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(Liquid + Liquid) Equilibria for Water + Ethanol + Citral Multicomponent System at 303.15 K

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Liquid−liquid equilibrium data for the system water + ethanol + citral (neral + geranial + impurities) at 303.15 K were obtained, considering that citral is composed by two geometrical isomers along with a complex mixture of impurities. All organic chemicals contained in the commercial citral were quantified by gas chromatography using a flame ionization detector rather than a thermal conductivity detector. Moreover, this last detector was used to quantify water and ethanol. To obtain the equilibrium data for this system, several mixtures that contain different ratios of the compounds, two with different ratios of (water + ethanol), one with the (neral + geranial) ratio corresponding to the commercial citral, and two with different ratios of (citral + ethanol), were studied. The influence of the equilibrium concentrations of ethanol and water on the neral and geranial distribution was also studied. Experimental results show that ethanol enhances the solubility of citral in water.

Introduction

Citrus oils are widely used by flavor, food, cosmetic, pharmaceutical, and chemical industries. They contain more than 200 compounds of which more than 100 have been identified and can be grouped into two fractions: (i) hydrocarbon terpenes, which constitute the major group (mass fraction > 0.90) and (ii) oxygenated terpenes, which are generally considered preferable because of their pleasant odor.[1] Citral (3,7-dimethyl-2,6-octadienal, also called lemonal, CAS No. 5392-40-5) belongs to this last group of compounds, has a characteristic pleasant smell, and is the most important constituent contributing to the aroma of lemon oil and many other essential oils. It is composed of a mixture of two geometrical isomers, geranial, the trans-configuration, approximately (55 to 70) % and neral, the cis-configuration, approximately (35 to 45) % with the brut formula $C_{10}H_{16}O$.[2]

The fraction of hydrocarbon terpenes has little contribution to the flavor and aroma. For this reason, it is a common industrial practice to remove hydrocarbon terpenes to concentrate the oil in oxygenated compounds such as citral. This removal of hydrocarbon terpenes is known as "deterpenation" or "folding" and is carried out to improve oil stability, increase oil solubility, and reduce storage and transport costs.[3] Deterpenation is currently done by distillation, solvent extraction, or chromatographic separation. Solvent extraction, employing hexane and chloroform as solvents, is probably the technique most frequently used by industry.[4] However, for a possible application of the extract in foods, cosmetics, etc., it would be preferable to use ethanol or water or their mixture as solvents.

A literature survey shows that there are some works on liquid−liquid equilibrium (LLE) data for systems containing terpenes, oxygenated compounds, water, and ethanol,[5−11] but only one for the water + ethanol + citral system.[11] This last work ignores citral's impurities and assumes that it is a single chemical component, when it actually consist of two geometrical isomers, whose respective peaks can be resolved using gas chromatography and a flame ionization detector (FID). On the other hand, it uses a pseudoternary plot to show its equilibrium diagram. Although it is a common practice to plot multicomponent systems as pseudoternary ones, this practice can lead to "misinterpretation and mistakes as a consequence of applying a nonadequate experimental methodology, leading to incomplete and even spurious sets of data", as expressed by Marcilla et al.[12]

To clarify these aspects, the [w_1 water + w_2 ethanol + citral (w_3 neral + w_4 geranial) + $(1- w_1 - w_2 - w_3 - w_4)$ impurities] multicomponent system was studied at $T = (303.15 \pm 0.05)$ K and atmospheric pressure with being w_i the mass fraction of component *i*. Impurities were not quantified in this work, and their concentration was obtained by mass balance.

Experimental Section

Materials. Water was bidistilled in an all-glass apparatus. Citral with claimed mass fraction purity > 0.95 and ethanol (mass fraction purity higher than 0.998, GC) were supplied by Fluka and Merck, respectively. However, chromatographic analysis of the commercial citral revealed that its mass fraction purity was only $w = 0.811$, with a mass fraction of neral and geranial of $w_3 = 0.3165$ and $w_4 = 0.4945$, respectively, and a mass fraction ratio between neral and geranial of $w_3/w_4 = 0.64$. Therefore, the commercial citral has a mass fraction of $w = 0.189$ of several nondetermined impurities. This level of impurities was apparently ignored in the previous work reported in the literature[11] probably due to the use of a thermal conductivity detector (TCD) instead of a FID to quantify the components, because FID provides a lower detection limit than TCD.

Citral supplied by Extrasynthese (France, chromatographic quality, with GC) with a nominal mass fraction purity of 98.5 % was used as a standard mixture to obtain calibration curves for neral and geranial, since the mass fraction ratio between these two isomers was reported by the manufacturer ($w_3/w_4 = 0.3747/0.6101$). The purity of the standard mixture, as well as the ratio between neral and geranial was confirmed in

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our laboratory using the chromatographic method described below.

Apparatus and Procedure. Several mixtures within the heterogeneous region were prepared, using 16 mL chromatographic vials as equilibrium cells. Each vial was equipped with a screw cap, septa, and a Teflon-coated magnetic stirrer bar to provide an intense and continuous stirring for at least 2 days using multipoint magnetic stirrers located at the bottom of a thermostatic device reported previously.[13] After phase equilibrium was attained, the magnetic stirrers were turned off, and both liquid phases were allowed to settle for 24 h before sampling. The chromatographic vials were filled up to approximately 90 % of their volume to maintain the vapor space at a minimum. The equilibrium temperature was measured with a calibrated mercury thermometer, uncertain to ± 0.02 K.

At the end of each experiment, samples were taken from both phases with hypodermic syringes and analyzed by means of gas chromatography. The external standard method was applied to obtain quantitative results. First, the needle was introduced through the septa to take samples of the upper phases. They were immediately placed in 2 mL chromatographic vials. Then, samples of the lower phases were taken introducing the needle and blowing air while this phase went through the upper phase to avoid its contamination. A Hewlett-Packard 6890 gas chromatograph with an automatic injector (Agilent G2613A) directly connected to a ChemStation (HP G2070AA) was used.

To obtain quantitative results, two chromatographic methods were used, as reported by Barrera Zapata et al.[14] for the water + acetonitrile + limonene system: (1) water and ethanol were quantified using a 30 m long × 0.25 mm id × 0.5 μm film thickness capillary column (INNOWax, cross-linked polyethylene glycol, HP 19091N-233). The temperature program was the following: initial temperature 343 K (hold 2 min), ramp 50 $\text{K}\cdot\text{min}^{-1}$, and the final temperature at 393 K for another one and a half minutes. The nitrogen carrier gas flow rate was electronically kept constant working with a split ratio of 20:1 and with the injector maintained at 453 K. Detection was carried out by a TCD at 523 K. (2) Neral and geranial were quantified using a 100 m long × 0.25 mm id × 0.5 μm film thickness capillary column (HP-1, crosslinked methyl siloxane, HP 19091Z-530). The temperature program was the following: initial temperature 363 K (hold 12 min), ramp 1 $\text{K}\cdot\text{min}^{-1}$, with final temperature at 523 K for another 10 min and a postrun at 573 K for 10 min. The nitrogen carrier gas flow rate was electronically kept constant working with a split ratio of 20:1 and with the injector maintained at 513 K. Detection was carried out by a FID at 523 K. Under these conditions, all chromatographic peaks corresponding to the components contained in the commercial citral (including impurities) can be resolved and their respective areas can be measured. Ethanol could not be quantified with the FID, because its chromatographic peak overlaps with those of some of the citral impurities. Three analyses were performed for each sample to obtain a mean mass fraction value with repeatability better than one percent.

A dual range Mettler AG245 balance with a uncertainty of ± 0.00001 g was used to weight all the components to make a calibration curve for each component, using the external standard method and taking into account the reported purity of the citral (Extrasynthese: 98.5 %) and the mass fraction ratio between neral and geranial, to obtain the real masses of the two isomers. Ten mixtures in the homogeneous region were used to obtain these calibration curves with a mass fraction range of (0 to 100) % for water and ethanol, (0.051 to 31.520) % for neral, and (0.083 to 51.322) % for geranial.

To determine which of the equations contained in the ChemStation software provides the best fit for the experimental data in the calibration curves, we prepared several mixtures with very well known concentrations by mass. These mixtures were analyzed with the two chromatographic methods above, using each of the equations included in the software. The best fitting equations with the TCD detector were the following:

$$y = 651.29\cdot x + 3.93 \text{ for ethanol, with a correlation factor of } r^2 = 0.9987, \text{ and}$$

$$y = 1361.94\cdot x + 3.94 \text{ for water, with a correlation factor of } r^2 = 0.9985$$

The best fitting equations with the FID detector were the following:

$$y = 148075.09\cdot x \text{ for neral, with a correlation factor of } r^2 = 0.9983, \text{ and}$$

$$y = 144016.91\cdot x \text{ for geranial, with a correlation factor of } r^2 = 0.9970$$

where y is the area counts of the peaks, and x is the mass of each component in the mixture.

These analyses show that the reported mass fraction values have an uncertainty of ± 0.001 for water and ethanol and ± 0.0001 for neral and geranial due to the different sensibility of both detectors.

The measurements were carried out starting from homogeneous well-known initial mixtures with different ratios of (water + ethanol), (neral + geranial), or (citral + ethanol) and adding to each one different quantities of the other components to reach the heterogeneous region. In this work, these initial mixtures were selected to determine tie lines within the whole heterogeneous region.

Results and Discussion

Table 1 lists LLE data, expressed in mass fractions, for [w_1 water + w_2 ethanol + w_3 neral + w_4 geranial + $(1- w_1 - w_2 - w_3 - w_4)$ impurities], corresponding to the initial mixtures with the following compositions: $M_1 = (w_2 = 0.406$ ethanol $+ w_1 = 0.594$ water), $M_2 = (w_2 = 0.243$ ethanol $+ w_1 = 0.757$ water), $M_3 = (w_3 = 0.3165$ neral $+ w_4 = 0.4945$ geranial), $M_4 = [(w_3 + w_4) = 0.615$ citral $+ w_2 = 0.241$ ethanol], and $M_5 = [(w_3 + w_4) = 0.477$ citral $+ w_2 = 0.411$ ethanol]. Because only water, ethanol, neral, and geranial were quantified, the sums of the mass fractions for each phase differ from unity, particularly when the neral and geranial concentrations are high. A mass balance for each tie line gives the citral's impurities concentration, which is not shown in Table 1. The neral/geranial ratios for each tie line and for both equilibrium phases are also included.

As can be seen from Table 1, the aqueous phase presents a very small concentration of impurities, which generally are within the uncertainty of the measurements, while their concentration is higher in the organic phase probably because they mainly consist of hydrocarbon terpenes with greater affinity with this phase.

Table 1 also shows that the neral/geranial ratio in the aqueous phase is generally not constant, while it remains practically constant in the organic one, within the experimental uncertainty, but it is smaller than that found in the commercial citral (Fluka) reported above. On the other hand, this ratio is greater for the aqueous phase than for the organic one, which is an indication that the distribution of both isomers is not the same in both

Table 1. Liquid + Liquid Equilibrium Data for the [w_1 Water + w_2 Ethanol + w_3 Neral + w_4 Geranial + (1− w_1 − w_2 − w_3 − w_4) Impurities] System at T = (303.15 ± 0.05) K[a]

aqueous phase					organic phase				
w_1	w_2	w_3	w_4	w_3/w_4	w_1	w_2	w_3	w_4	w_3/w_4
M_1 = (w_2 = 0.406 ethanol + w_1 = 0.594 water)									
0.611	0.375	0.0045	0.0071	0.63	0.104	0.359	0.1675	0.2844	0.59
0.625	0.363	0.0037	0.0058	0.64	0.114	0.363	0.1636	0.2762	0.59
0.638	0.352	0.0031	0.0048	0.65	0.105	0.373	0.1637	0.2754	0.59
0.640	0.351	0.0029	0.0045	0.64	0.088	0.318	0.1864	0.3131	0.60
0.664	0.331	0.0017	0.0027	0.63	0.112	0.370	0.1625	0.2730	0.60
0.683	0.313	0.0015	0.0023	0.65	0.093	0.327	0.1826	0.3050	0.60
0.720	0.277	0.0008	0.0012	0.67	0.077	0.253	0.2105	0.3527	0.60
0.754	0.244	0.0006	0.0009	0.67	0.062	0.217	0.2268	0.3800	0.60
0.777	0.222	0.0005	0.0007	0.71	0.052	0.183	0.2404	0.4027	0.60
0.802	0.196	0.0004	0.0005	0.80	0.047	0.163	0.2483	0.4159	0.60
M_2 = (w_2 = 0.243 ethanol + w_1 = 0.757 water)									
0.769	0.230	0.0004	0.0006	0.67	0.047	0.190	0.2387	0.4035	0.59
0.772	0.227	0.0004	0.0006	0.67	0.044	0.178	0.2436	0.4109	0.59
0.775	0.224	0.0005	0.0007	0.71	0.049	0.178	0.2424	0.4072	0.60
0.781	0.218	0.0004	0.0005	0.80	0.052	0.178	0.2421	0.4058	0.60
0.785	0.214	0.0003	0.0005	0.60	0.050	0.173	0.2445	0.4096	0.60
0.793	0.206	0.0004	0.0006	0.67	0.058	0.168	0.2432	0.4071	0.60
M_3 = (w_3 = 0.3165 neral + w_4 = 0.4945 geranial)									
0.596	0.387	0.0056	0.0089	0.63	0.125	0.425	0.1415	0.2367	0.60
0.620	0.368	0.0038	0.0059	0.64	0.095	0.331	0.1802	0.3025	0.60
0.667	0.326	0.0023	0.0035	0.66	0.077	0.299	0.1960	0.3286	0.60
0.686	0.308	0.0019	0.0027	0.70	0.077	0.284	0.2006	0.3363	0.60
0.725	0.273	0.0009	0.0013	0.69	0.060	0.233	0.2225	0.3723	0.60
0.738	0.260	0.0008	0.0011	0.73	0.057	0.218	0.2279	0.3817	0.60
0.782	0.217	0.0005	0.0006	0.83	0.040	0.146	0.2560	0.4286	0.60
0.792	0.207	0.0004	0.0005	0.80	0.043	0.153	0.2524	0.4232	0.60
0.849	0.150	0.0002	0.0003	0.67	0.032	0.094	0.2749	0.4601	0.60
0.874	0.125	0.0003	0.0003	1.00	0.030	0.074	0.2817	0.4716	0.60
0.875	0.125	0.0002	0.0002	1.00	0.023	0.007	0.3049	0.5110	0.60
0.975	0.024	0.0001	0.0001	1.00	0.023	0.006	0.3067	0.5098	0.60
M_4 = [(w_3 + w_4) = 0.615 citral + w_2 = 0.241 ethanol]									
0.790	0.209	0.0002	0.0004	0.50	0.040	0.154	0.2521	0.4258	0.59
0.757	0.242	0.0005	0.0007	0.71	0.051	0.202	0.2338	0.3947	0.59
0.728	0.269	0.0009	0.0013	0.69	0.061	0.230	0.2221	0.3744	0.59
0.718	0.280	0.0008	0.0013	0.62	0.064	0.238	0.2185	0.3685	0.59
0.683	0.312	0.0015	0.0023	0.65	0.069	0.264	0.2088	0.3516	0.59
0.661	0.333	0.0020	0.0031	0.65	0.080	0.276	0.2021	0.3397	0.59
M_5 = [(w_3 + w_4) = 0.477 citral + w_2 = 0.411 ethanol]									
0.868	0.131	0.0001	0.0002	0.50	0.025	0.070	0.2846	0.4768	0.60
0.803	0.196	0.0003	0.0004	0.75	0.032	0.112	0.2652	0.4542	0.58
0.798	0.201	0.0003	0.0004	0.75	0.040	0.157	0.2495	0.4256	0.59
0.763	0.235	0.0005	0.0007	0.71	0.044	0.192	0.2406	0.4017	0.60
0.739	0.258	0.0008	0.0012	0.67	0.053	0.240	0.2195	0.3745	0.59
0.702	0.294	0.0014	0.0021	0.67	0.067	0.288	0.2012	0.3417	0.59
0.657	0.336	0.0024	0.0037	0.65	0.089	0.340	0.1778	0.3028	0.59
0.623	0.364	0.0042	0.0066	0.64	0.098	0.360	0.1692	0.2867	0.59
0.575	0.402	0.0075	0.0119	0.63	0.144	0.406	0.1405	0.2374	0.59
0.496	0.449	0.0175	0.0286	0.61	0.204	0.468	0.1024	0.1732	0.59

[a] w_i denotes the mass fraction of component *i*.

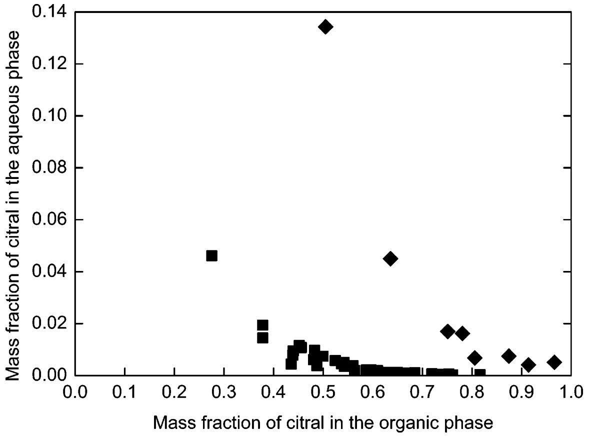

Figure 1. Mass fraction of citral in the aqueous phase against mass fraction of citral in the organic phase at T = 303.15 K. ♦, this work; ■, ref 11. The citral concentrations in this work were obtained adding the mass fractions of neral and geranial listed in Table 1.

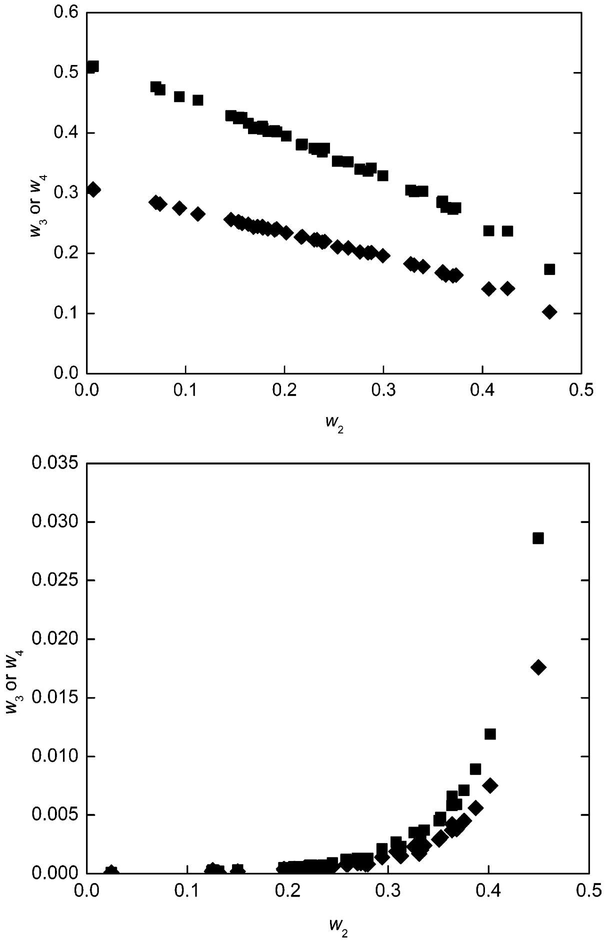

Figure 2. (a) Equilibrium mass fraction of ♦, neral (w_3) or ■, geranial (w_4) in the organic phase against the equilibrium mass fraction of ethanol (w_2) in the same phase at T = 303.15 K. (b) Equilibrium mass fraction of ♦, neral (w_3) or ■, geranial (w_4) in the aqueous phase against the equilibrium mass fraction of ethanol (w_2) in the same phase at T = 303.15 K.

equilibrium phases. A ratio greater than that found in the commercial citral (Fluka), means that neral has a greater affinity for the aqueous phase than geranial.

In view of the experimental results shown in Table 1 and the above statement, citral cannot be considered as a single component, because their two isomers are differently distributed between both equilibrium phases.

A comparison of our data with previous results[11] can be made plotting the mass fractions of citral (neral + geranial) in the aqueous phase against the mass fractions of citral in the organic one. Because in this work the mass fractions of neral and geranial were obtained independently, our mass fractions of citral were calculated adding the neral and geranial mass fractions for each tie line reported in Table 1 (from M_1 to M_5) in each phase. Figure 1 shows this comparison. As can be seen, previous results (taken from Table 3, ref 11) are very different from ours. This is due to the different methodology used to obtain the equilibrium concentrations. On the other hand, a careful observation of Figure 2 of the previous work[11] shows that no tie line rests on the binodal curve, just as it happens when quaternary or multicomponent systems are plotted as pseudoternary ones.[15]

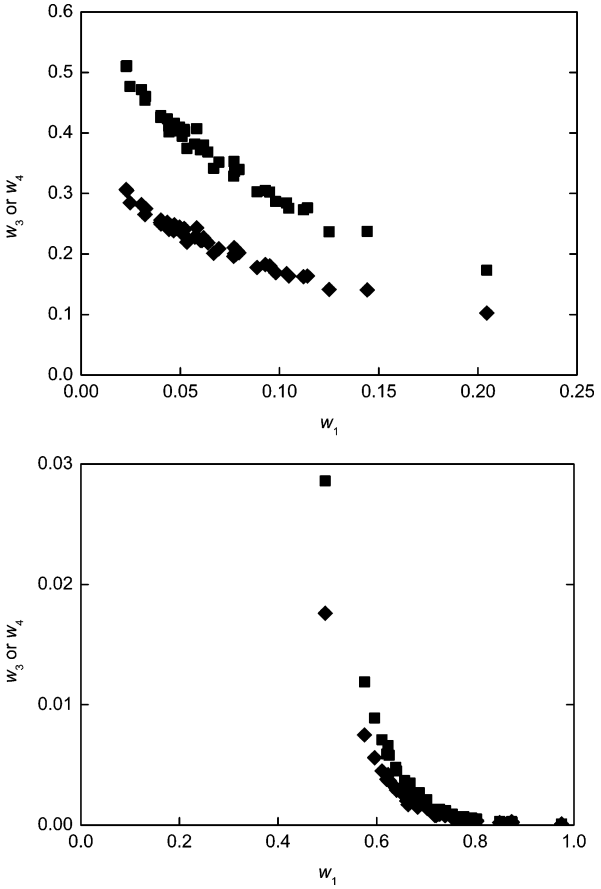

Figure 3. (a) Equilibrium mass fraction of ♦, neral (w_3) or ■, geranial (w_4) in the organic phase against the equilibrium mass fraction of water (w_1) in the same phase at $T = 303.15$ K. (b) Equilibrium mass fraction of ♦, neral (w_3) or ■, geranial (w_4) in the aqueous phase against the equilibrium mass fraction of water (w_1) in the same phase at $T = 303.15$ K.

Plots of the equilibrium mass fractions of neral (w_3) or geranial (w_4) in the organic and aqueous phases against the equilibrium mass fraction of ethanol in the same phases (w_2) are shown in Figure 2a,b, respectively, while Figure 3a,b show plots of the equilibrium concentration of both isomers against the equilibrium mass fraction of water in both phases for all sets of data listed in Table 1 at $T = (303.15 \pm 0.05)$ K.

As can be seen from Figure 2a, the equilibrium concentrations of neral and geranial in the organic phase decrease when the ethanol concentration increases in this same phase, while an opposite situation is observed for the aqueous phase, as shown in Figure 2b. This last plot also shows that the concentration of both isomers significantly increases when the equilibrium mass fraction of ethanol surpasses $w_2 = 0.3$, but their mass fractions become relatively important only when the mass fraction of ethanol in the aqueous phase is higher than $w_2 = 0.4$. The concentrations of both isomers are very small in this phase (ranges: $w_3 \cong 0.00$ to 0.02 for neral, and $w_4 \cong 0.00$ to 0.03 for geranial).

The equilibrium mass fractions of both isomers in the organic phase are plotted in Figure 3a against the equilibrium mass fraction of water in this same phase. This plot shows a similar trend as that observed in Figure 2a but with a faster decrease when water concentration increases. On the other hand, Figure 3b shows a behavior that is opposite to that observed in Figure 2b, because in this case the mass fractions of both isomers quickly decrease when the mass fraction of water increases.

Furthermore, for the organic phase (see Figure 2a), both isomer concentrations decrease when the ethanol concentration increases because they are partially transferred to the aqueous phase. However, their values are at least one order of magnitude greater than those in the aqueous phase (see Figure 2b).

Conclusion

Liquid−liquid equilibrium for the [w_1 water + w_2 ethanol + citral (w_3 neral + w_4 geranial) + $(1 - w_1 - w_2 - w_3 - w_4)$ impurities] multicomponent system was studied at $T = (303.15 \pm 0.05)$ K and atmospheric pressure.

Our experimental results show that systems containing citral should be considered as multicomponent ones, because citral always contains a very high level of impurities, which are not easy to separate by a distillation process. Also, citral should never be considered as a single component because neral and geranial are distributed in different ways between both equilibrium phases. Furthermore, when citral is quantified by gas chromatography, it is very important to use a chromatographic quality chemical to take into account its own impurities and to know its neral/geranial ratio to be able to determine the real masses of each isomer when the calibration curves are made. Otherwise, the equilibrium concentrations will be wrong.

Another important aspect to consider is the choice of the detector used to quantify citral by gas chromatography. The TCD is not appropriate for this purpose because of its low sensibility, which does not allow visualizing many of the impurities present in the commercial citral.

The experimental results show that the best conditions to extract citral (neral + geranial), using ethanol as solvent and water as cosolvent, correspond to solvent mixtures with the highest ethanol concentration compatible with two equilibrium liquid phases, because high ethanol concentrations produce high mass fractions of neral and geranial in the aqueous phase (see Figure 2b).

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