Thermodynamics properties, VLE and H^E, of the systems 2-pentanol and cyclohexane or methylbenzene for contributing to the knowledge of new biofuels

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ABSTRACT

Accurate experimental data of vapour–liquid equilibria (VLE) and excess enthalpies (H^E) are reported for the binary systems (2-pentanol + cyclohexane) and (2-pentanol + methylbenzene). An isothermal total pressure cell was used for measuring the VLE at $T = 313.15$ K. The data were correlated using Margules, Wilson, NRTL and UNIQUAC equations. The excess enthalpies were measured at two different temperatures $T = (298.15$ and $313.15)$ K using an isothermal flow calorimeter and were correlated by the Redlich–Kister equation. The binary system 2-pentanol + methylbenzene exhibits an azeotrope and both systems present a positive deviation from the ideality. Furthermore, an endothermic behaviour is observed when 2-pentanol is mixed with these hydrocarbons.

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1. Introduction

Energy saving is an immediate and economic measure which takes part of any energy policy since it is the key of sustainability, fuel supply and competitiveness. As part of the target of the Directive «20-20-20» [1], European Union has insisted on energy efficiency with a minimum content of 10% of biofuels in gasoline and diesel fuels.

Thermodynamic properties of biofuels are in general different from fossil fuels. Moreover, literature data do not have information about uncertainties and chemical composition lacking on metrological traceability. To facilitate the wider use of biofuels in road transport, the biofuels and the blends need to become increasingly compatible with existing logistics as well as future ones; but a good characterization of the thermodynamic properties is needed to obtain an in-depth understanding. In the particular case of this study, it will be performed the characterization of liquid biofuels with the reference hydrocarbons, being the main objectives: knowledge of the thermodynamic behaviour of the liquid and vapour phase (vapour pressure, temperature and phase compositions) of the new liquid fuels, through the measurement of the vapour–liquid equilibrium of binary mixtures of bioalcohols with fossil reference hydrocarbons as well as the energy of mixing of the same mixtures through calorimetric measurements.

The renewable oxygenated additives are mainly alcohols and ethers, in this case 2-Pentanol can be considered a compound for second generation of biogasolines due to its high octane rating (up to 100 Research Octane Number-RON), better water tolerance and very high heat of combustion.

Continuing with the study of the behaviour of this component, its mixture with n-heptane or 2,2,4-trimethylpentane was already published [2], the paper reports accurate experimental data of vapour–liquid equilibria and excess enthalpies of the mixtures (2-pentanol + cyclohexane) and (2-pentanol + methylbenzene).

In a previous paper [3], binary mixtures with 1-pentanol + cyclohexane and 1-pentanol + methylbenzene were measured. Both papers will contribute to get a better knowledge of second generation biofuels, and a comparison of their behaviour is discussed.

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Table 1
Material description.

Chemical name	Source	Mass fraction purity	Purification method
2-Pentanol	Sigma–Aldrich	≥0.997	None
Cyclohexane	Sigma–Aldrich	≥0.997	None
Methylbenzene	Sigma–Aldrich	≥0.997	None

2. Experimental section

2.1. Materials

The compounds were purchased from Sigma–Aldrich and were of the highest purity available, chromatography quality reagents with a purity >0.99 (GC) for 2-pentanol, >0.995 (GC) for cyclohexane and >0.998 (GC) for methylbenzene. Their purities were also checked by gas chromatography and all were found to be >0.997. The details are summarized in Table 1. The alcohols were treated with molecular sieve to avoid the water absorption and analyzed with a Karl–Fisher test to ensure the low alcohols water content. In addition, the pure compounds are degassed using a modified distillation method as was detailed in previous papers [4,5].

2.2. Experimental techniques

An isothermal total pressure cell was used for measuring the vapour–liquid equilibrium of the binary mixtures and it was described in a previous paper [4,5]. Experimental values were obtained in two overlapping runs starting from opposite ends of the composition range. The equilibrium properties measured directly and their standard uncertainties (k = 1) are: injected volume ±0.03 mL, temperature ±10 mK and total pressure ±5 Pa. The overall mole fraction is determined accurately from the volumetric displacement of the injector pistons, the temperature of the injectors and the densities for the pure components. The estimated standard uncertainty for mole fractions is ±0.0005.

Excess enthalpies were measured with a quasi-isothermal flow calorimeter, developed in our laboratory [6]. It 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, at constant rate, energy from the flow cell and a control-heater compensates this energy and additionally the energy liberated (exothermic mixing) or absorbed (endothermic mixing) by the mixing process. The properties measured directly and their corresponding standard uncertainties are: flow rate

Table 2
VLE data: total pressure, liquid mole fraction and calculated vapour mole fraction using Margules equation for 2-pentanol (1) + cyclohexane (2) at T = 313.15 K.[a]

x_1	$y_{1,calc}$	p/kPa	x_1	$y_{1,calc}$	p/kPa
0.0000	0.0000	24.575	0.5010	0.0730	20.565
0.0497	0.0293	24.563	0.5510	0.0790	19.753
0.1000	0.0377	24.330	0.5511	0.0790	19.765
0.1502	0.0421	24.036	0.6008	0.0862	18.832
0.2004	0.0460	23.708	0.6013	0.0863	18.834
0.2507	0.0501	23.328	0.6513	0.0953	17.759
0.3006	0.0543	22.899	0.7013	0.1070	16.497
0.3489	0.0585	22.421	0.7513	0.1225	15.008
0.4007	0.0631	21.879	0.8016	0.1448	13.234
0.4007	0.0631	21.875	0.8513	0.1788	11.140
0.4508	0.0678	21.263	0.9007	0.2391	8.672
0.4509	0.0678	21.259	0.9498	0.3765	5.820
0.5009	0.0730	20.558	1.0000	1.0000	2.294

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

Table 3
VLE data: total pressure, liquid mole fraction and calculated vapour mole fraction using Margules equation for 2-pentanol (1) + methylbenzene (2) at T = 313.15 K.[a]

x_1	$y_{1,calc}$	p/kPa	x_1	$y_{1,calc}$	p/kPa
0.0000	0.0000	7.877	0.5004	0.2053	7.176
0.0498	0.0592	8.055	0.5499	0.2207	6.979
0.0995	0.0912	8.042	0.5504	0.2209	6.896
0.1495	0.1122	8.003	0.5999	0.2388	6.743
0.1996	0.1281	7.958	0.6005	0.2390	6.744
0.2499	0.1416	7.875	0.6506	0.2604	6.464
0.2998	0.1540	7.780	0.7006	0.2865	6.074
0.3497	0.1660	7.628	0.7628	0.3287	5.653
0.3997	0.1782	7.532	0.8008	0.3626	5.255
0.4004	0.1784	7.534	0.8507	0.4223	4.716
0.4498	0.1911	7.355	0.9008	0.5125	4.051
0.4504	0.1913	7.378	0.9509	0.6675	3.268
0.4999	0.2051	7.193	1.0000	1.0000	2.302

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

±0.15% (≤10 mL/min); temperature ±10 mK; the heating and cooling systems have an stability better than 2.4 μW, and it results in an uncertainty of ±0.0001 in the composition of the mixture and the expanded uncertainty in the excess molar enthalpy is better than ±1% for a cover factor k = 2 which means a confidence level of 0.95.

3. Results

The use of an static technique for measuring the equilibrium means that vapour phase need not be sampled for analysis and data are thermodynamically consistent "per se" [7]. Data reduction was done by Barker's method according to well established procedures [8,9]. The non-ideality of the vapour 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_{ii}, B_{ij}) were calculated by the Hayden and O'Connell method [10] using the parameters given by Dymond and Smith [11].

VLE data were correlated by the Margules equation up to six-parameter [12]:

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

In addition, Wilson [13], NRTL [14] and UNIQUAC [15] models were used for data reduction, whose expressions are given by Eqs. (2)–(4), respectively:

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

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

$$\frac{G_m^E}{RT} = \sum_i x_i \ln\left(\frac{\phi_i}{x_i}\right) + \left(\frac{z}{2}\right)\sum_i q_ix_i \ln\left(\frac{\vartheta_i}{q_i}\right) - \sum_i q_ix_i \ln\left(\sum_j \vartheta_j A_{ji} \right) \tag{4}$$

where A_{ij}, A_{ji} and α (only for NRTL model) are the adjustable parameters, and $G_{ji} = \exp(-\alpha_{ji}A_{ji})$; $\vartheta_i = q_ix_i/\sum_j q_jx_j$; $\phi_i = r_ix_i/\sum_j r_jx_j$ and z = 10.