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## LLE OF BINARY MIXTURES 3-PHENYL-1-PROPANOL + ALKANES

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### 1. Introduction

A liquid mixture is more complex the greater the number of interactions that originate between the different active groups (functional groups): significant parts that constitute the characteristic links of the chain of each type of molecules.

The determination of the liquid-liquid equilibrium (LLE) of binary mixtures is a way of approaching the study of molecular interactions. Thermodynamic stability analysis indicates that a liquid mixture separates into two liquid phases if doing so can decrease its Gibbs energy. This phenomenon is important in many separation processes such as extraction and extractive distillation. The partial miscibility is a manifestation of the non-ideal behavior of liquids and its prediction is a test for the theories of dissolutions.

In this work, LLE curves have been determined for the 3-phenyl-1-propanol ( $C_6H_5-(CH_2)_2-CH_2OH + CH_3(CH_2)_n-CH_3$  mixtures ( $n = 5,6,7,8,9$ ) using critical opalescence procedure. 3-phenyl-1-propanol belongs to the class of organic compounds known as benzene and substituted derivatives. This substance is a sweet, anise, and balsam-tasting compound. 3-phenyl-1-propanol is found, on average, in the highest concentration within bilberries. It has also been detected, but not quantified in, several different foods, such as evergreen blackberries, mushrooms, highbush blueberries, pomes, and alcoholic beverages. This could make 3-phenyl-1-propanol a potential biomarker for the consumption of these foods.

This work is part of the investigation of the proximity effects presented in liquid mixtures involving aromatic polar compounds. These proximity effects occur between the aromatic ring ( $C_6H_5$  – group) and the polar X group of the aromatic compound. These effects are intramolecular effects and lead to interactions between the phenyl ring and the X group which are substantially different from those between the mentioned groups when they belong to different molecules [1]. In this framework, mixtures including aromatic amines [2-8], aromatic alkanals, ketones, alkanooates [9-12], aromatic nitriles, 2-phenoxyethanol[13], or aromatic alkanols [14-16] have been studied.

## 2. Materials and methods

Information about the source, purity, water content and density,  $\rho$ , of the pure compounds used in the experimental part of this research is included in Table 1. The chemicals were used as received without further purification. Prior to use, the liquids are stored in containers with molecular sieve (Union Carbide Type 4D, Fluka). Density results were obtained from a vibrating-tube densimeter and a sound analyser, Anton Paar model DSA-5000. The repeatability and the relative standard uncertainty of the values are, respectively,  $5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ , and  $0.002 \text{ kg} \cdot \text{m}^{-3}$ . The results are in good agreement with those reported in the literature (Table 1). The water content of the samples is determined by the Karl-Fisher method and the values are also shown in Table 1.

Table 1. Properties of pure compounds at 298.15 K and atmospheric pressure<sup>a</sup>

Compound	Molar fraction <sup>b</sup>	$\rho / \text{kgm}^{-3}$ Exp.	$\rho / \text{kgm}^{-3}$ Lit.	Water content <sup>c</sup>
3-phenyl-1-propanol	$\geq 99\%$	997.780	1032[17]	57 ppm
n-Octane	$\geq 99\%$	698.682	698.62[18]	38 ppm
n-Decane	$\geq 99\%$	726.347	726.28[18]	20 ppm
n-Dodecane	$\geq 98\%$	745.508	745.31[18]	25 ppm
n-Tetradecane	$\geq 99\%$	759.275	759.29[18]	25 ppm
n-Hexadecane	$\geq 99\%$	770.221	770.06[18]	33 ppm

<sup>a</sup> standard uncertainties are:  $u(T)=0.01 \text{ K}$ ;  $u(P)=1 \text{ kPa}$ ; the relative standard uncertainty for density,  $\rho$ ,  $u(\rho)=0.002$  and 0.02 for water content; <sup>b</sup> provided by the supplier from GC analysis; <sup>c</sup> in mass fraction.

The mixtures are prepared by weighing with a measurement precision of 0.0001 g, inside Pyrex tubes with an internal diameter of 0.9 cm and a length of 4 dm. These tubes are immediately sealed at atmospheric temperature and pressure. The conversion to molar magnitudes is based on the 2013 Relative Atomic Mass Table published by the IUPAC Commission of Isotopes Abundances and Atomic Weights (CIAAW) [19]. The uncertainty in the calculation of the mole fractions is less than 0.0005. The weighing precision is 0.0001, but due that the most volatile component partially evaporates in the free volume of the ampoule ( $\cong 1.17 \times 10^{-6} \text{ m}^3$ ) this value is slightly lower.

The LLE curves were determined by means of the observation of the turbidity produced on cooling ( $1.2 \text{ K h}^{-1}$ ) when a second phase takes place. Details on the experimental method applied and on the apparatus calibration can be found elsewhere [20]. Figure 1 shows the change in the appearance of the mixture when the phase separation occurs. The equilibrium temperatures were measured using a Pt-1000 resistance. Two or three runs are conducted for a better assessment of these temperatures. The thermometer was calibrated according to the ITS-90 scale of temperature using the triple point of the water and the fusion point of Ga as fixed points. The precision of the equilibrium temperature measurements is  $\pm 0.001 \text{ K}$ . The corresponding estimated standard uncertainty depends on the region where measurements are conducted. In the flat region of the LLE curves (top of the curves), the uncertainty of the temperature is 0.1 K. Outside from this region (tails of the curves), it is 0.2 K. For the equilibrium mole fractions, the standard uncertainty is 0.0005. This value is estimated taking into account that the more volatile component is partially evaporated to the mentioned free volume of the ampoule.

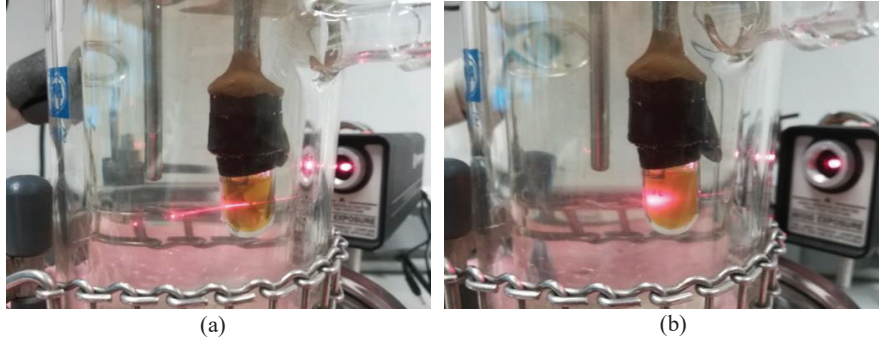


Figure 1. Detail of the experimental procedure: (a) one phase mixture; (b) the cooling of the mixture causes the appearance of the second phase

### 3. Experimental Results

The directly measured liquid-liquid equilibrium temperatures,  $T$ , vs.  $x_1$ , the mole fraction of the 3-phenyl-1-propanol +  $n$ - $C_n$  ( $n=8,10,12,14,16$ ) systems are presented in Figure 2 and Table 2. As can be observed in Figure 2, some features of the LLE curves of the studied mixtures are: (i) they show a rather flat maximum; (ii) the curves become progressively skewed to higher values when alkane size increases; (iii) The UCST values increase more or less linearly with the number of C atoms of the  $n$ -alkane (Table 2); (iv) the asymmetry of the curves shifts from the alkane-rich zone to the alcohol-rich zone as the number of carbons in the alkane increases.

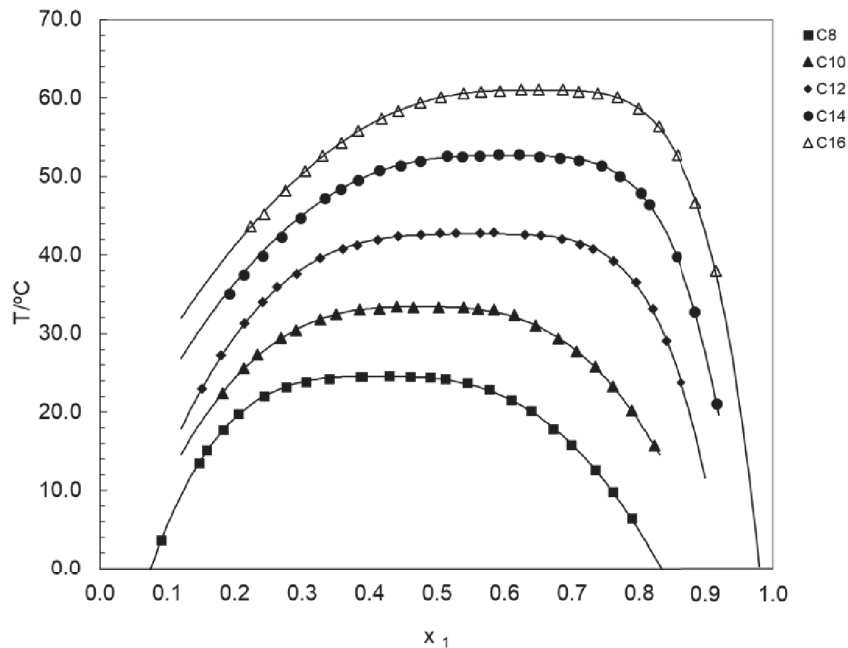


Figure 2. LLE for 3-phenyl-1-propanol (1) +  $n$ -alkane (2) mixtures. Points, experimental results (■)  $n$ -octane, (▲)  $n$ -decane, (◆)  $n$ -dodecane; (●)  $n$ -tetradecane; (△)  $n$ -heptane. Solid lines are the result of the fitting of the experimental data by means of equation (1) using the parameters collected in Table 3.

The experimental data of each system were correlated by eq. 1 [21; 22]:

$$T = T_c + k|y - y_c|^m \quad (1),$$

$$y = (\alpha \cdot x_1)/(1 + x_1 \cdot (\alpha - 1)) \quad (2),$$

$$y_c = (\alpha \cdot x_c)/(1 + x_{1c} \cdot (\alpha - 1)) \quad (3).$$

where  $m$ ,  $k$ ,  $\alpha$ ,  $T_c$ , and  $x_{1c}$ , are the parameters which must be fitted against the experimental data from an adjustment based on a Marquardt algorithm [23] with all the points weighted equally. Table 3 gives the values of the parameters, and the standard deviations for the LLE temperatures,  $\sigma(T)$ , calculated from equation 4:

$$\sigma(T) = \left[ \frac{\sum(T_{exp} - T_{calc})^2}{N-p} \right]^{1/2} \quad (5).$$

$N$  is the number of experimental data and  $p$  the number of the fitting parameters in Eq. 1. Equation 1, fits perfectly the experimental data, as it is shown in Figure 2.

Table 2: Experimental data of the LLE of the binary systems 3-phenyl-1-propanol + n-alkanes at atmospheric pressure.

3-phenyl-1-propanol (1) + n-octane (2)				3-phenyl-1-propanol (1) + n-decane (2)			
$x_1$	T(K)	$x_1$	T(K)	$x_1$	T(K)	$x_1$	T(K)
0.0908	276.84	0.4604	297.66	0.1821	295.52	0.5395	306.44
0.1469	286.62	0.4894	297.56	0.2128	298.72	0.5609	306.26
0.1586	288.26	0.5123	297.41	0.2339	300.47	0.5841	306.19
0.1823	290.95	0.5444	296.92	0.2688	302.61	0.6144	305.47
0.2054	292.89	0.5769	296.01	0.2910	303.56	0.6460	304.12
0.2438	295.16	0.6102	294.69	0.3262	304.93	0.6801	302.48
0.2766	296.29	0.6389	293.31	0.3500	305.57	0.7062	300.87
0.3052	296.97	0.6720	291.01	0.3851	306.21	0.7349	298.93
0.3402	297.41	0.6990	288.96	0.4141	306.23	0.7607	296.39
0.3862	297.63	0.7347	285.76	0.4406	306.57	0.7893	293.31
0.3901	297.62	0.7604	282.95	0.4647	306.47	0.8219	288.87
0.4292	297.79	0.7888	279.55	0.5025	306.50	0.5395	306.44
3-phenyl-1-propanol (1) + n-dodecane (2)				3-phenyl-1-propanol (1) + n-			
$x_1$	T(K)	$x_1$	T(K)	$x_1$	T(K)	$x_1$	T(K)
0.1516	296.08	0.5283	315.91	0.1917	308.22	0.5632	325.82
0.1792	300.34	0.5637	315.97	0.2133	310.63	0.5911	325.98
0.2147	304.40	0.5845	316.00	0.2416	313.03	0.6208	325.99
0.2411	307.12	0.6300	315.75	0.2694	315.50	0.6514	325.70
0.2628	309.09	0.6540	315.70	0.2974	317.86	0.6816	325.53

0.2916	310.70	0.6848	315.13	0.3335	320.37	0.7105	325.23
0.3262	312.78	0.7121	314.49	0.3574	321.52	0.7435	324.51
0.3610	313.88	0.7311	313.86	0.3832	322.71	0.7711	323.21
0.3822	314.43	0.7618	312.36	0.4147	323.95	0.8020	321.05
0.4116	315.09	0.7951	309.66	0.4453	324.55	0.8148	319.66
0.4420	315.54	0.8199	306.24	0.4751	325.14	0.8562	312.94
0.4761	315.79	0.8404	302.18	0.5141	325.81	0.8844	305.93
0.5046	315.90	0.8632	296.94	0.5374	325.72	0.9168	294.16
phenyl-1-propanol (1) + n-hexadecane (2)							
$x_1$	T(K)	$x_1$	T(K)				
0.2228	316.79	0.5934	334.04				
0.2437	318.38	0.6251	334.21				
0.2752	321.38	0.6501	334.25				
0.3040	323.85	0.6861	334.19				
0.3306	325.84	0.7097	333.89				
0.3579	327.49	0.7385	333.71				
0.3825	328.98	0.7673	333.23				
0.4176	330.57	0.7992	331.81				
0.4427	331.52	0.8296	329.55				
0.4748	332.53	0.8576	325.88				
0.5058	333.24	0.8854	319.78				
0.5392	333.77	0.9152	311.08				

The standard uncertainties,  $u$ , are:  $u(x)=\pm 0.0005$ ;  $u(T)=\pm 0.05$  K;  $u(P)=\pm 0.01$  kPa;

Table 3. Coefficients in eq. (1) for the fitting of the ( $x_1$ , T) experimental pairs.

$N$	$m$	$k$	$\alpha$	$T_c(K)$	$x_{1c}$	$\sigma(T)$ (K)
		3-phenyl-1-propanol (1) + n-Octane (2)				
24	3.028	-439	1.341	297.70	0.4113	0.08
		3-phenyl-1-propanol (1) + n-decane (2)				
26	2.870	-369	1.010	306.55	0.4747	0.11
		3-phenyl-1-propanol (1) + n-Dodecane (2)				
26	3.761	-991	0.661	315.80	0.5610	0.11
		3-phenyl-1-propanol (1) + n-Tetradecane (2) (2)				
26	3.357	-660	0.522	325.83	0.6078	0.09
		3-phenyl-1-propanol (1) + n-Hexadecane (2)				
26	3.307	-605	0.455	334.15	0.650	0.10

As can be seen in Figure 3, the ELL curves of the 3-phenyl-1-propanol + n-alkane systems show a higher UCTS that increases as the length of the alkane increases, in a practically linear way (Figure 4). The asymmetry of the curves changes from the alkane rich zone to the alcohol rich zone with the length of the n-alkane, as does the value  $x_{1C}$  (Figure 4), being the curve practically symmetric for the mixture of 3-phenyl-1-propanol with n-dodecane.

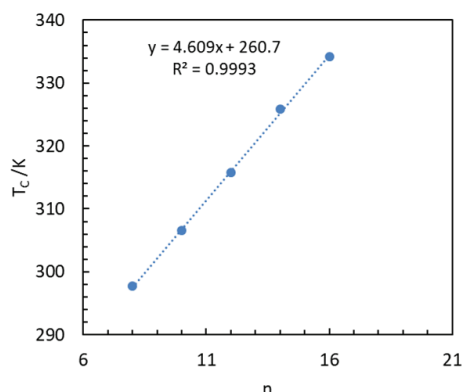


Figure 3.  $T_c$  vs  $n$  ( $n=8,10,12,14,16$ )

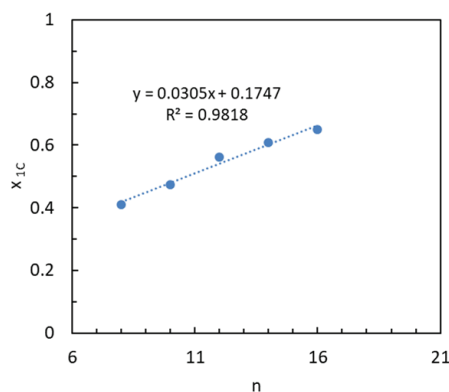


Figure 4.  $T_c$  vs  $x_{1C}$  ( $n=8,10,12,14,16$ )

#### 4. Conclusions

Thermophysical properties of binary liquid mixtures have been very useful in obtaining information on the intermolecular interactions and geometrical effects in the systems. The liquid-liquid equilibrium (LLE) curves for 3-phenyl-1-propanol ( $C_6H_5-(CH_2)_2-CH_2OH$ ) + n-alkane ( $CH_3(CH_2)_nCH_3$ ) mixtures ( $n = 6,8,10,12,14$ ) have been obtained by the critical opalescence method using a laser scattering technique. All of the systems show an upper critical solution temperature (UCST). In addition, the LLE curves have a rather horizontal top, and their symmetry depends on the alkane size. The UCST increases almost linearly with  $n$ .

Mixtures containing aromatic alkanols and n-alkanes show LLE curves, with moderately high UCTS values. In contrast, systems involving 1-alkanols + n-alkanes are characterized by rather low  $H_m^E$  values and these curves are skewed toward low alcohol concentrations. This fact is explained in terms of the alcohol self-association, which is scarcely broken by alkanes[16]. The dipolar interactions between alkanol molecules are strengthened by the presence of the  $C_6H_5-$  and  $-OH$  groups in the same molecule. The replacement of the n-alkane by an aromatic compound, in mixtures with a given 1-alkanol, increases  $H_m^E$ . In summary, intermolecular effects between the  $-OH$  and aromatic groups increase  $H_m^E$  values compared to those of 1-alkanol + n-alkane systems, while intramolecular effects between the mentioned groups lead to solutions become more immiscible[16].

The strength of the intramolecular effects between the  $C_6H_5-$  and the X groups depends on the polar group considered and its length. For hexadecane mixtures, UCTS (phenol)=360.7 K [24]; UCTS (phenyl-methanol)=340.5 K[15]; UCTS (2-phenyl-ethanol)=343.6 K [16]; UCTS (3-phenyl-1-propanol)=334.5 K (this work), and UCTS (2-hydroxybenzaldehyde) = 313.1 K [11]. Mixtures of 1-hexanol or 1-heptanol with alkanes are miscible at 298.15 K at any composition, as well the mixtures of benzaldehyde with alkanes from n-heptane to n-hexadecane. The aromatic ring enhances the interactions alkanol + alkanol, and the presence of the aldehyde group attenuates these interactions increasing the intermolecular effects between aldehyde-alkanol groups.



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