



Characterizing second generation biofuels: Excess enthalpies and vapour-liquid equilibria of the binary mixtures containing 1-pentanol or 2-pentanol and n-hexane



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ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form

27 May 2016

Accepted 30 May 2016

Available online 1 June 2016

Keywords:

VLE

Excess enthalpies

1-Pentanol

2-Pentanol

Hexane

ABSTRACT

Experimental data of excess enthalpies and vapour-liquid equilibria (VLE) are reported for the binary systems (1-pentanol + n-hexane) and (2-pentanol + n-hexane). An isothermal flow calorimeter was used to determine excess enthalpies at $T = (298.15 \text{ and } 313.15) \text{ K}$ and the results were fitted using Redlich-Kister equation. Vapour-liquid equilibria data were measured using an isothermal total pressure cell at $T = 313.15 \text{ K}$. Barker's method allows to correlate these data using Margules, Wilson, NRTL and UNIQUAC equations. An endothermic behavior is observed when 1-pentanol or 2-pentanol is mixed with n-hexane whose effect increases at higher temperatures and both systems present a positive deviation from the Raoult's law.

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1. Introduction

Energy policies in the European Union focus on the promotion of the use of biofuels, as is established in Directive «20-20-20» [1], which determines a minimum content of 10% of biofuels overall gasoline and diesel fuels.

Properties of these new biofuels change in comparison with fossil fuels, therefore a characterization of these properties is required in order to enhance their use. In this sense, our research group is involved in the measurement of thermodynamic and thermophysical properties, such as density, viscosity, heat capacity, excess enthalpy or vapour-liquid equilibria, of mixtures of interest for the formulation of biofuels.

In this paper, 1-pentanol and 2-pentanol are studied as oxygenated additives of renewable origin due to their qualities such as high octane rating or high combustion heat, and n-hexane was chosen as hydrocarbon. Excess enthalpies and vapour-liquid

equilibria of the mixtures (1-pentanol + n-hexane) and (2-pentanol + n-hexane) are reported.

2. Experimental section

2.1. Materials

1-Pentanol, 2-pentanol and n-hexane were chromatography quality reagents of the highest purity available from Sigma-Aldrich. Their purities were >0.997 (GC), >0.98 (GC) and >0.99 (GC), respectively and were also checked by gas chromatography being better than 0.997. The details are summarized in Table 1.

2.2. Experimental techniques

Both techniques, used in this work, were described in detail in previous papers [2,3] and a brief summary of their main characteristics is reported below.

A quasi-isothermal flow calorimeter, developed in our laboratory, was used to determine excess enthalpies [2]. The technique is based on the accurate measurement of the energy required to maintain the mixing vessel at a constant temperature, using a Peltier cooler to remove a constant heat rate from the flow cell, and

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Table 1
Material description.

Chemical name	Source	Mass fraction purity (GC) ^a	Purification method
1-Pentanol	Sigma-Aldrich	≥0.997	None
2-Pentanol	Sigma-Aldrich	≥0.997	None
n-Hexane	Sigma-Aldrich	≥0.997	None

^a From the supplier.

a control-heater to compensate this energy and 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 ±0.15% (≤10 mL/min); temperature ±10 mK; the heating and cooling systems have a stability better than 2.4 μW. The estimated expanded uncertainties, for a cover factor $k=2$, are: ±0.0002 in the composition and ±1% in the excess molar enthalpy.

Vapour-liquid equilibrium measurements were carried out with an isothermal total pressure cell [3]. The equilibrium properties measured directly and their standard 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, obtaining an estimated standard uncertainty for composition of ±0.0005. Experimental values were obtained in two overlapping runs starting from opposite ends of the composition range and the repeated central compositions are used for checking the quality of the measurements.

3. Results

Excess enthalpies were measured at $T=(298.15$ and $313.15)$ K for the binary mixtures (1-pentanol + n-hexane) and (2-pentanol + n-hexane). These data, reported in Table 2 and in Fig. 1, were correlated using a modified Redlich-Kister [4] equation:

$$\frac{H_m^E}{J \cdot \text{mol}^{-1}} = x(1-x) \sum_{i=1}^n \frac{A_i(2x-1)^{i-1}}{[1+C(2x-1)]} \quad (1)$$

The parameters of equation (1) and the standard deviations are given in Table 3. The optimal number of parameters was selected by examining F-test [5].

As regards the use of a static technique for measuring VLE, the vapour phase need not be sampled for analysis and the data are thermodynamically consistent “per se” [6]. Barker’s method [7,8] was applied for data reduction and the virial equation of state was used for modelling vapour phase non-ideality. Second virial coefficients (B_{ii} , B_{ij}) were calculated by the Hayden and O’Connell method [9] using the parameters given by Dymond and Smith [10]. The average values of the experimental vapour pressures (p_i^{sat}) for the pure compounds and their comparison with the literature [11–22], the molar volumes of pure liquids (V_i^{L}) and the second virial coefficients (B_{ii} , B_{ij}) are indicated in Table 4.

Margules equation up to six-parameter [23], Wilson [24], NRTL [25] and UNIQUAC [26] models were applied for correlating the experimental data. The expressions are given by Eqs. (2)–(5), respectively:

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

Table 2
Experimental excess molar enthalpies H_m^E as a function of the mole fraction x_1 for the binary systems^a at atmospheric pressure.

x_1	$H_m^E/J \cdot \text{mol}^{-1}$	x_1	$H_m^E/J \cdot \text{mol}^{-1}$	x_1	$H_m^E/J \cdot \text{mol}^{-1}$
1-Pentanol (1) + n-hexane (2) at $T = 298.15$ K					
0.0000		0.3522		0.7015	
0.0504	0.0	0.4030	537.8	0.7514	290.1
0.0999	329.3	0.4528	524.2	0.8021	235.6
0.1509	413.2	0.5035	505.8	0.8518	178.8
0.2010	465.6	0.5535	477.6	0.9004	126.6
0.2524	501.3	0.6025	441.6	0.9499	69.6
0.3027	526.9	0.6525	397.1	1.0000	21.0
	533.6		346.3		0.0
1-Pentanol (1) + n-hexane (2) at $T = 313.15$ K					
0.0000		0.3503		0.7016	
0.0504	0.0	0.4032	724.5	0.7515	415.4
0.1000	455.1	0.4530	711.6	0.8019	340.1
0.1510	569.2	0.5039	688.6	0.8517	264.8
0.2011	637.7	0.5539	652.0	0.9004	200.0
0.2525	680.1	0.6027	605.1	0.9499	128.2
0.3007	705.9	0.6527	547.3	1.0000	67.4
	720.9		487.4		0.0
2-Pentanol (1) + n-hexane (2) at $T = 298.15$ K					
0.0000	0.0		834.8		637.0
0.0500	442.7	0.3527		0.7018	
		0.4013	847.5	0.7519	546.9
0.1016	575.7	0.4530	848.7	0.7992	449.7
0.1523	663.0	0.5018	835.9	0.8509	341.3
0.2021	724.9	0.5518	813.0	0.8999	229.2
0.2509	770.3	0.6027	769.7	0.9496	108.9
0.3012	808.2		709.8	1.0000	0.0
		0.6528			
2-Pentanol (1) + n-hexane (2) at $T = 313.15$ K					
0.0000	0.0		1027.2		774.8
0.0501	559.9	0.3530		0.7019	
		0.4015	1032.7	0.7519	670.0
0.1017	740.8	0.4533	1028.7	0.7992	562.8
0.1524	851.9	0.5022	1006.4	0.8509	427.9
0.2022	923.7	0.5521	977.5	0.9016	284.5
0.2512	970.7	0.6031	928.2	0.9513	133.1
0.3014	999.3		855.0	1.0000	0.0
		0.6531			

^a Standard uncertainties ($k=1$): $u(x_1) = 0.0001$, $u(T) = 10$ mK, $u_i(H_m^E) = 0.5\%$.

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