Liquid−Liquid Equilibria for the Water + Ethanol + Citral and Water + Ethanol + Limonene Systems at 293 K

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Isobaric liquid−liquid equilibrium (LLE) data were determined at atmospheric pressure and at 293 K for limonene + water and citral + water binary systems (solubility data) as well as for water + ethanol + citral and water + ethanol + limonene ternary systems (tie lines and miscibility gaps). Ethanol enhances the mutual solubility between water and citral and between water and limonene. The miscibility gap disappears for an ethanol mass fraction equal to about 0.45 for the first system and about 0.73 for the second one. The binary and ternary experimental data were fitted by means of the UNIQUAC model. New and previously unavailable UNIQUAC interaction parameters were determined. The quality of the fit is good.

Introduction

In lemon essential oil mixtures, limonene and citral are two of the main components of the terpene hydrocarbon class and of the oxygenated terpene class, respectively (Guzman, 1988). Oxygenated compounds are generally considered preferable due to odor. In order to improve the quality of essential oils, some processes have therefore been developed to enrich the mixture in oxygenated compounds (Bandyopadhyay, 1981; Broderick, 1955), solvent extraction probably being the most commonly used by industry. Because of their intrinsic characteristics of selectivity between terpenes and oxygenated compounds, the solvents most often employed are hexane, chloroform, and aqueous solutions of ethanol (Pangborn and Russel, 1976).

The light components of the essential oil mixtures are completely soluble in ethanol but not quite completely soluble in water. The solvent obtained by adding ethanol to water maintains the polar characteristics of water, but its polarity is mitigated by the presence of the alcohol.

Alcoholic extracts of lemon essential oils are particularly requested by industry for the following reasons: (1) they are highly soluble in aqueous solutions and can therefore be used readily to make drinks and perfumes; (2) they enhance the aromatic strength of the mixture; (3) oxidation reactions are reduced in the presence of the alcohol.

Unfortunately, the study of the solvent extraction technique is limited by the lack of data on the thermodynamic behavior of systems containing terpenes, oxygenated terpenes, water, and ethyl alcohol. Examination of the literature yields data on the solubility of limonene in water at temperatures from 273 to 293 K (Massaldi and King, 1973) and liquid−liquid equilibrium (LLE) data of the 3,δ-carene + α-pinene + polar compounds (Antosik and Stryjek, 1992). Furthermore, some qualitative information on extractive conditions of limonene + citral mixtures is also reported (Bandyopadhyay, 1989; Pangborn and Russel, 1976; Licandro et al., 1990). But, no systematic evaluation has yet been performed on the selectivity capacity of aqueous solutions of ethyl alcohol in relation to the percentage of water in the solvent or to the mass flow ratio between the solvent and essential oil mixture.

To this end we explore the behavior of aqueous solutions of ethyl alcohol with limonene (hydrocarburic compound) and citral (oxygenated compound).

Solubilities for the binary systems of water + limonene and water + citral are reported at atmospheric pressure and at 293 K. For the ternary systems of water + ethanol + limonene and water + ethanol + citral tie-lines, miscibility gaps, and distribution coefficients are determined at atmospheric pressure and at 293 K.

The thermodynamic consistency of the tie lines is ascertained by applying the independent material balance check.

The LLE results obtained are fitted by means of the UNIQUAC activity coefficient model, and new and not previously available UNIQUAC interaction parameters for limonene + water, citral + water, ethanol + limonene, and citral + ethanol are determined.

Experimental Section

Materials. The following chemicals were used: *d*-limonene (used as purchased from Jansen) with a claimed purity of 97%, citral (used as purchased from Fluka Chemika) with a claimed purity of 97% (GC), ethanol (used as purchased from Fluka Chemika) with a claimed purity of 99.8% and a water content of <0.2%, and redistilled and deionized water (Carlo Erba).

The Merck KOH (0.1 M) and the Carlo Erba $NH_2OH{\cdot}Cl$ (99% purity) reagents were used to measure the citral content. The titration capacity of $NH_2OH{\cdot}Cl$ was checked before every run by titrating weighted masses of citral.

Procedures. Binary LLE measurements for the water + limonene and water + citral systems were determined at atmospheric pressure and at 293 K. For each system, mixtures of the two components were mixed vigorously by means of a magnetic stirrer in a thermostated equilibrium cell with temperature regulated to an accuracy of ±0.1 K. After 60 min the stirrer was switched off and the solution in the cell was allowed to settle for at least another 60 min in order to obtain complete separation of the two phases. Preliminary experiments indicate that higher contact times do not result in higher concentrations of the organic components in the aqueous phase and vice versa. Samples of the two liquid phases were taken through septum seals by means of a hypodermic syringe.

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For the water + limonene system analysis of the aqueous phase was carried out by determining the absorbance at 220 nm with a Perkin-Elmer spectrophotometer (Lambda 5). To determine the concentration of limonene in water, a weighted amount of the aqueous phase was diluted with an equal amount of ethanol; then a spectrophotometric analysis was performed and the mass fraction of limonene was determined with an accuracy of $w = \pm 4 \times 10^{-6}$. The dilution of the aqueous phase was necessary in order to reproduce the calibration conditions: in fact, owing to the low solubility of limonene in water, the calibration curve was obtained by using solutions of limonene in a water + ethanol mixture (50% by weight).

Calibration solutions were gravimetrically prepared by means of an electronic balance accurate to ±0.1 mg.

The concentration of water in limonene was determined by injecting weighted amounts of solution in a gas chromatograph (HP 5890A) equipped with a thermal conductivity detector. The components were separated by a 1/4 in. × 6 ft stainless steel column packed with Chromosorb 102 (80/100 mesh). The gas chromatograph response peaks were integrated by using a HP 3394A integrator. The operative conditions were injection temperature, 523 K; oven temperature, 423 K for 6 min, from 423 to 483 within 4 min; detector temperature, 523 K; and carrier gas, He, 30 cm^3/min.

A calibration curve was obtained as a function of weighted amounts of water injected.

Samples of the organic phase (5 μL) were injected in the gas chromatograph in order to measure the amount of water, while the mass of limonene was determined by material balance. The accuracy in the estimation of the water mass fraction was $w = \pm 4 \times 10^{-6}$.

For the water + citral system the solubility of citral in water was obtained spectrophotometrically by determining the absorbance of the solution at 285 nm. Weighted samples of the aqueous phase were diluted with an equal amount of water and then were analyzed. The mass fraction of citral was determined with an accuracy of $w = \pm 7 \times 10^{-6}$. For this system the calibration curve was obtained by using solutions of citral in water with a concentration lower than that of saturation.

The mass fraction of water in citral was obtained with the same GC procedure used to determine the solubility of water in limonene, and an accuracy of the water mass fraction of $w = \pm 1 \times 10^{-4}$ was estimated.

In each system, the reproducibility was very near the accuracy of the experiments.

Isobaric ternary LLE data were determined for the two systems of water + ethanol + citral and water + ethanol + limonene at 293 K. For each system the equilibria were established in an equilibrium cell equipped with a magnetic stirrer and a jacket for circulating the thermostating water at the desired temperature. The miscibility gap was obtained separately from the determination of tie lines. One portion of the binodal curve was determined by starting from a known mixture of water and ethanol (20 g) and adding measured volumes of limonene (citral) and the other portion by starting from known mixtures of limonene (citral) and ethanol (20 g) and adding measured volumes of water. The third component was added by a volumetric pump with an accuracy of ±0.02 cm^3. The end point of the titration was detected by visual inspection of the transition from a homogeneous to a heterogeneous mixture. The estimated error through the whole curve was partly due to uncertainty in the observation and has been calculated as $w = \pm 1 \times 10^{-3}$ for the added component and $w = \pm 1 \times 10^{-5}$ for the other components. All the measurements were repeated twice for each mixture; errors in the experimental readings resulted in differences in w values that were within the w accuracy.

Table 1. Mutual Solubility for the Binary Systems Water (1) + Limonene (3) and Water (1) + Citral (3)

water (1) + limonene (3)		water (1) + citral (3)	
w_1	w_3	w_1	w_3
275×10^{-6}	999.7×10^{-3}	8900×10^{-6}	991.1×10^{-3}
999.98×10^{-3}	20×10^{-6}	999.5×10^{-3}	514×10^{-6}

In order to determine the tie lines for each system, known amounts of the three components were fed into the same thermostated equilibrium cell and mixed vigorously by means of the magnetic stirrer for at least 1 h. After the stirrer was turned off the mixtures were allowed to settle in the cell for at least 2 h. Samples of the two liquid phases were then taken and analyzed. For the water + ethanol + limonene system, sample composition was determined by means of a gas chromatograph (see above) . Two calibrating curves were determined to ensure correspondence between the integrator areas and the actual composition of the mixtures, the first one being ethanol related to water and the second one limonene related to ethanol. The estimated error is $\pm 3.2 \times 10^{-3}$ g for the quantity of water and $\pm 8 \times 10^{-3}$ g for the quantity of limonene. The estimated accuracy is $w = \pm 5 \times 10^{-4}$ for the water mass fraction and $w = \pm 2 \times 10^{-3}$ for the limonene mass fraction.

For the water + ethanol + citral system, the ethanol and water contents were determined by means of gas chromatographic analysis while the citral content was determined by means of the $NH_2OH{\cdot}HCl$ method. This is the conventional method of analysis to determine the aldehyde content in an essential oil mixture (Hanna et al., 1968). By adding $NH_2OH{\cdot}HCl$ to the samples (7 g) and titrating the products of the reactions with known volumes of KOH by means of a volumetric pump, it is possible to determine the quantity of citral in the sample. The estimated error is $\pm 3.2 \times 10^{-3}$ g for the quantity of water and $\pm 7 \times 10^{-4}$ g for the quantity of citral. The accuracy is $w = \pm 5 \times 10^{-4}$ for the mass fraction of water and $w = \pm 1 \times 10^{-4}$ for the mass fraction of citral.

The results of the analysis on both systems were also checked by means of an independent material balance in order to verify that the feed composition lays on the tie line determined by the compositions of the two liquid phases in equilibrium. The mean geometric distance of the feed composition from the corresponding tie line is 4.7×10^{-3} for the water + ethanol + limonene system and 2.8×10^{-3} for the water + ethanol + citral system.

All the experiments were carried out in an inert atmosphere of dry nitrogen to avoid exposure to moisture and oxygen.

Results and Discussion

Table 1 gives the mutual solubility results at atmospheric pressure and at 293 K for the two binary systems water + limonene and water + citral. Limonene shows a lower solubility in water than that of citral, and water is more soluble in citral than in limonene.

The experimental tie lines for the water + ethanol + limonene and water + ethanol + citral systems at atmospheric pressure and at 293 K are given in Table 2 and 3, respectively.

Tables 4 and 5 show the binodal-curve results for the two mentioned ternary systems, while the calculated binodal curves can be seen in Figures 1 and 2 along with the experimental tie lines.

All the liquid−liquid equilibrium results were fitted by using the UNIQUAC activity coefficient model. New

Table 2. Experimental Tie Lines for Water (1) + Ethanol (2) + Limonene (3) at 293 K and at Atmospheric Pressure and Mean and Maximum Values of the Correlation Deviations

water rich phase		terpene rich phase	
w_1	w_2	w_1	w_2
0.1291	0.7161	0.0016	0.0589
0.2276	0.7083	0.0024	0.0366
0.2469	0.6978	0.0032	0.0406
0.3231	0.6524	0.0008	0.0184
0.3444	0.6329	0.0013	0.0203
0.3949	0.5927	0.0006	0.0147
0.4443	0.5460	0.0006	0.0142
0.5218	0.4767	0.0004	0.0108
0.5794	0.4191	0.0006	0.0066
0.7561	0.2439	0.0007	0.0041
0.8509	0.1439	0.0015	0.0022
$\Delta\langle w\rangle_1 = 0.029^a$	$\Delta\langle w\rangle_2 = 0.019$	$\Delta\langle w\rangle_1 = 0.004$	$\Delta\langle w\rangle_2 = 0.004$
$\Delta w_1^{max} = 0.080^a$	$\Delta w_2^{max} = 0.050$	$\Delta w_1^{max} = 0.014$	$\Delta w_2^{max} = 0.003$

[a] $\Delta\langle w\rangle_j = \{\sum_j(w_j^{calc} - w_j^{exp})\}/N$. $\Delta w_j^{max} = \max\{|w_j^{calc} - w_j^{exp}|\}$.

Table 3. Experimental Tie Lines for Water (1) + Ethanol (2) + Citral (3) at 293 K and at Atmospheric Pressure and Mean and Maximum Correlation Deviations

water rich phase		terpene rich phase	
w_1	w_2	w_1	w_2
0.4239	0.4418	0.1518	0.3432
0.5283	0.4267	0.0954	0.2688
0.6049	0.3775	0.0626	0.1862
0.6334	0.3504	0.0405	0.1788
0.6530	0.3402	0.0369	0.1574
0.7102	0.2823	0.0240	0.1017
0.8235	0.1724	0.0178	0.0683
0.8870	0.1079	0.0121	0.0217
$\Delta\langle w\rangle_1 = 0.017^a$	$\Delta\langle w\rangle_2 = 0.018$	$\Delta\langle w\rangle_1 = 0.007$	$\Delta\langle w\rangle_2 = 0.016$
$\Delta w_1^{max} = 0.031^a$	$\Delta w_2^{max} = 0.039$	$\Delta w_1^{max} = 0.008$	$\Delta w_2^{max} = 0.030$

[a] $\Delta\langle w\rangle_j = \{\sum_j(w_j^{calc} - w_j^{exp})\}/N$. $\Delta w_j^{max} = \max\{|w_j^{calc} - w_j^{exp}\}$.

Table 4. Experimental Miscibility Gap for Water (1) + Ethanol (2) + Limonene (3) at 293 K and at Atmospheric Pressure

w_1	w_2	w_1	w_2
0.001	0.0324	0.030	0.4674
0.009	0.1906	0.070	0.6456
0.009	0.1882	0.084	0.6868
0.012	0.2370	0.106	0.7091
0.017	0.2974	0.114	0.7189
0.019	0.3597	0.149	0.7326
0.019	0.4904	0.185	0.7301
0.021	0.3529	0.256	0.6987
0.022	0.3596	0.282	0.6817
0.024	0.5869	0.322	0.6526
0.027	0.4261	0.372	0.6122

Table 5. Experimental Miscibility Gap for Water (1) + Ethanol (2) + Citral (3) at 293 K and at Atmospheric Pressure

w_1	w_2	w_1	w_2
0.021	0.1050	0.387	0.4434
0.024	0.1027	0.412	0.4472
0.054	0.2019	0.447	0.4464
0.091	0.2585	0.450	0.4445
0.208	0.3783	0.500	0.4367
0.259	0.4082	0.511	0.4318
0.298	0.4197	0.574	0.4044
0.355	0.4372	0.653	0.3402
0.371	0.4389		

UNIQUAC interaction parameters were obtained from the fitting of the experimental data, while the UNIQUAC volume and surface parameters were determined by using the method developed by Bondi (1968).

Use of the binary and ternary LLE results made it possible to estimate previously unavailable interaction parameters between each solvent (water and ethanol) and limonene or citral.

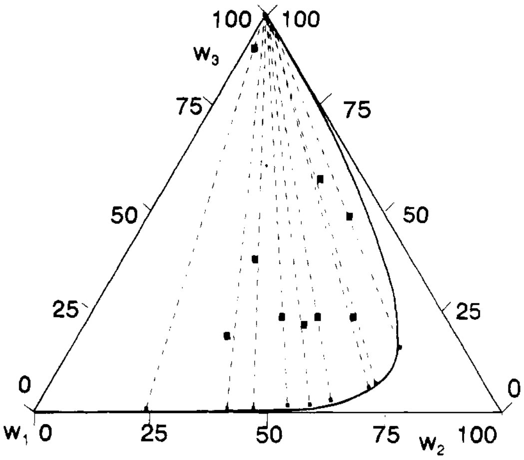

Figure 1. Ternary liquid–liquid equilibrium of water (1) + ethanol (2) + limonene (3) at 293 K: (•----•) experimental tie line, (■) overall compositions for tie line. The miscibility gap is calculated by means of the UNIQUAC model, and the parameter values are reported in Tables 6 and 7.

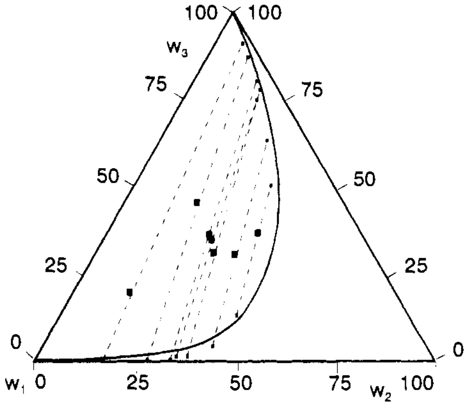

Figure 2. Ternary liquid–liquid equilibrium of water (1) + ethanol (2) + citral (3) at 293 K: (•----•) experimental tie line, (■) overall compositions for tie line. The miscibility gap is calculated by means of the UNIQUAC model, and the parameter values are reported in Tables 6 and 7.

Table 6. UNIQUAC Surface (q) and Volume (r) Parameters Values

	water	*ethanol*	*limonene*	*citral*
r	0.92	2.1055	6.736	6.829
q	1.40	1.972	5.592	5.884

Table 7. UNIQUAC Binary Interaction Parameters for the Water (1) + Ethanol (2) + Limonene (3) and Water (1) + Ethanol (2) + Citral (3) Systems at 293 K

	water (1) + ethanol (2) + limonene (3)		water (1) + ethanol (2) + citral (3)	
i–j	$(u_{ij}/R)/K$	$(u_{ji}/R)/K$	$(u_{ij}/R)/K$	$(u_{ji}/R)/K$
1–2	−167.38	−185.30	−167.38	−185.30
1–3	275.31	966.11	96.27	1209.49
2–3	−98.363	426.08	−199.6	−64.98

In this work we did not estimate specific values for the binary UNIQUAC interaction parameters of the ethanol + water system, but we assumed the values available in the literature ("common parameters", Sorensen and Arlt, 1980). The common parameters were those established from the correlation of all the ternary LLE results on systems containing water and ethanol reported in the cited collection.

Table 6 gives the values for the UNIQUAC surface and volume parameters and Table 7 the binary interaction parameters. The parameter estimation was carried out by the least-squares method by minimizing the following

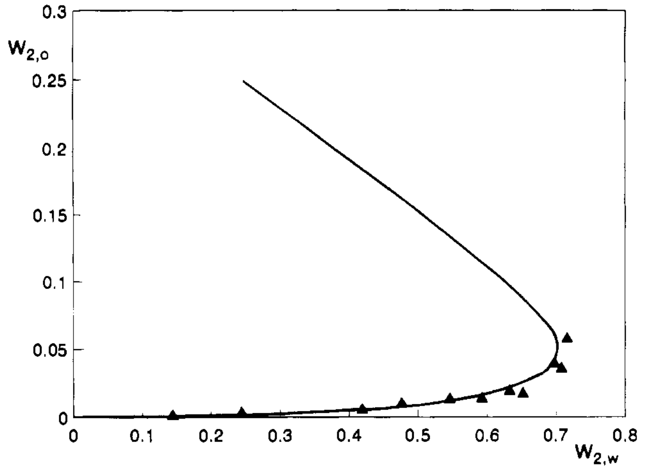

Figure 3. Trend of ethanol mass fraction in the organic phase vs ethanol mass fraction in the aqueous phase for the system water + ethanol + limonene at 293 K.

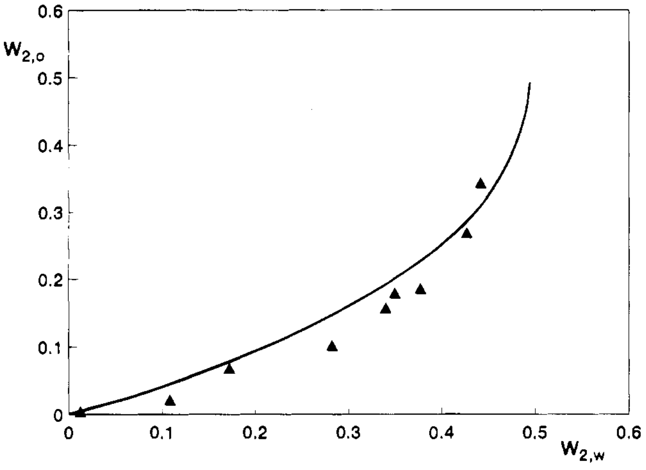

Figure 4. Trend of ethanol mass fraction in the organic phase vs ethanol mass fraction in the aqueous phase for the system water + ethanol + citral at 293 K.

objective function:

$$F = 100\{[(\sum_{k=1}^{N} \min \sum_{j=1}^{3}\sum_{i=1}^{2}(w_{\mathrm{jik}}^{\mathrm{exp}} - w_{\mathrm{jik}}^{\mathrm{calc}})^2/6N)]^{1/2} + [\sum_{j=1}^{2}\sum_{i=1}^{2}(w_{\mathrm{ji}}^{\mathrm{exp}} - w_{\mathrm{ji}}^{\mathrm{calc}})^2/4]^{1/2}\}$$

where N is the number of tie lines for the system (equal to 11 and 8 for the system with limonene and citral, respectively), the subscript k refers to the tie lines, i to the liquid phases in equilibrium, and j to the components, and w_{ijk}^{exp} are the experimental mass fractions and w_{ijk}^{calc} the mass fractions of the calculated tie line lying closest to the experimental tie line considered. In the second term of the same equation w_{ij}^{exp} are the experimental solubilities and w_{ij}^{calc} are the calculated solubilities of the two binary systems water + limonene and water + citral, respectively.

Figures 3 and 4 show the experimental and calculated distributions of the ethanol mass fraction between the two phases for the two ternary systems under investigation.

The root mean squares deviation between experimental and calculated mass fractions is equal to 2.3% for the water + ethanol + limonene system and to 1.8% for the water + ethanol + citral system.

The miscibility gap results show a strong effect of ethanol on the aqueous solutions of organic components. Complete miscibility is observed for an ethanol concentration greater than about 0.73 for the limonene system and about 0.45 for the citral system. Ethanol enhances both limonene (citral) solubility in the aqueous phase and water solubility in the organic phase.

Figures 1 and 2 show that the theoretical model furnishes very good predictions for the LLE data of both systems: the predictions of the miscibility gap and of the distribution coefficients are fully satisfactory.

Conclusions

Liquid–liquid equilibria were measured at 293 K and at atmospheric pressure for water + limonene and water + citral binary systems and for water + ethanol + limonene and water + ethanol + citral ternaries. The systems were correlated by means of the UNIQUAC activity coefficient model, which was fitted to the experimental results. New UNIQUAC interaction parameters between each solvent and each terpene compound were found. The accuracy of the calculation is reported by means of the RMSD and of the mean and maximum values of the differences between calculated and experimental equilibrium compositions.

The results for the ternary systems show that aqueous solutions of ethanol can be used as a solvent in the extraction process of oxygenated compounds from lemon essential oils.

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