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Liquid-liquid equilibrium data of limonene + octanal + solvent systems

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1,3-butanediol has been tested as solvent for essential oil desterpenation process. For this reason, liquid-liquid equilibrium data of the system limonene+octanal+1,3-butanediol have been obtained at two different temperatures. These data were satisfactorily correlated with NRTL activity coefficient model in order to obtain the binary interaction parameters of the mixture. Besides, an extraction column was simulated, by using ASPEN PLUS® software, to determine the influence of several variables on the amount and purity of the recovered limonene.

1. Introduction

Nowadays, the importance of the food industry is increasing and this involves the generation of a great amount of subproducts. Orange and lemmon crusts, from which essential oils can be obtained, are between the most important.

Essential oils are constituted mainly by two fractions, one containing terpene hydrocarbons (over 90% limonene) and the other, oxygenated terpenoid compounds such as linalool or octanal. Although oxygenated compounds are generally considered preferable due to odor, limonene can be also applied in chemical industry as solvent (in sustitution, for example, of chloride solvents) and, moreover, the epoxide of limonene is an important reaction intermediate in organic synthesis. For this reason, it is interesting to separate limonene and the oxygenated fraction (Kirk and Othmer, 1996).

The separation of limonene and the oxygenated fraction can be developed either by distillation or liquid-liquid extraction. Due to the high boiling point of this compounds, distillation involves working under vacuum conditions or with steam stripping so, in most of the cases, extraction (which can be done at room temperature and pressure) is the preferred procedure. For designing an extraction column, the first step is to determine the liquid-liquid equilibrium of the different components, to determine the number of theoretical stages to reach a specified separation degree.

In literature, equilibrium diagrams have been obtained with solvents as ethanol/ water (Arce et al., 2004a), aminoalcohols (Arce et al., 2004b), or glycols (Sevgili et al., 2008) for the ternary mixtures limonene/linalool/solvent, but there is not any work concerning limonene and octanal separation, although this last compund is largely employed as an

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additive for cosmetics (Kirk and Othmer, 1996). In this work, 1,3-butanediol is proposed as solvent for octanal separation from limonene, by means of an extraction process.

2. Experimental section

2.1 Materials

All materials used were analytical grade, and were purchased from Aldrich

2.2 Apparatus and procedure

Firstly, the solubility curve was determined at room temperature, according to the cloud point method (Othmer et al., 1940). Thus, the regions of miscibility and immiscibility of the mixture were established.

Afterwards tie-lines were obtained at 298.15 K and 313.15 K. For this purpose, several mixtures with an overall composition covering the immiscibility region were placed, in a water-jacketed thermostatted equilibrium cell, entirely made of glass. The system was stirred for 1 h and then left overnight in order to reach equilibrium. A sample of each phase was taken and analyzed using a Perkin Elmer A/S gas chromatograph, equipped with a 60 m x 0,32 mm x 1 μm DB1 capillary column and a flame ionization detector.

3. Results and discussion

3.1 Liquid-liquid equilibrium data

Table 1 shows the liquid-liquid equilibrium data for limonene (1) + octanal (2) + 1,3-butanediol (3) systems, at 298.15 and 313.15 K. Preliminary experiments with 1,2-propenediol as solvent were also carried out but the efficiency of this last solvent in the extraction process is clearly lower than the one of 1,3-butanediol.

Table 1. Experimental tie-line mole fraction data for limonene (1) +octanal (2) + 1,3-butanediol (3) system.

Limonene rich-phase			1,3-Butanediol rich-phase		
x_1	x_2	x_3	x_1	x_2	x_3
		$T = 298.15$ K			
0,6799	0,2250	0,0951	0,0693	0.1378	0,7929
0,7021	0,1984	0,0995	0,0375	0.0836	0,8789
0,7124	0,2035	0,0841	0,0567	0.1032	0,8401
0,7730	0,1595	0,0675	0,0311	0.0691	0,8998
0,7816	0,1768	0,0417	0,0356	0.0548	0,9096
0,8013	0,1385	0,0602	0,0147	0.0167	0,9686
		$T = 313.15$ K			
0.6832	0.2078	0.1090	0.0539	0.0913	0.8548
0.7351	0.1813	0.0836	0.0422	0.0722	0.8855
0.7606	0.1503	0.0891	0.0429	0.0544	0.9027
0.7624	0.1702	0.0674	0.0391	0.0697	0.8912

Limonene rich-phase			1,3-Butanediol rich-phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.7904	0.1472	0.0624	0.0360	0.0539	0.9102
0.7963	0.1289	0.0748	0.0297	0.0335	0.9368
0.8402	0.0969	0.0628	0.0228	0.0179	0.9593
0.8727	0.0694	0.0579	0.0201	0.0089	0.9711
0.9060	0.0442	0.0499	0.0208	0.0042	0.9750

The reliability of the data was evaluated by means of Othmer and Tobias (1942) correlation, as shown in Equation 1, where x_{11} is the mole fration of limonene in the limonene-rich phase, x_{33} is the mole fration of glycol in the glycol-rich phase, and *a* and *b* are constants.

$$\ln\left(\left(1-x_{11}\right)/x_{11}\right)=a+b\cdot\ln\left(\left(1-x_{33}\right)/x_{33}\right) \tag{1}$$

These results appear in Figure 1. As it can be seen, there is a linear tendency, indicating the consistency of the tie-line data. The values of the Othmer and Tobias constants appear in Table 2.

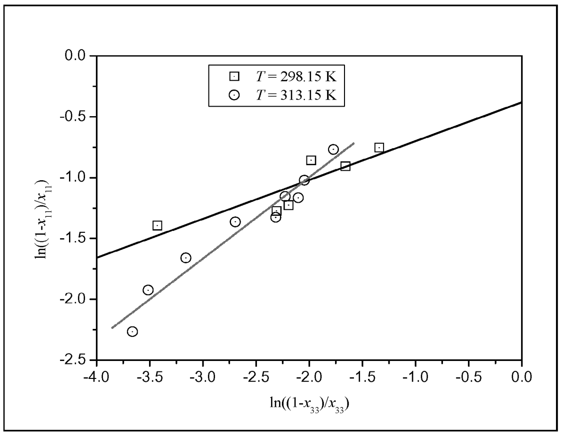

Figure 1. Othmer and Tobias plot for limonene (1) + octanal(2) + 1,3-butanediol (3) system.

Table 2. a and b constants of Othmer and Tobias equation, and correlation factor R^2, for limonene (1) +octanal (2) + 1,3-butanediol (3) system.

	A	*b*	R^2
$T = 298.15$ K	-0.3808	0.3195	0.7687
$T = 313.15$ K	0.3385	0.6681	0.9521

These data were correlated to the NRTL (Renon and Prausnitz, 1968) activity coefficients model, by using ASPEN PLUS® commercial software. This software employs an objective function called "maximum likelihood" which minimizes the difference between experimental and fitted data for all the variables involved in the fitting (pressure, temperature, and liquid composition of both components). The binary interaction parameters of two components, *i* and *j*, are defined according Equation 2, while the value of α parameter of NRTL equation was fixed in 0.3.

$$\tau_{ij} = a_{ij} + b_{ij}/T \tag{2}$$

NRTL b_{ij} binary interaction parameters are shown in Table 3. These parameters were obtained by adjusting the data of both temperatures at the same time, so the dependence on temperature is taken into account. a_{ij} parameters were assumed equal to zero and were no fitted; otherwise, there would be twelve adjustable parameters for each system, what means that a large number of experimental points would be necessary.

Figure 2 shows the experimental tie-line data along with the regressed values obtained with NRTL model. As it can be seen, NRTL model accurately fits the experimental data by considering only the b_{ij} parameters. In order to support this statement the total root-mean-square deviation, along with the limonene mole fraction in glycol rich phase, and the glycol mole fraction in limonene rich phase ones, are shown in Table 4. In all cases, the deviation value is less than 10%.

Table 3. NRTL b_{ij} binary interaction parameters, for limonene (1) +octanal (2) + 1,3-butanediol (3) system.

b_{12}	163.48
b_{21}	-41.01
b_{13}	1332.64
b_{31}	794.39
b_{32}	50.92
b_{23}	345.56

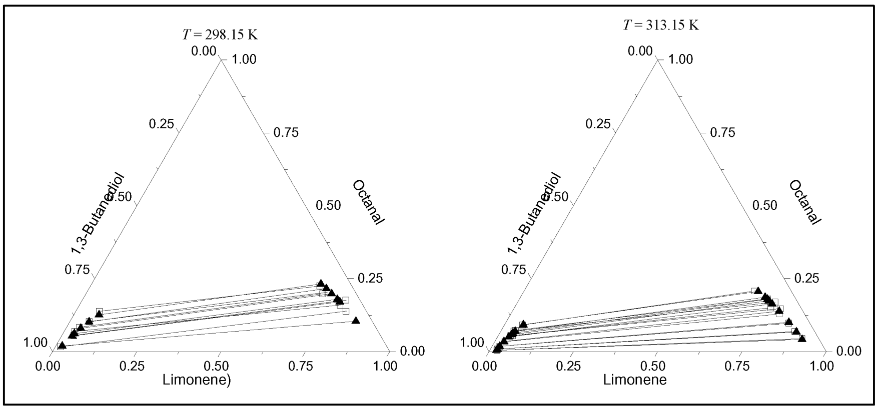

Figure 2. Ternary Liquid-Liquid diagram for limonene (1) + octanal (2) + 1,3-butanediol at both T = 298.15 K and T = 313.15 K. □, experimentally determined, ▲, values obtained with NRTL model.

Table 4. Octanal mole fraction in glycol rich phase, $\sigma(x_{23}) = [x_{23}(exp.) - x_{23}(calc.)]^2$,and octanal mole fraction in limonene rich phase, $\sigma(x_{21}) = [x_{21}(exp.) - x_{21}(calc.)]^2$, root-mean-square deviations.

	T = 298.15 K	T = 313.15 K
100. $\sigma(x_{23})$	8.36	6.08
100. $\sigma(x_{21})$	6.54	4.17

3.2 Results of simulation

The obtained binary interaction parameters were used in the simulation of an extraction column by using ASPEN PLUS® software. An inlet stream of 1000 kmol/h with 0.95 limonene mole fraction and 0.05 octanal mole fraction was fed to an extraction column, along with a solvent stream, at 30ºC and atmospheric pressure. Two products streams were obtained: a raffinate one, which contains most of the limonene, and an extract stream, which contains mainly the solvent along with the extracted octanal.

Figure 3 shows the recovery degree of limonene (limonene mole flow in raffinate, divided by limonene mole flow in the inlet stream) and octanal (octanal mole flow in the extract, divided by octanal mole flow in the inlet stream), as a function of the number of theoretical stages (while maintaining the solvent/feed ratio in a value of one), and as a function of the solvent/feed ratio (for a value of the number of theoretical stages of 10).

In the first case, it can be seen that the limonene recovery does not vary with the number of theoretical stages, but the octanal recovery increases until a constant value around of 70%, when the number of theoretical stages is 10 or higher. The purity of the limonene (mole fraction) in the raffinate is, in all cases, above 0.95.

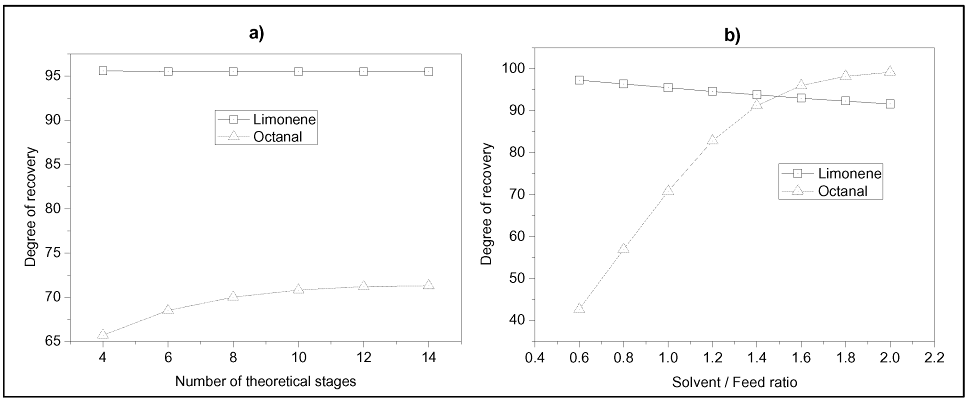

Figure 3. Limonene (□) and octanal (o) degree of recover,as a function of a) stage number and b) solvent/feed ratio.

In the second case, the octanal recovery increases very much when increasing the amount of solvent fed to the column so, with a solvent/feed ratio of 2 is possible to recover almost 100% of the octanal. Besides, when increasing the solvent/feed ratio, althought the amount of limonene recovered in the raffinate stream decreases due to the fact that some of the limonene is extracted along with the octanal, the purity of the limonene in the raffinate stream increases. In all cases, the purity of the limonene (mole fraction) in the raffinate is higher than 0.96 but, by using a solvent/feed ratio of 2, it is possible to obtain limonene with 0.995 purity.

4. Conclusions

1,3-Butanediol has been used as a solvent for limonene and octanal separation by means of an extraction process. For this reason, liquid-liquid equilibrium data have been obtained for the system limonene+octanal+1,3-butanediol, at two different temperatures, in order to determine the NRTL binary interaction parameters, which aare necessary to simulate an extraction column.

The NRTL model accurately fits the data at both 298.15 K and 313.15 K with deviations less than 10%. Regarding to simulation results, an extraction column with 10 theoretical stages and a solvent/feed ratio of 1 can recover the 70% of the octanal in the extract and the 95% of the limonene in the raffinate. By using a solvent/feed ratio of 2, it is possible to obtain limonene with purity (mole fraction) higher han 0.995.

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