the binary data. The binary systems involved in the ternary have been already published [1, 2, 7].

On the other hand, the Wilson [39], NRTL [40] and UNIQUAC [41] models have been used for fitting ternary systems. The expressions for the excess Gibbs energy are given respectively by:

$$\frac{G^E}{RT} = -\sum_i x_i \ln \left(\sum_j x_j A_{ij} \right) \text{ where } A_{ij} = \frac{V_j^L}{V_i^L} \exp \left[\frac{-\lambda_{ij}}{RT} \right] \quad (4)$$

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j A_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \text{ where } A_{ij} = \frac{b_{ij}}{RT} \quad (5)$$

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\varphi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\vartheta_i}{q_i} - \sum_i q_i x_i \ln \left(\sum_j \vartheta_j A_{ji} \right) \text{ where } A_{ij} = \exp \left[-\frac{(u_{ij} - u_{ji})}{RT} \right] \quad (6)$$

where $G_{ji} = \exp(-\alpha_{ji} A_{ji})$, $\vartheta_i = q_i x_i / \sum_j q_j x_j$, $\varphi_i = r_i x_i / \sum_j r_j x_j$; $z = 10$. The dimensionless adjustable parameters are A_{ij} and A_{ji} .

The dimensional adjustable parameters λ_{ij} , b_{ij} and $(u_{ij} - u_{ji})$ of Wilson, NRTL and UNIQUAC models for the new ternary system are given in Table 6. The parameter α_{ji} of the NRTL model has also been adjusted.

Table 6

Parameters of the models used for the ternary systems at $T = 313.15$ K. together with the Root Mean Square Deviation of Pressure (rms ΔP (kPa)) and the Maximum Value of the Deviation (max) ΔP (kPa).

	Wilson	NRTL	UNIQUAC	Wohl
<i>1-butanol (1) + cyclohexane (2) + methylbenzene (3)</i>				
C_0				4.5034
C_1				-2.3470
C_2				1.2061

A ₁₂	0.0693	1.0568	1.4986	
A ₂₁	0.6470	2.2646	0.3315	
A ₁₃	0.1212	0.7039	1.2502	
A ₃₁	0.7076	1.8031	0.4600	
A ₂₃	1.0107	0.7070	0.6554	
A ₃₂	0.6097	-0.2050	1.2686	
α ₁₂		0.5840		
α ₁₃		0.6107		
α ₂₃		0.3000		
rmsΔP / kPa	0.094	0.101	0.136	0.138
maxΔP / kPa	0.337	0.353	0.412	0.425

2-butanol (1) + cyclohexane (2) + methylbenzene (3)

C ₀				4.3960
C ₁				-2.3173
C ₂				0.2062
A ₁₂	0.0965	0.8718	1.4289	
A ₂₁	0.6447	1.9958	0.3737	
A ₁₃	0.2654	1.2541	1.0207	
A ₃₁	0.5092	1.3354	0.6261	
A ₂₃	0.9090	0.4531	0.6371	
A ₃₂	0.6916	-0.0210	1.3007	
α ₁₂		0.5718		
α ₁₃		0.7263		
α ₂₃		0.3000		
rmsΔP / kPa	0.056	0.067	0.110	0.146
maxΔP / kPa	0.159	0.175	0.359	0.376

$$rms = \sqrt{\frac{(P_{\text{exp}} - P_{\text{cal}})^2}{n - p}}$$

n: number of data points measured

p: number of adjustable parameters model.

max ΔP = max (calculated pressure-experimental pressure)

5. DISCUSSION

The azeotropic behaviour of two of the constituent binaries containing 1- butanol either with cyclohexane or with methylbenzene [1] disappears when the third component, respectively methylbenzene or cyclohexane is added giving non-azeotropic ternary mixtures of 1-butanol+ cyclohexane + methylbenzene at 313.15 K for the whole domain. As shown in table 4 and Figure 2, the total vapour pressure increases monotonically from the value, 2.494 kPa, of the saturation pressure of the less volatile compound, 1-butanol, to the saturation pressure, 24.573 kPa, of the more volatile compound, cyclohexane.

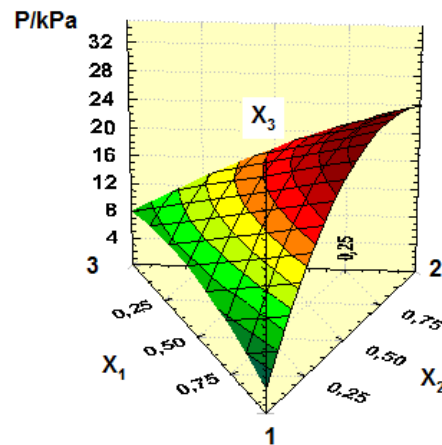


Figure 2. 3D diagram of the pressure surface reduced by Wilson model for the ternary system 1-butanol (1) + cyclohexane (2) + methylbenzene (3) at $T = 313.15$ K.

An analogous azeotropic behaviour is shown when, with the same binary constituent mixtures, the alcohol is 2-butanol. The addition of the respective third component cancels this behaviour generating a non-azeotropic ternary mixture at 313.15 K. This is shown in table 5 and Figure 3, changing monotonically the values of pressure from pure 2-butanol, 6.048 kPa, now higher than 1-butanol, to that of pure cyclohexane, as more volatile compound in the mixture.

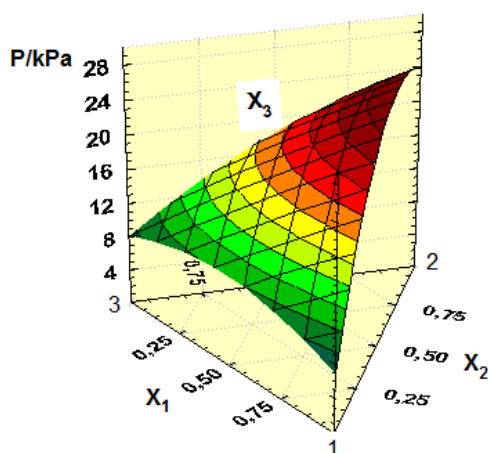


Figure 3. 3D diagram of the pressure surface reduced by Wilson model for the ternary system 2-butanol (1) + cyclohexane (2) + methylbenzene (3) at $T = 313.15$ K.

Table 6 summarizes the results of data correlations for both ternaries, containing the values of the adjustable parameters of the different models used, together with the root-mean-square deviation of the difference between the experimental and the calculated pressures ($\text{rms } \Delta P$) and the maximum value of this difference ($\text{max } \Delta P$). The best result in both cases is given by Wilson model with a $\text{rms } \Delta P$ of 0.094 kPa and $\text{max } \Delta P$ of 0.337 kPa, for the case of 1-butanol and a better one, 0.058 kPa and 0.164 kPa respectively, for the case with 2-butanol. NRTL, UNIFAC and Wohl correlations separate progressively from the optimal case as can be observed.

Molar excess Gibbs energies, G^E , at 313.15 K can be calculated from the compositions and activity coefficients given in tables 4 and 5 for the ternaries containing 1-butanol and 2-butanol respectively. The corresponding resulting values are represented graphically (Figure 4 and 5) as a surface when plotting G^E as a function of the liquid composition.

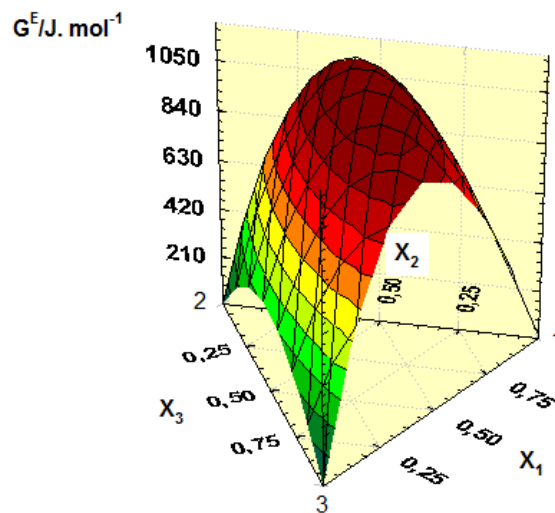


Figure 4. 3D diagram of the excess Gibbs surface reduced by the Wilson equation for the ternary system 1-butanol (1) + cyclohexane (2) + methylbenzene (3) at $T = 313.15$ K.

The result is a positive deviation from ideality which increases monotonically from the two more ideal binary curves to the less ideal binary mixture, 1-butanol or 2-butanol + cyclohexane, with a maximum of 1060 J/mol close to equimolar concentration for the 1-butanol case and a rather similar value, 1052 J/mol for 2-butanol. It can be seen that the binary cyclohexane + toluene shows the more ideal behaviour of the three component binaries with a lower maximum value of 255 J/mol at nearly equimolar concentration. From these results we conclude phenomenologically that the influence of the -OH group position in the alcohol have little influence, giving smaller values of the G^E for the mixtures containing 2-butanol in relation to the ones with 1-butanol, of the order of 0.5% lower.

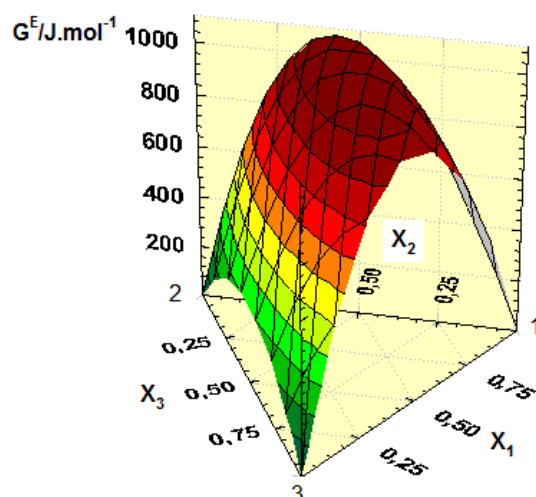


Figure 5. 3D diagram of the excess Gibbs surface reduced by the Wilson equation for the ternary system 2-butanol (1) + cyclohexane (2) + methylbenzene (3) at $T = 313.15$ K.

Concerning comparison with literature related results, we have found no isothermal data to compare with, only isobaric results at conditions of temperature and pressure far from ours, as will be discussed in detail. The ternary 1-butanol (1) + cyclohexane (2) + methylbenzene (3), Draiko et al. [42] report ebulliometric data at 101.3 kPa (1 atm) using a Swietoslowski ebulliometer giving resulting boiling points between 353.15 K (80 C) and 379.15 (106 C), referring the constituent binary measurements to data from other authors measured in the sixties. In relation to our second ternary, 2-butanol (1) + cyclohexane (2) + methylbenzene (3), only isobaric vapor-liquid equilibria using a modified Othmer-type ebulliometer with recirculation of both phases at 740 mmHg (approx. 100 kPa) has been published [43] with boiling points between 351.15 K (78 C) and 378.15 (105 C).

Due to the lack of experimental data for the isothermal VLE ternary systems, we have carried out a direct comparison for the binary constituents and their pure compounds available in the literature [1, 2, 44]. In Figure 6 and 7, the difference between the experimental data and the literature data (relative deviations) as function of the experimental vapor pressure is shown. As a result, a maximum relative deviation of 1.3% was observed for the binary systems cyclohexane + methylbenzene with a total relative average deviation of 0.5% from our experimental data.

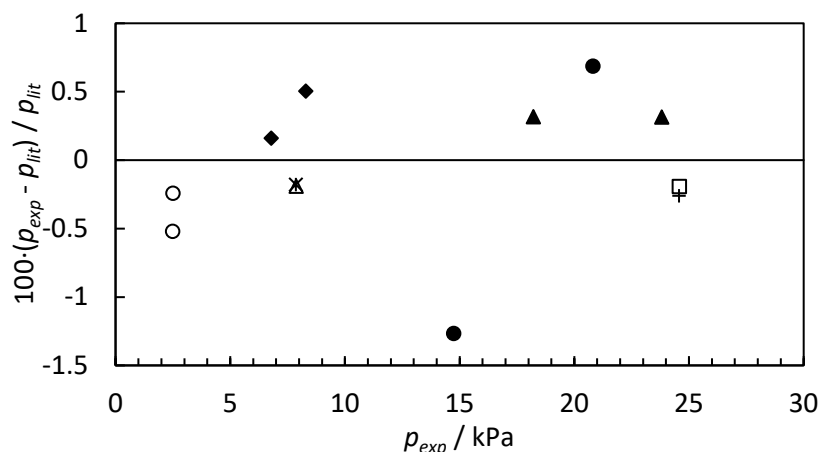


Figure 6. Relative deviations between our experimental VLE data (p_{exp}) and literature values (p_{lit}): From Belabbaci et al [1], (○) 1-butanol; (◆) 1-butanol + methylbenzene; (▲) 1-butanol + cyclohexane; (⊗) methylbenzene; (+) cyclohexane. From Alonso et al [44], (●) cyclohexane + methylbenzene; (□) cyclohexane; (△) methylbenzene.

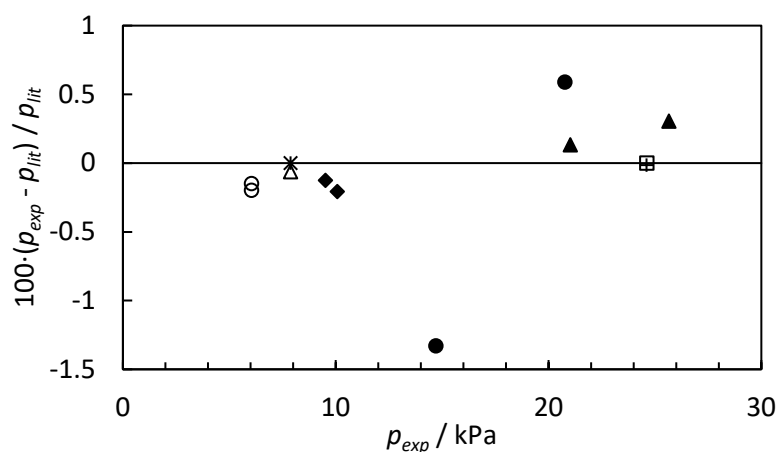


Figure 7. Relative deviations between our experimental VLE data (p_{exp}) and literature values (p_{lit}): From Belabbaci et al [2], (○) 2-butanol; (◆) 2-butanol + methylbenzene; (▲) 2-butanol + cyclohexane; (⊗) methylbenzene; (+) cyclohexane. From Alonso et al [44], (●) cyclohexane + methylbenzene; (□) cyclohexane; (△) methylbenzene.

In contrast to the reported isobaric VLE data, we complement them with isothermal VLE data. The contribution of our new results is at significant different conditions than those references reported, they are at constant temperature of 313.15 K (40 °C) and vapor pressures ranging from 2.5 to 25 kPa. The isothermal total pressure cell used, assures a static equilibrium between

phases as opposed to equilibrium stills which achieves a state of dynamic equilibrium hoping it close to true thermodynamic equilibrium. As a consequence of Duhem's theorem, disturbing sampling of the phases is not, in fact, necessary as has been proved by Van Ness and Abbott [6] and confirmed by numerous related papers, allowing data reduction the calculation of the excess Gibbs function. This means that the uncertainties in temperature, pressure and determined phase compositions are much lower conferring to isothermal data the desired information for testing models and fitting model parameters from reliable accurate data. Our estimated expanded uncertainties (k=2) are: $U(P)/P=2 \cdot 10^{-4} + 4 \text{ Pa}$, $U(T)=0.02 \text{ K}$, $U(x_i)=0.001$, in contrast to the ones reported for the isobaric measurements of: $U(P)=260 \text{ Pa}$, $u(T)=0.2 \text{ K}$, $U(x_i)=0.002$, $U(y_i)=0.01$. Accuracy on data is better provided by isothermal techniques, by the way the measurements are performed.

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List of symbols

A_{ij} , A_{ji} , b_{ij} , b_{ji} , $(u_{ij}-u_{jj})$ and $(u_{ji}-u_{ii})$ adjustable parameters of the correlation models

B_{ii} , B_{ij} , B_{jj} second virial coefficients

C_0 , C_1 , C_2 parameters in Eq. (2)

g^E molar excess Gibbs energy

i, j constituent identification: 1, 2 or 3

lit. literature value

max maximum value of the indicated quantity

P total pressure

P_i^{sat} vapor pressure of pure constituent i

R universal gas constant

rms root mean square

T absolute temperature

V_i^L molar volume of pure liquid $i= 1, 2, 3$

x mole fraction, liquid phase

Greek letters

Δ signifies difference

λ_{ij} , λ_{ji} , η_{ij} , η_{ji} parameters in Eq. (3)

α_{ji} adjustable parameter the NRTL model

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