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Thermodynamic behaviour of second generation biofuels: Vapour–liquid equilibria and excess enthalpies of the binary mixtures 2-pentanol and *n*-heptane or 2,2,4-trimethylpentane

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ABSTRACT

Accurate experimental data of vapour–liquid equilibria (VLE) and excess enthalpies are reported for the binary systems (2-pentanol + 2,2,4-trimethylpentane) and (2-pentanol + *n*-heptane). 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. Both binary systems exhibit a positive deviation from the ideality with azeotropes, and an endothermic behaviour has been observed when the 2-pentanol is mixed with these hydrocarbons.

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1. Introduction

The European target of decrease the dependency on the petroleum is been achieved by the use of biofuels and it also reduces CO_2 emissions and supports the agricultural community. There is a wide variety of biogenic products that can be added to fuels and the quality of these products becomes more and more important, requiring an accurate knowledge of the thermodynamic properties of the new fuel blends.

The 2-pentanol is considered a compound for the 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, the paper reports accurate experimental data of vapour–liquid equilibria and excess enthalpies of the mixtures (2-pentanol + 2,2,4-trimethylpentane) and (2-pentanol + *n*-heptane).

In previous papers [1,2], binary mixtures of hydrocarbons with 1-pentanol were measured; this paper will continue the contribution to a better knowledge of second generation biofuels.

2. Experimental

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 2,2,4-trimethylpentane and *n*-heptane. Their purities were also checked by gas chromatography and all were found to be >0.997. The details are summarized in Table 1.

2.2. Experimental techniques

An isothermal total pressure cell has been used for measuring the vapour–liquid equilibrium of the binary mixtures, and it has been described in a previous paper [3]. Experimental values were obtained in two overlapping runs starting from opposite ends of the composition range. The equilibrium properties measured directly and their uncertainties 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 uncertainties for mole fractions are ±0.0005.

Excess enthalpies have been measured with a quasi-isothermal flow calorimeter, developed in our laboratory [4]. It is based on the accurate measurement of the energy required to maintain the

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Nomenclature

List of symbols

A_i	adjustable parameters of Redlich
A_{ij}, A_{ji}	adjustable parameters of the VLE correlation models, Eqs. (2)
B_{ii}, B_{ij}, B_{jj}	second virial coefficients
C	adjustable parameter of Redlich
$G_m{}^E$	excess molar Gibbs energy
$H_m{}^E$	excess molar enthalpy
i, j constituent identification	1id=6#or 2
lit.	literature value
max	maximum value of the indicated quantity
P	total pressure
P_i^s	vapour 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, vapour phase

Greek letters

Δ	signifies difference
α_{ij}	adjustable parameter in NRTL model, Eq.id=6#(3)
λ_{ij}, λ_{ji}	adjustable parameters in Eq.id=6#(1)
η_{ij}, η	adjustable parameters in Eq.id=6#(1)

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 uncertainties are flow rate ±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 extended relative uncertainty in the excess molar enthalpy is better than ±1% for a cover factor of 2 ($k = 2$) which means a confidence level of 0.95.

3. Results

The use of a static technique for measuring the equilibrium means that the vapour phase need not be sampled for analysis and the data are thermodynamically consistent "*per se*" [5]. Data reduction was done by Barker's method according to well established procedures [6,7]. 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 [8] using the parameters given by Dymond and Smith [9].

Table 2
Total pressure VLE data for the binary system 2-pentanol (1) + 2,2,4-trimethylpentane (2) at 313.15 K.[a]

x_1	$y_{1,\ \mathrm{calc}}$	P (kPa)	x_1	$y_{1,\ \mathrm{calc}}$	P (kPa)
0.0000	0.0000	12.973	0.5008	0.1353	11.787
0.0499	0.0560	13.256	0.5502	0.1436	11.461
0.0988	0.0740	13.231	0.5509	0.1438	11.463
0.1490	0.0839	13.162	0.6001	0.1533	11.058
0.1996	0.0917	13.041	0.6007	0.1535	11.085
0.2501	0.0991	12.904	0.6508	0.1652	10.636
0.2999	0.1063	12.694	0.7008	0.1797	10.110
0.3501	0.1134	12.526	0.7512	0.1987	9.449
0.4002	0.1205	12.320	0.8012	0.2248	8.640
0.4006	0.1205	12.288	0.8513	0.2642	7.612
0.4500	0.1276	12.059	0.9009	0.3314	6.302
0.4506	0.1277	12.054	0.9501	0.4749	4.596
0.5001	0.1352	11.784	1.0000	1.0000	2.305

[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.

VLE data were correlated by the Margules equation up to six parameter [10]:

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

also Wilson [11], NRTL [12] and UNIQUAC [13] models were used for the correlation, which expressions are given by Eqs. (2)–(4), respectively:

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

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

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

where, $G_{ji} = \exp(-\alpha_{ji}A_{ji})$; $\vartheta_i = q_ix_i/\sum_j q_jx_j$; $\phi_i = r_ix_i/\sum_j r_jx_j$ and $z = 10$.

Tables 2 and 3 give the experimental values of total pressure, the liquid phase composition and the calculated vapour phase composition by Margules equation for the binary systems (2-pentanol + 2,2,4-trimethylpentane) and (2-pentanol + *n*-heptane) at $T = 313.15$ K, respectively, and both sets of data have been represented in Fig. 1. The average values of the experimental vapour pressures (P_i^s) for the pure compounds and their comparison with the literature, the molar volumes of pure liquids (V_i^L) and the second virial coefficients (B_{ii}, B_{ij}) are indicated in Table 4. The results of VLE data correlation are summarized in Table 5; it contains the values of the adjustable parameters for the different models, the root mean square of the difference between the experimental and the calculated pressures (rms ΔP) and the maximum value of this difference (max $|\Delta P|$).

Table 1
Material description.

Chemical name	Source	Mass fraction purity	Purification method
2-Pentanol	Sigma–Aldrich	≥0.997	None
2,2,4-Trimethylpentane	Sigma–Aldrich	≥0.997	None
Heptane	Sigma–Aldrich	≥0.997	None

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