Vapor-liquid equilibria and excess enthalpies of the binary systems 1-pentanol or 2-pentanol and 1-hexene or 1,2,4-trimethylbenzene for the development of biofuels

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Abstract

Accurate experimental data of vapor-liquid equilibria (VLE) and excess enthalpies are reported for four binary systems: (1-pentanol + 1-hexene), (2-pentanol + 1-hexene), (1-pentanol + 1,2,4-trimethylbenzene) and (2-pentanol + 1,2,4-trimethylbenzene). An isothermal total pressure cell was used for measuring VLE at $T = 313.15$ K. The data were fitted using Margules, Wilson and NRTL equations. Excess enthalpies were measured at two different temperatures $T = (298.15 \text{ and } 313.15)$ K using an isothermal flow calorimeter and were correlated by the Redlich-Kister equation. All systems present a positive deviation from the Raoult's Law. An azeotropic behavior with maximum pressure is observed for the mixtures 1-pentanol or 2-pentanol with 1,2,4-trimethylbenzene. In addition, an endothermic behavior, which increases with temperature, is obtained when the alcohols are mixed with these hydrocarbons.

Keywords:

VLE; excess enthalpies; 1-pentanol; 2-pentanol; 1-hexene; 1,2,4-trimethylbenzene.

1. Introduction

Continuing with the target of the Directive «20-20-20» [1] on decreasing CO_2 emissions, 195 nations agreed to adopt a new global climate agreement in Paris [2] which will take effect in 2020. About 25 % of the EU CO_2 emissions come from the transport sector. Within this sector, road transport is the biggest emitter accounting more than 70 % of all greenhouse gas emissions. One of the main strategies is the promotion of low-emission alternative energy for transport, such as biofuels.

Their thermodynamic properties are different and, as a consequence, experimental characterization of these properties is required in order to introduce their use and the development of new predictive models. For years, our research group is involved in the measurement of thermodynamic and thermophysical properties of gases and liquids, such as density, viscosity, heat capacity, excess enthalpy and vapour-liquid equilibria, of mixtures of interest for the formulation of biofuels.

The methodology consists in measuring properties of binary systems (as the simplest mixture) containing an oxygenated additive of renewable origin and a hydrocarbon representative of fossil fuels.

In a series of publications, vapor-liquid equilibria (VLE) and excess enthalpy of mixtures of 1-pentanol or 2-pentanol plus different hydrocarbons such as hexane, heptane, 2,2,4-trimethylpentane, cyclohexane, or toluene [3-10] were presented.

1-pentanol and 2-pentanol were selected for this study because both are considered compounds of the second generation biogasolines due to their high octane rating (up to 100 Research Octane Number - RON), better water tolerance and very high heat of combustion.

In this paper, 1,2,4-trimethylbenzene and 1-hexene were chosen as surrogates of aromatic hydrocarbons and olefins, respectively. Excess enthalpies and vapor-liquid equilibria of the mixtures (1-pentanol + 1,2,4-trimethylbenzene), (2-pentanol + 1,2,4-trimethylbenzene), (1-pentanol + 1-hexene) and (2-pentanol + 1-hexene) are reported.

2. Experimental Section

2.1 Materials

The compounds were purchased from Sigma-Aldrich with the highest purity available, gas chromatography (GC) quality reagents with a purity >0.997 (GC) for 1-pentanol, >0.98 (GC) for 2-pentanol, > 0.97 (GC) for 1-hexene and > 0.98 (GC) for the 1,2,4-trimethylbenzene. Their purities were double-checked by GC and all were found better than 0.997. The material description is summarized in Table 1.

Table 1

Material description.

Chemical name	Source	Mass fraction purity[a]	Purification method
1-Pentanol	Sigma-Aldrich	≥0.997	None
2-Pentanol	Sigma-Aldrich	≥0.997	None
1-Hexene	Sigma-Aldrich	≥0.997	None
1,2,4-Trimethylbenzene	Sigma-Aldrich	≥0.997	None

[a] Stated by the supplier and checked by gas chromatography

2.2 Experimental Techniques

An isothermal total pressure cell, which is based on the design of Van Ness et al. [11], can be used to measure VLE of binary and ternary mixtures [12] and the schema of the technique is shown in Fig. 1.

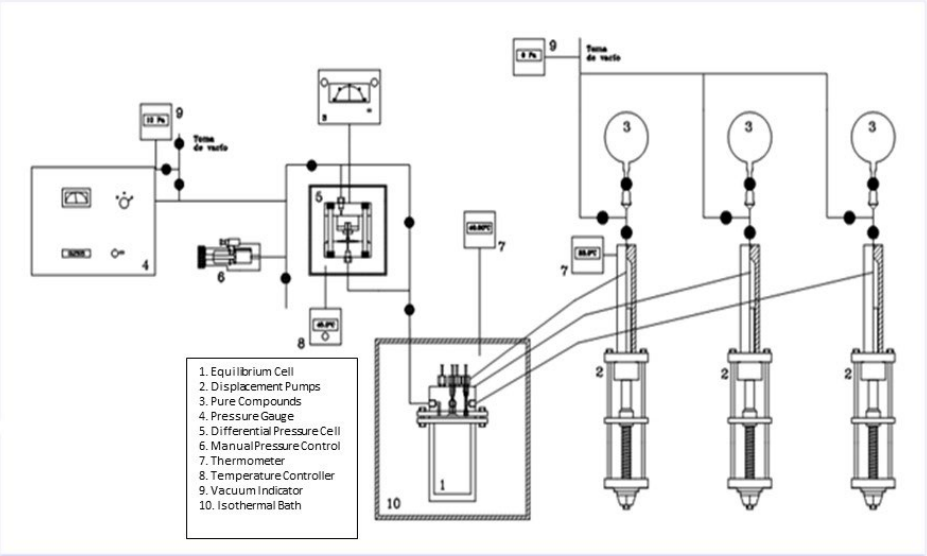

Figure 1. Schematic view of the VLE apparatus

Three positive displacement pumps, of 100 mL volume, allow to inject known volumes of pure degassed compounds into the cell with a standard uncertainty of 0.03 mL, the estimated expanded uncertainty of the mole fraction was estimated $U(x) = 0.001$ for a cover factor $k = 2$ (a level of confidence of approximately 95 %) and was calculated taking into account the contributions to the uncertainty of density, pressure and temperature.

This cell is a cylindrical stainless steel piece with a volume of 180 mL with an externally-operated magnetic stirrer. It is immersed in a thermostatic bath whose temperature is measured by a calibrated standard Pt-100 connected to an a/c resistance bridge with a standard uncertainty ($k = 1$) u (T) =10 mK. Total pressure is indirectly measured through a differential pressure cell and null indicator. When atmospheric air balances the vapor pressure at the differential pressure cell, a Bourdon fused quartz precision pressure gauge indicates the pressure with a standard uncertainty of u (P) = 5 Pa, this value is only referred to our pressure equipment. Temperature and pressure devices were calibrated with our own standards traceable to I.S. units at TERMOCAL laboratory.

Experimental values for binary mixtures are obtained in two overlapping runs starting from opposite ends of the composition range, the repeated central composition points are used to test the quality of the measurements because it is not possible to repeat a point due to the measure procedure.

Excess enthalpies were measured using a bespoke quasi-isothermal flow calorimeter developed in our laboratory [13]. A schematic view of the calorimeter is shown in the Fig. 2.

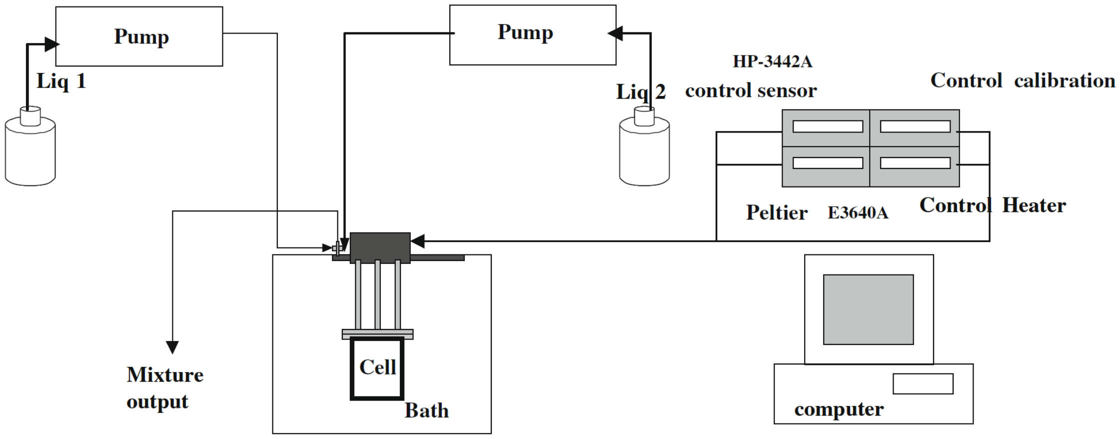

Figure 2. Schematic view of the isothermal flow calorimeter

Two precision isocratic pumps with dual floating pistons in series, deliver the pure compounds into the cell at a programmable constant flow rate. The fluids pass through a loop immersed in a water bath to ensure that they reach the bath temperature prior to entering the cell, which is also inside the thermostatic bath.

Isothermal calorimetry is based on the accurate measurement of the energy required to maintain the mixing vessel at a constant temperature. To achieve this condition, a Peltier cooler removes energy at constant rate from the flow cell, and a control-heater compensates this energy and, additionally, the energy rejected (exothermic mixing) or absorbed (endothermic mixing) by the mixing process. The excess enthalpy is calculated applying an energy balance to the cell.

The cell is a stainless steel vessel containing a copper block where all the energy in the process is exchanged by conduction. At the top of the copper block, there are the Peltier cooler and the control heater. The mixture flows through a stainless steel tube which is coiled around the copper block. During the experiments, the refrigeration power is set and held constant by a DC power supply and the control heater is connected to a function generator of arbitrary waveform to change the power input into the cell. The calorimeter is controlled using the value of a 10 kΩ NTC thermistor connected to a multimeter and located at the top of the flow cell (outlet of the flow cell). The apparatus is completely automated (data acquisition, monitoring and controlling) using the VEE-Agilent program through the computer.

The standard uncertainties ($k = 1$) of the measured magnitudes are: $u(T) = 10$ mK, flow rate $u_r(\dot{V}) = 0.15$ % which results in an expanded uncertainty ($k = 2$) $U(x) = 0.0002$ for the mixture composition, and a relative expanded uncertainty ($k = 2$) $U_r(H^E) = 1.0$ % for excess enthalpy.

Both techniques were deeply described and validated in previous papers [12,13] and the quality of the measurements provided using them has been proven for this type of mixtures [4-10].

3. Results

The use of a static technique for VLE means that vapor phase do not need to be sampled for analysis and data are thermodynamically consistent “per se” [14]. Four binary mixtures (1-pentanol + 1-hexene), (2-pentanol + 1-hexene), (1-pentanol + 1,2,4-trimethylbenzene) and (2-pentanol + 1,2,4-trimethylbenzene) were measured at $T = 313.15$ K. Barker’s method [15,16] was applied for data reduction and the virial equation of state was used for modelling the non-ideality of the vapor phase. Second virial coefficients (B_{ii}, B_{ij}) were calculated by Hayden and O'Connell method [17] using the parameters given by Dymond and Smith [18].

Average values of the experimental vapor pressures (P_i^s) of pure compounds, molar volumes of pure liquids (V_i^L) and second virial coefficients (B_{ii}, B_{ij}) are given in Table 2, where vapor pressures are compared with the literature values [19-30].

Table 2

Average values of the experimental vapor pressures (P_i^s) for the pure compounds and literature values (P_i^s(lit.)), molar volumes of pure liquids (V_i^L) and second virial coefficients (B_{ii}, B_{ij}) at T = 313.15 K used for the calculations.

	1-Pentanol (i=1)	2-Pentanol (i=2)	1-Hexene (i=3)	1,2,4-Trimethylbenzene (i=4)
P_i^s /kPa	0.905[a]	2.295[a]	44.934	0.730
P_i^s (lit.) /kPa	0.918[b]	2.260[d]	44.952[h]	0.702[l]
	0.872[c]	2.281[e]	44.979[i]	
	0.891[d]	2.298[f]	45.030[j]	
		2.280[g]	44.954[k]	
V_i^L/(cm^3·mol^{-1})[m]	110.1	111.2	128.0	88.15
B_{ii} /(cm^3·mol^{-1})[n]	-3001	-2560	-1518	-4348
B_{i3} /(cm^3·mol^{-1})[n]	-1893	-1766	-1518	
B_{i4} /(cm^3·mol^{-1})[n]	-3290	-3048		-4348

[a] Average of 7 runs, measured in previous works [4-10]

[b] Reference 19.

[c] Reference 20.

[d] Reference 21.

[e] Reference 22.

[f] Reference 23.

g Reference 24.

[h] Reference 25.

[i] Reference 26.

[j] Calculated from Antoine equation using constants reported by Reid et al. [27].

[k] Reference 28.

[l] Reference 29.

[m] Reference 30.

[n] Calculated by Hayden et al.[17] from Dymond et al.[18].

Margules equation up to six-parameter [31], Wilson [32] and NRTL [33] models were applied to correlate the experimental data. The expressions of these models are given by Eqs. (1) - (4), respectively:

$$G_m^E/RT = \left[A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j + (\eta_{ji}x_i + \eta_{ij}x_j)x_i^2x_j^2\right]x_ix_j \tag{1}$$

$$G_m^E/RT = -\sum_i x_i \ln\left(\sum_j x_j A_{ij}\right) \tag{2}$$

$$G_m^E/RT = \sum_i x_i \left(\sum_j A_{ji}G_{ji}x_j \middle/ \sum_k G_{ki}x_k\right) \tag{3}$$

where G_{ji}=exp(-$\alpha_{ji}A_{ji}$).

In Table 3, the experimental values of total pressure, liquid phase composition and vapor phase composition, calculated by Margules equation, are shown for all the binary systems at T = 313.15 K. Also, the sets of data are represented in Fig. 3.

Table 3

Total pressure VLE data, P, liquid mole fraction, x_i, and calculated vapor mole fraction, $y_{1,calc}$, using Margules equation for the binary systems at $T = 313.15$ K.[a]

x_1	$y_{1,calc}$	P(kPa)	x_1	$y_{1,calc}$	P(kPa)
		1-pentanol (1) + 1-hexene (2)			
0.0000	0.0000	44.914	0.5019	0.0171	36.529
0.0492	0.0075	43.855	0.5517	0.0184	35.097
0.0995	0.0096	43.191	0.5521	0.0184	35.144
0.1503	0.0106	42.546	0.6021	0.0200	33.446
0.2007	0.0115	41.892	0.6024	0.0200	33.498
0.2511	0.0124	41.184	0.6527	0.0220	31.526
0.3014	0.0133	40.452	0.7025	0.0247	29.174
0.3516	0.0142	39.624	0.7528	0.0284	26.304
0.4014	0.0151	38.751	0.8028	0.0338	22.866
0.4016	0.0151	38.713	0.8526	0.0428	18.716
0.4517	0.0161	37.717	0.8999	0.0593	14.050
0.4518	0.0161	37.672	0.9493	0.1072	8.159
0.5017	0.0171	36.487	1.0000	1.0000	0.913
		2-pentanol (1) + 1-hexene (2)			
0.0000	0.0000	44.954	0.5018	0.0434	35.350
0.0498	0.0147	43.919	0.5514	0.0471	33.891
0.1004	0.0203	43.129	0.5519	0.0471	33.874
0.1502	0.0235	42.445	0.6014	0.0515	32.194
0.2007	0.0263	41.709	0.6022	0.0516	32.175
0.2521	0.0290	40.857	0.6522	0.0571	30.220
0.3011	0.0316	39.951	0.7024	0.0641	27.937

0.3513	0.0344	38.940	0.7523	0.0736	25.288
0.4013	0.0372	37.850	0.8022	0.0872	22.180
0.4015	0.0372	37.838	0.8520	0.1088	18.481
0.4514	0.0401	36.671	0.9018	0.1497	14.000
0.4516	0.0401	36.656	0.9509	0.2531	8.634
0.5016	0.0434	35.363	1.0000	1.0000	2.281

1-pentanol (1) + 1,2,4-trimethylbenzene (2)

0.0000	0.0000	0.730	0.5003	0.4971	1.175
0.0500	0.3638	1.076	0.5500	0.5214	1.181
0.0997	0.3928	1.107	0.5502	0.5215	1.173
0.1499	0.4053	1.135	0.6000	0.5507	1.176
0.1997	0.4184	1.150	0.6002	0.5508	1.171
0.2498	0.4314	1.160	0.6503	0.5832	1.166
0.2996	0.4427	1.168	0.6912	0.6102	1.160
0.3498	0.4529	1.175	0.7503	0.6488	1.144
0.3999	0.4640	1.180	0.8004	0.6823	1.120
0.4002	0.4641	1.171	0.8505	0.7228	1.091
0.4499	0.4781	1.182	0.9005	0.7825	1.041
0.4502	0.4782	1.171	0.9503	0.8769	0.989
0.5000	0.4970	1.182	1.0000	1.0000	0.918

2-pentanol (1) + 1,2,4-trimethylbenzene (2)

0.0000	0.0000	0.730	0.5016	0.7475	2.079
0.0504	0.4515	1.227	0.5500	0.7626	2.086
0.1002	0.5566	1.477	0.5517	0.7631	2.127
0.1504	0.6065	1.624	0.5999	0.7781	2.127

0.2000	0.6378	1.715	0.6016	0.7787	2.148
0.2509	0.6619	1.802	0.6499	0.7939	2.167
0.3010	0.6816	1.864	0.7000	0.8103	2.212
0.3512	0.6993	1.932	0.7501	0.8282	2.238
0.4000	0.7154	1.966	0.8000	0.8489	2.244
0.4015	0.7159	1.976	0.8501	0.8747	2.265
0.4499	0.7313	2.024	0.9003	0.9079	2.283
0.4515	0.7318	2.011	0.9504	0.9506	2.278
0.5000	0.7470	2.067	1.0000	1.0000	2.268

[a] Standard uncertainties (k=1): $u(x_1) = 0.0005$, $u(y_{1,\mathrm{calc}}) = 0.0005$, $u(P) = 5$ Pa; $u(T) = 10$ mK.

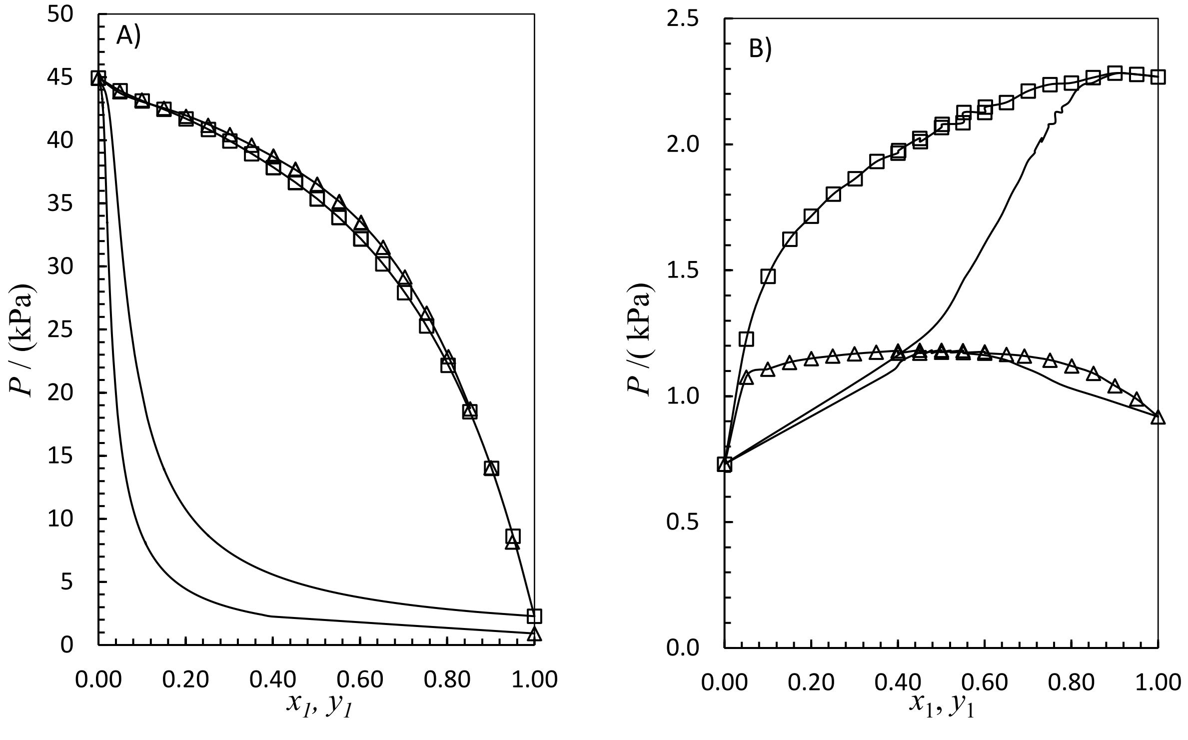

Figure 3: Experimental VLE data at $T = 313.15$ K for the binary systems; A) 1-pentanol (1) + 1-hexene (2) (Δ) and 2-pentanol (1) + 1-hexene (2) (□); B) 1-pentanol (1) + 1,2,4-trimethylbenzene (2) (Δ) and 2-pentanol (1) + 1,2,4-trimethylbenzene (2) (□). Lines

represent calculated values using Margules equation with the parameters given in Table 4.

Finally, VLE correlation results are summarized in Table 4 which contains the values of the dimensionless adjustable parameters for the different models, the root mean square of pressure residuals (defined as the differences between experimental and calculated pressures) and the maximum value of this residual. The mixtures containing 1,2,4-trimethylbenzene present an azeotrope which was calculated and given in the table.

Table 4

Fitted parameters of the models (Eqs. 1-3) used for the correlation of the binary systems at T=313.15 K, root mean square pressure deviation (rms ΔP) and the maximum deviation value (max $|\Delta P|$). The ΔP term is defined as the difference between the experimental and calculated pressure and the subscript "az" means azeotrope.

	Margules	Wilson	NRTL
	1-pentanol (1) + 1-hexene (2)		
A_{12}	2.6379	0.1103	0.7145
A_{21}	1.2387	0.6840	1.9874
λ_{12}	4.4954		
λ_{21}	0.5331		
η_{12}	6.1458		
η_{21}	0.6473		
α_{12}			0.5769
rms ΔP /(kPa)	0.061	0.184	0.206
max $|\Delta P|$ /(kPa)	0.131	0.418	0.469
	2-pentanol (1) + 1-hexene (2)		

A_{12}	2.2684	0.1658	0.7081
A_{21}	1.1642	0.7373	1.7105
λ_{12}	3.4969		
λ_{21}	0.5007		
η_{12}	4.3217		
η_{21}	0.4965		
α_{12}			0.6673
rms ΔP /(kPa)	0.043	0.279	0.140
max$\lvert \Delta P \rvert$ /(kPa)	0.079	0.528	0.293
1-pentanol (1) + 1,2,4-trimethylbenzene (2)			
A_{12}	3.1148	0.0422	0.7801
A_{21}	1.1267	0.7475	2.5264
λ_{12}	7.2318		
λ_{21}	-1.7501		
η_{12}	12.7162		
η_{21}	-8.6270		
α_{12}			0.5754
rms ΔP /(kPa)	0.008	0.009	0.008
max$\lvert \Delta P \rvert$ /(kPa)	0.028	0.028	0.028
$x_{1,\mathrm{az}}$	0.4948	0.4998	0.5117
P_{az} / kPa	1.181	1.184	1.182
2-pentanol (1) + 1,2,4-trimethylbenzene (2)			
A_{12}	1.9782	0.2360	0.8258
A_{21}	1.1972	0.6063	1.4598

λ_{12}	1.9108		
λ_{21}	-0.6108		
η_{12}	1.3168		
η_{21}	-2.2594		
α_{12}			0.6763
rms ΔP /(kPa)	0.012	0.017	0.012
max$\lvert \Delta P \rvert$ /(kPa)	0.028	0.032	0.028
$x_{1,\mathrm{az}}$	0.9527	0.9607	0.9382
P_{az} / kPa	2.283	2.285	2.294

In the case of excess enthalpies, the four binary systems were measured at two temperatures: 298.15 K and 313.15 K. The experimental data as a function of the composition are reported in Table 5.

Table 5

Experimental excess molar enthalpies H_m^E as a function of the mole fraction x_1 for the binary systems[a].

x_1	H_m^E (J·mol^{-1})	x_1	H_m^E (J·mol^{-1})	x_1	H_m^E (J·mol^{-1})
1-pentanol (1) + 1-hexene (2) at $T = 298.15$ K					
0.0000	0.0	0.3530	626.6	0.7019	324.873
0.0507	397.4	0.4030	610.8	0.7526	263.3
0.1006	497.8	0.4523	579.4	0.8008	199. 9
0.1522	560.2	0.5030	540.4	0.8482	145.8
0.2030	598.1	0.5529	495.2	0.9020	87.1
0.2531	619.6	0.6040	443.7	0.9513	38.0

0.3022	630.3	0.6523	381.7	1.0000	0.0
1-pentanol (1) + 1-hexene (2) at T = 313.15 K					
0.0000	0.0	0.3526	807.2	0.7019	456.8
0.0506	507.6	0.4026	794.8	0.7526	371.6
0.1005	664.0	0.4519	763.9	0.8025	284.8
0.1520	749.3	0.5026	717.9	0.8517	211.4
0.2027	802.4	0.5524	666.4	0.9019	132.3
0.2528	815.9	0.6035	603.2	0.9513	58.1
0.3021	829.0	0.6519	531.4	1.0000	0.0
2-pentanol (1) + 1-hexene (2) at T = 298.15 K					
0.0000	0.0	0.3512	963.4	0.7020	731.1
0.0503	488.7	0.4032	979.2	0.7510	630.6
0.0999	659.2	0.4525	978.8	0.8004	513.9
0.1511	766.5	0.5030	962.2	0.8500	391.4
0.2015	845.3	0.5529	928.2	0.9007	240.0
0.2513	901.7	0.6018	876.9	0.9507	112.3
0.3027	940.4	0.6523	810.8	1.0000	0.0
2-pentanol (1) + 1-hexene (2) at T = 313.15 K					
0.0000	0.0	0.3513	1179.0	0.7020	859.8
0.0500	589.5	0.4034	1181.7	0.7510	751.8
0.0999	821.0	0.4509	1163.0	0.8012	622.5
0.1512	957.0	0.5014	1135.7	0.8506	480.4
0.2017	1060.8	0.5513	1094.7	0.9012	310.4
0.2516	1113.6	0.6005	1036.5	0.9509	155.1
0.3028	1160.0	0.6523	949.9	1.0000	0.0

1-pentanol (1) + 1,2,4-trimethylbenzene (2) at T = 298.15 K

0.0000	0.0	0.3481	1015.0	0.6985	641.4
0.0503	520.0	0.3998	1005.1	0.7494	539.4
0.0995	733.9	0.4481	979.0	0.7991	434.5
0.1500	855.0	0.4995	934.2	0.8492	325.3
0.1995	918.6	0.5495	880.4	0.8997	220.6
0.2501	974.9	0.5985	811.8	0.9505	105.8
0.2997	1006.6	0.6482	733.2	1.0000	0.0

1-pentanol (1) + 1,2,4-trimethylbenzene (2) at T = 313.15 K

0.0000	0.0	0.3481	1257.2	0.6986	847.5
0.0503	581.5	0.3998	1254.6	0.7495	723.3
0.0995	864.0	0.4482	1232.6	0.7991	593.7
0.1500	1036.3	0.4995	1182.5	0.8492	452.3
0.1995	1141.2	0.5496	1122.0	0.8997	305.1
0.2502	1207.4	0.5986	1046.9	0.9505	148.0
0.2997	1241.7	0.6482	951.4	1.0000	0.0

2-pentanol (1) + 1,2,4-trimethylbenzene (2) at T = 298.15 K

0.0000	0.00	0.3485	1466.22	0.6988	1208.05
0.0499	601.23	0.3979	1496.47	0.7480	1082.49
0.1012	911.08	0.4482	1507.98	0.7979	921.70
0.1490	1103.21	0.4996	1489.56	0.8482	734.34
0.2006	1240.85	0.5496	1458.97	0.8990	519.43
0.2487	1345.70	0.6006	1396.39	0.9502	270.90
0.2980	1415.52	0.6502	1310.22	1.0000	0.00

2-pentanol (1) + 1,2,4-trimethylbenzene (2) at T = 313.15 K

0.0000	0.0	0.3507	1641.0	0.6987	1331.9
0.0499	621.9	0.3979	1668.0	0.7479	1191.4
0.0987	991.9	0.4504	1672.8	0.7978	1016.2
0.1490	1235.2	0.4996	1660.1	0.8481	811.2
0.1982	1395.6	0.5476	1615.6	0.8989	578.0
0.2509	1508.4	0.6005	1545.4	0.9501	300.3
0.3002	1598.1	0.6482	1449.6	1.0000	0.0

[a] Standard uncertainties (k=1): $u(x_1) = 0.0001$, $u(T) = 10$ mK, $u_r(H_m^E) = 0.005$.

Experimental data were correlated using a modified Redlich-Kister equation [35] adding a parameter C to fit better the asymmetric behavior:

$$H_m^E/(\mathrm{J \cdot mol^{-1}}) = x_1(1-x_1)\sum_{i=1}^{n} A_i(2x_1-1)^{i-1}/[1+C(2x_1-1)] \qquad (4)$$

The optimal number of parameters was selected by examining F-test [36].These parameters and the standard deviation of the fitting are summarized in Table 6.

Table 6

Parameters of Redlich-Kister equation (Eq. 4) and standard deviation of excess molar enthalpies σ for the measured systems.

T / K	C	A_1	A_2	A_3	A_4	A_5	σ
		(J·mol^{-1})					
			1-pentanol (1) + 1-hexene (2)				
298.15	0.96379	2178.58	417.03	-1151.23	-179.80	156.08	1.8
313.15	0.92917	2881.90	745.49	-907.65	-520.77	-180.20	3.9
			2-pentanol (1) + 1-hexene (2)				
298.15	0.96725	3847.07	2825.25	-161.21	-1236.76	-1135.83	3.6

313.15	0.95754	4554.35	2955.92	102.19	-533.66	-986.64	4.3
1-pentanol (1) + 1,2,4-trimethylbenzene (2)							
298.15	0.86600	3748.68	1269.68	-988.92	-437.78	440.33	3.0
313.15	0.81871	4734.31	1766.93	-502.23	-566.67	88.28	2.0
2-pentanol (1) + 1,2,4-trimethylbenzene (2)							
298.15	0.85353	5966.65	4090.31	691.90	-122.59	0.00	2.4
313.15	0.62729	6624.39	2911.90	964.67	-655.94	690.38	3.3

In Fig. 4, experimental excess enthalpies and the calculated values, using the modified Redlich-Kister equation, are plotted as a function of the composition.

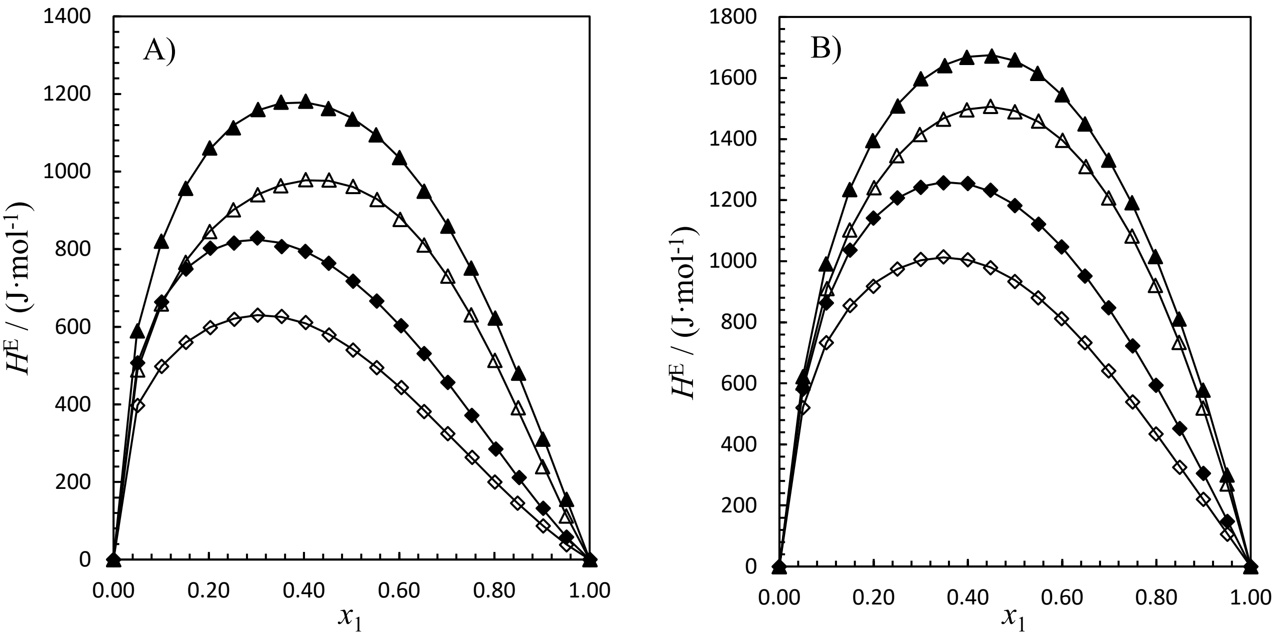

Figure 4: Experimental excess molar enthalpies as a function of the composition for the binary systems; A) 1-pentanol (1) + 1-hexene (2) (◊) at *T*=298.15 K and (♦) at *T*=313.15 K; 2-pentanol (1) + 1-hexene (2) (Δ) at *T*=298.15 K and (▲) at *T*=313.15 K; B) 1-pentanol (1) + 1,2,4-trimethylbenzene (2) (◊) at *T*=298.15 K and (♦) at *T*=313.15 K; 2-pentanol (1) + 1,2,4-trimethylbenzene (2) (Δ) at *T*=298.15 K and (▲) at *T*=313.15 K. The lines represent calculated values using Redlich–Kister equation.

4. Discussion and conclusions

Regarding VLE behavior, there is a big difference between the vapor pressure of 1-hexene and the alcohols but these VLE data are well correlated by the models. In both mixtures, six-parameter Margules equation provides the best fitting with a root mean square pressure residual of 61 Pa with a maximum deviation of 131 Pa for (1-pentanol + 1-hexene) and a root mean square pressure residual of 43 Pa with a maximum deviation of 79 Pa for (2-pentanol + 1-hexene). The fitting using Wilson model is better than using NRTL for the system with 1-pentanol and the opposite happens for the system with 2-pentanol. Concerning the mixtures containing 1,2,4-trimethylbenzene, whose vapor pressure is lower than the alcohols, six-parameter Margules equation and NRTL provide the best fitting with a root mean square pressure residual of 8 Pa and 12 Pa for 1-pentanol and 2-pentanol, respectively and a maximum deviation of 28 Pa for both. Wilson model gives similar results.

As can be seen in Fig. 3 where total pressure is plotted as a function of composition, the four binary systems present a positive deviation from Raoult's law. Furthermore, maximum pressure azeotropes are observed for the systems with 1,2,4-trimethylbenzene due to highly non-ideal behavior of aromatic hydrocarbons and alcohols mixtures. The azeotropes were calculated using the correlation models obtaining the pressures of 1.18 kPa at 1-pentanol mole fraction of 0.5 and 2.28 kPa at 2-pentanol mole fraction around 0.95, with slight differences between the three models.

In relation to excess enthalpies, an endothermic effect due to the mixing process is observed for all binary mixtures and this effect always increases with temperature. The highest excess enthalpies are obtained for the system (2-pentanol + 1,2,4-trimethylbenzene) at T= 313.15 K with H_m^E = 1673 J·mol^{-1} and the value decreases to

H_m^E = 1508 J·mol^{-1} at T = 298.15 K for a mole fraction of 2-pentanol of 0.45. Then, the second highest excess enthalpies are observed for the system (1-pentanol + 1,2,4-trimethylbenzene) at T= 313.15 K with H_m^E = 1257 J·mol^{-1} and decreasing to H_m^E = 1015 J·mol^{-1} at T = 298.15 K for a mole fraction of 1-pentanol of 0.35.

Concerning the effect of mixing of 1-pentanol or 2-pentanol with 1-hexene, the endothermic behavior is higher for the mixture (2-pentanol + 1-hexene) with maximum excess enthalpies of H_m^E = 1182 J·mol^{-1} at T= 313.15 K and H_m^E = 979 J·mol^{-1} at T = 298.15 K for a mole fraction of 2-pentanol of 0.40. For the system 1-pentanol + 1-hexene, the maximum values of excess enthalpies are H_m^E = 829 J·mol^{-1} at T= 313.15 K and H_m^E = 630 J·mol^{-1} at T = 298.15 K for a mole fraction of 1-pentanol of 0.30.

The mixing effect of this kind of mixtures is the result of the competition between hydrogen bonding in alcohols and dispersion forces of hydrocarbons. The endothermic behavior is due to the fact that chemical forces of the hydrogen bonds in the alkanol are stronger than the dispersion forces of the hydrocarbon and also the effect is enhanced with increasing temperature. In addition, the stronger endothermic character of 2-pentanol mixtures in comparison to 1-pentanol mixtures has been observed in our previous work [4-10] and also reported by J.C. Young et al. [37] where they explain the strongest excess enthalpy of secondary alcohols as a combination of the degree of self-association (number of hydrogen bonds) which follows the trend of 1°>2°>3°, and of the facility of disrupting those bonds which follows the reverse trend of 3°>2°>1°, resulting then a trend of 2°>3°>1° in the excess enthalpies.

For all these systems, the correlation using the modified Redlich-Kister equation (Eq. (4)) gives standard deviations within the uncertainty of the measurements.

We have not found VLE or excess enthalpy data in the literature for comparison and, therefore, the data reported are completely new.

Finally, different excess functions are calculated and plotted in Fig. 5 for all the binary mixtures at T =313.15 K. Excess enthalpies were fitted by Eq. (4), excess Gibbs energies were evaluated using six-parameter Margules equation, and excess entropies were calculated through the expression $T{\cdot}S^{\mathrm{E}} = H^{\mathrm{E}} - G^{\mathrm{E}}$.

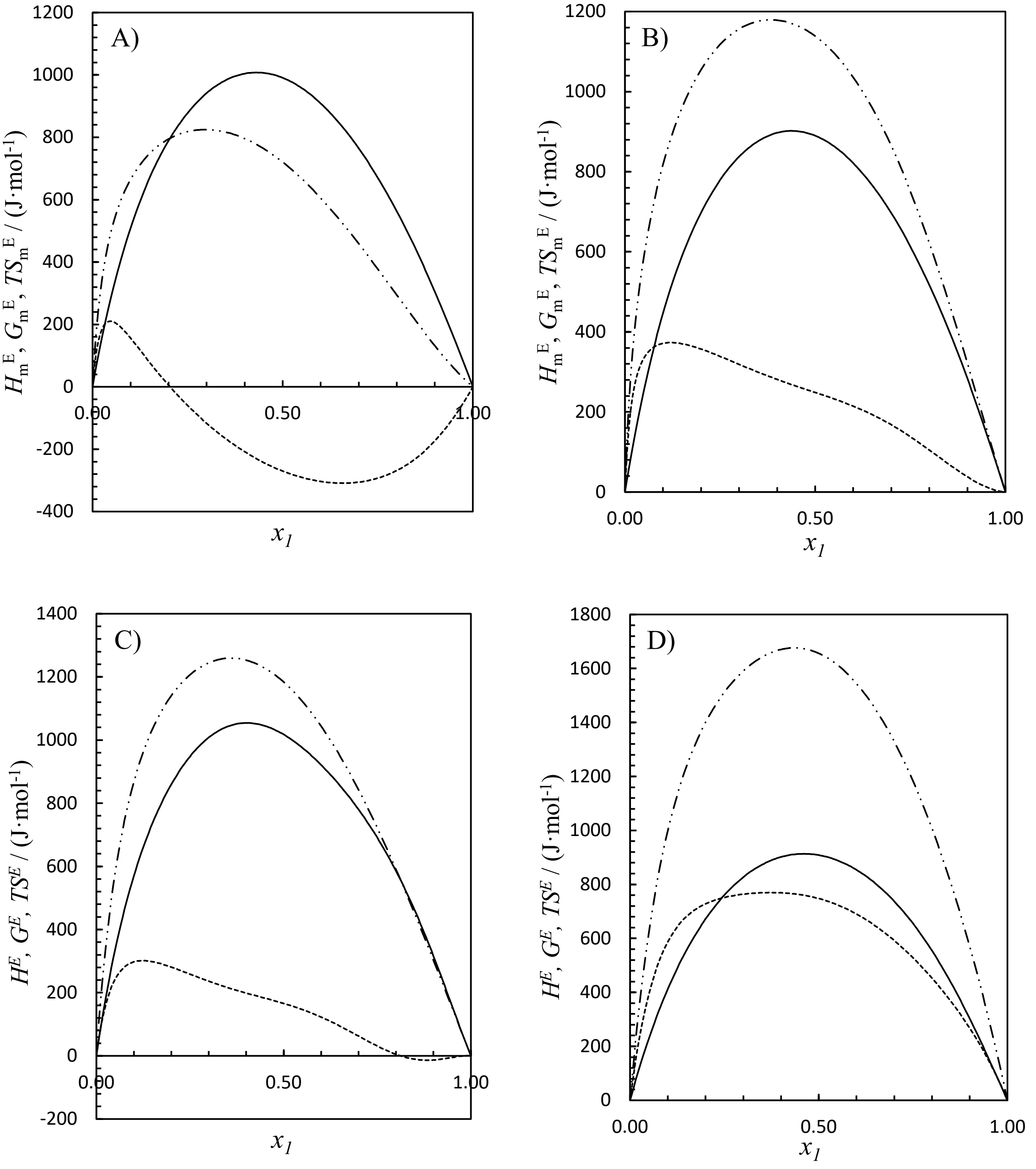

Figure 5: Excess functions, G_m^E (—), H_m^E (— ·· —) and TS_m^E (----), at 313.15 K for the systems: A) 1-pentanol + 1-hexene; B) 2-pentanol + 1-hexene; C) 1-pentanol + 1,2,4-trimethylbenzene; D) 2-pentanol + 1,2,4-trimethylbenzene.

As regards the mixtures with 1-hexene, the excess enthalpy is lower than the excess Gibbs energy for a mole fraction of 1-pentanol greater than 0.2, which results in negative values of the excess entropy in this composition range. However, for the system (2-pentanol + 1-hexene) its excess Gibbs energy is higher than its excess enthalpy in all the composition range, and so its excess entropy is always positive.

Focusing on the mixtures 1-pentanol or 2-pentanol with 1,2,4-trimethylbenzene. The excess entropy of the system (1-pentanol + 1,2,4-trimethylbenzene) is positive up to a mole fraction of alcohol of 0.8, due to the fact that the excess enthalpy is higher than the excess Gibbs energy for this composition range, but negative for a mole fraction from 0.8 to 1 (the excess Gibbs energy is slightly higher than the excess enthalpy). In the case of (2-pentanol + 1,2,4-trimethylbenzene), the excess enthalpy is much higher than the excess Gibbs energy, therefore the excess entropy is positive in all the composition range.

Comparing the systems in a different way, when 1-pentanol is mixed with 1-hexene or 1,2,4-trimethylbenzene, different behavior between both systems is observed. Maximum excess Gibbs energies are similar: $G_m^E = 1054\ \mathrm{J \cdot mol^{-1}}$ at a mole fraction of 1-hexene of 0.60 and $G_m^E = 1006\ \mathrm{J \cdot mol^{-1}}$ at a mole fraction of 1,2,4-trimethylbenzene of 0.55 but excess enthalpies are quite different, maximum excess enthalpies are: $H_m^E = 829\ \mathrm{J \cdot mol^{-1}}$ at a mole fraction of 1-hexene of 0.70 and $H_m^E = 1257\ \mathrm{J \cdot mol^{-1}}$ at a mole fraction of 1,2,4-trimethylbenzene of 0.65. It means that the excess entropy in the system 1-pentanol + 1-hexene is negative for mole fractions from 0.2 to 1, however, the excess entropy in the system 1-pentanol + 1,2,4-trimethylbenzene is positive in the composition range up to 0.8.

In contrast, when 2-pentanol is mixed with 1-hexene or 1,2,4-trimethylbenzene, maximum excess Gibbs energies are also similar: $G_m^E = 901$ J·mol^{-1} and $G_m^E = 913$ J·mol^{-1} at a mole fraction of hydrocarbon of 0.55 for both systems but much lower than the excess enthalpies, giving positive excess entropies in all the composition range.

List of symbols

A_i	adjustable parameters of Redlich-Kister equation, Eq. (4)
A_{ij}, A_{ji}	adjustable parameters of the VLE correlation models, Eqs. (1-3)
B_{ii}, B_{ij}, B_{jj}	second virial coefficients
C	adjustable parameter of Redlich-Kister equation, Eq. (4)
calc	calculated
G_m^E	excess molar Gibbs energy
H_m^E	excess molar enthalpy
i,j	constituent identification: 1 or 2
lit.	value of literature
max	maximum value of the indicated quantity
P	total pressure
P_i^s	vapor pressure of pure constituent i
R	universal gas constant
rms	root mean square
S_m^E	excess molar entropy
T	absolute temperature
V_i^L	molar volume of pure liquid i=1, 2
x	mole fraction, liquid phase
y	mole fraction, vapor phase

Greek letters

Δ	signifies difference
α_ij	adjustable parameter in NRTL model, Eq. (3)
λ_ij, λ_ji	adjustable parameters in Eq. (1)
η_ij, η_ji	adjustable parameters in Eq. (1)

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