J. Chem. Eng. Data **2001,** *46,* 546−550

Liquid−Liquid Equilibrium of the Water + Citric Acid + Short Chain Alcohol + Tricaprylin System at 298.15 K

Luciana Lintomen,[†] Renata T. P. Pinto,[†] Eduardo Batista,[‡] Antonio J. A. Meirelles,[‡] and Maria Regina W. Maciel*,[†]

Chemical Engineering School/Separation Process Development Laboratory and Food Engineering School/Physical Separation Laboratory, State University of Campinas—UNICAMP, Cidade Universitária " Zeferino Vaz",
C.P. 6066, Zip Code 13081-970, Campinas, SP, Brazil

In the past few years, new processes for citric acid recovery have been studied. Among these processes, liquid−liquid extraction has had special attention. The extraction process is attractive due to the fact that, if a good solvent is used, it presents high selectivity and efficiency, it does not affect the thermal stability of products, and it requires low energy consumption. In this work, experimental data for the liquid−liquid equilibria of water−citric acid−solvent systems were obtained. The following solvents were tested: 2-butanol, 1-butanol, and mixed solvents containing those alcohols and tricaprylin. The parameters for the NRTL and UNIQUAC models were obtained by fitting the thermodynamic models to the experimental data.

Introduction

The worldwide production of citric acid exceeds 500 000 ton/year. In contrast with a lot of products that previously were obtained by microbiological methods and nowadays are obtained by synthetic methods, this acid continues to be manufactured mainly by fermentation. Seventy percent of all citric acid produced is used by the food industry, and 18% is used by the pharmaceutical industry. Its use in the food industry represents 55−65% of the total acidulants' market, in which 20−25% corresponds to phosphoric acid and 5% to malic acid.

The fermentation process technology for the industrial production of organic acids has been known for more than a century. Citric acid is one of the macrofermentation processes of larger success within the bioproduct industries. The citric acid produced usually has as raw material the sugar because of the large availability of it in Brazil. The microorganisms used in the fermentation are yeast (*Candida lipolytica*) or fungus (*Aspergillus niger*).[1]

The economical impact, however, is still limited largely due to difficulties in the product recovery. To enhance market share of these bioproducts on an industrial scale, substantial improvements in separation technology are necessary. The classical method for recovering citric acid is based on the precipitation of calcium salts, by addition of calcium hydroxide in the fermentation broth. The solid is filtrated and treated with sulfuric acid (H_2SO_4) for the preferential precipitation of sulfate calcium. The free organic acid in the filtrate is purified using activated carbon or ion exchange, and concentrated by evaporation. The acid crystallizes with great difficulty and very low efficiency.

Compared to the usual separation processes, liquid−liquid extraction seems to be a very promising alternative. The success of a liquid−liquid extraction process relies on solvent selection. Mixed solvents composed of tertiary amines and alcohol are suggested as appropriated solvents.[2,3] The disadvantage of their use is their great toxicity and, consequently, higher purification costs. Welsh and Williams[4] studied several kinds of vegetable oils, as solvents to the recovery of organic compounds from aqueous solutions, like corn oil, canola oil, olive oil, and others. The authors verified that short chain alcohols and organic acids presented low recovery and small distribution coefficients, when the vegetable oils are used as single solvents.

Therefore, there is great appeal to the search for new solvents, mainly combinations of solvents. The main difficulty is the analysis of mixed solvents due to the lack of equilibrium data.

The aim of this work is to obtain new solvents for the recovery of citric acid by liquid−liquid extraction. Liquid−liquid equilibrium data for the following systems were experimentally obtained: water−citric acid−short chain alcohol (2-butanol or 1-butanol) and water−citric acid−short chain alcohol−tricaprylin. The intention is to study the influence of the solvent and the effect of the diluent structure on the formation of the two-phase region and on the selectivity and distribution coefficient of citric acid. Having the data, the NRTL and UNIQUAC parameters were determined.

Experimental Section

Citric acid monohydrate (99.5 mass % purity), 1-butanol, and 2-butanol (99.5 vol % purity) were purchased from Merck and were used without further purification. The tricaprylin, from Sigma Aldrich (97.6 mass % purity)[5] was also used. Distilled water was used in all experiments. For the determination of the experimental liquid−liquid equilibrium data, an equilibrium cell, according to the methodology described by Silva et al.,[6] was used. The equilibrium cell temperature was kept at (298.15 ± 0.1) K by a thermostatic bath (Paar Physica, Viscoterm VT2). Tie lines were obtained by preparing ternary and quaternary mix-

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* To whom correspondence should be addressed. Telephone: +55-0-19-7883900 or +55-0-19-7883971. Fax: +55-19-7993910. E-mail: wolf@feq.unicamp.br.

[†] Chemical Engineering School/Separation Process Development Laboratory.

[‡] Food Engineering School/Physical Separation Laboratory.

10.1021/je000226h CCC: $20.00

Table 1. Experimental Tie Lines at 298.15 K of the System Water (1) + Citric Acid (2) + 2-Butanol (3)

overall composition			bottom phase			top phase		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
0.5451	0.0000	0.4549	0.8140	0.0000	0.1860	0.3588	0.0000	0.6412
0.5340	0.0109	0.4551	0.7819	0.0134	0.2047	0.3549	0.0097	0.6354
0.5435	0.0204	0.4361	0.7680	0.0250	0.2070	0.3671	0.0178	0.6151
0.5350	0.0355	0.4295	0.7309	0.0403	0.2288	0.4125	0.0301	0.5574

Table 2. Experimental Tie Lines at 298.15 K of the System Water (1) + Citric Acid (2) + 1-Butanol (3)

overall composition			bottom phase			top phase		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
0.5354	0.0000	0.4646	0.9334	0.0000	0.0666	0.2019	0.0000	0.7981
0.5281	0.0255	0.4464	0.8967	0.0370	0.0663	0.2143	0.0138	0.7719
0.5308	0.0433	0.4259	0.8722	0.0617	0.0661	0.2186	0.0226	0.7588
0.5227	0.0517	0.4256	0.8609	0.0738	0.0653	0.2163	0.0252	0.7585
0.5867	0.0743	0.3390	0.8297	0.1052	0.0651	0.2161	0.0418	0.7421
0.4323	0.1555	0.4122	0.7124	0.2177	0.0699	0.2263	0.0925	0.6812

Table 3. Experimental Tie Lines at 298.15 K of the System Water (1) + Citric Acid (2) + 2-Butanol (3) + 5% Tricaprylin (4)

overall composition				bottom phase				top phase			
w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4
0.4681	0.0000	0.4816	0.0502	0.8256	0.0000	0.1744	0.0000	0.2265	0.0000	0.6896	0.0839
0.4720	0.0101	0.4699	0.0480	0.8036	0.0148	0.1809	0.0007	0.2332	0.0070	0.6780	0.0818
0.4713	0.0200	0.4605	0.0481	0.7937	0.0286	0.1769	0.0008	0.2345	0.0145	0.6681	0.0829
0.4648	0.0302	0.4570	0.0480	0.7736	0.0427	0.1802	0.0035	0.2339	0.0197	0.6612	0.0852
0.4572	0.0399	0.4512	0.0518	0.7610	0.0568	0.1772	0.0050	0.2349	0.0260	0.6448	0.0943
0.4270	0.1017	0.4181	0.0532	0.6208	0.1354	0.2417	0.0021	0.2453	0.0553	0.5801	0.1193
0.4149	0.1265	0.4087	0.0499	0.5758	0.1580	0.2556	0.0106	0.2423	0.0746	0.5584	0.1247

Table 4. Experimental Tie Lines at 298.15 K of the System Water (1) + Citric Acid (2) + 1-Butanol (3) + 5% Tricaprylin (4)

overall composition				bottom phase				top phase			
w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4
0.4745	0.0000	0.4778	0.0477	0.9347	0.0000	0.0653	0.0000	0.1763	0.0000	0.7460	0.0777
0.4718	0.0101	0.4711	0.0470	0.9169	0.0165	0.0660	0.0006	0.1720	0.0051	0.7424	0.0805
0.4682	0.0203	0.4631	0.0484	0.9010	0.0330	0.0651	0.0009	0.1753	0.0106	0.7323	0.0818
0.4662	0.0301	0.4584	0.0453	0.8838	0.0485	0.0651	0.0026	0.1808	0.0149	0.6394	0.1649
0.4595	0.0400	0.4532	0.0473	0.8696	0.0644	0.0640	0.0020	0.1773	0.0213	0.7195	0.0819
0.4294	0.1006	0.4184	0.0516	0.7760	0.1601	0.0627	0.0012	0.1884	0.0494	0.6628	0.0994
0.4039	0.1534	0.3946	0.0481	0.6951	0.2334	0.0618	0.0097	0.1727	0.0746	0.6461	0.1066

tures of known overall composition lying within the two-phase region. The components were weighed using an analytical electronic balance (Sartorius, A200 S model, with precision ±0.0001 g). The mixture was stirred vigorously for 30 min and, then, allowed to attain equilibrium for over a period of 12 h. After this period, the two phases became clear and transparent with the interface well defined. The samples were carefully taken from each phase and analyzed.

Citric acid concentration was determined by potentiometric titration of samples of known mass against 0.1 M sodium hydroxide,[7] with an automatic buret (Metrohm, Dosimat 715 model, with precision ±0.002 mL); these measurements were performed at least in duplicate. The total solvent (alcohol + water) concentration was determined by evaporation in an oven at 60 °C till constant weight. Later, water and alcohol concentrations were determined by gas chromatography using a Varian CG 3400 instrument with a 1 m × (31.75 × 10^{-4}) m Porapak-Q 80/100 mesh packed column. The column temperature was 180 °C, and the detection was carried out by thermal conductivity (TCD) with helium at a flow rate of 30 mL/min. For the quantitative results the external standard method was applied, well-known water and alcohol samples being the standard compounds used for this purpose. Each sample was measured three times, and the average value was considered. The tricaprylin concentration was obtained by difference. The standard deviations (σ) were 0.11 mass % for citric acid, 0.04 mass % for the alcohols, 0.12 mass % for tricaprylin, and 0.03 mass % for water.

Results and Discussion

Tables 1−5 show the experimental tie lines. All the concentrations are expressed in mass fraction.

Using the equilibrium data, the distribution coefficient (K) and the selectivity (S) can be calculated. The distribution coefficient is defined by the separation factor of the citric acid between the two liquid phases in equilibrium.

$$K_2 = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \tag{1}$$

where x is the mole fraction, the superscript I denotes the aqueous phase, and the superscript II denotes the solvent-rich phase; the index 2 is used to denote the solute (citric acid).

The selectivity is defined as the ratio of the distribution coefficients of the acid and water.

$$S_{21} = \frac{K_2}{K_1} \tag{2}$$

where the index 1 denotes the water. As can be seen by

Table 5. Experimental Tie Lines of the System Water (1) + Citric Acid (2) + 2-Butanol (3) + 10% Tricaprylin (4) at 298.15 K

overall composition				bottom phase				top phase			
w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4
0.4468	0.0000	0.4547	0.0985	0.8339	0.0000	0.1647	0.0014	0.1759	0.0000	0.6604	0.1637
0.4440	0.0099	0.4448	0.1013	0.8173	0.0163	0.1653	0.0011	0.1940	0.0056	0.6233	0.1771
0.4443	0.0201	0.4378	0.0978	0.7994	0.0318	0.1678	0.0010	0.1758	0.0108	0.6405	0.1729
0.4361	0.0296	0.4357	0.0986	0.7831	0.0468	0.1683	0.0018	0.1826	0.0150	0.6534	0.1490
0.4388	0.0415	0.4200	0.0997	0.7605	0.0639	0.1727	0.0029	0.1702	0.0201	0.6229	0.1868
0.3961	0.1256	0.3828	0.0955	0.5938	0.1769	0.2204	0.0089	0.1529	0.0540	0.5588	0.2343
0.3873	0.1495	0.3641	0.0991	0.5640	0.2009	0.2308	0.0043	0.1348	0.0547	0.5321	0.2784

Table 6. NRTL and UNIQUAC Parameters for the System Water (1) + Citric Acid (2) + 2-Butanol (3) + 1-Butanol (4) + Tricaprylin (5) at 298.15 K

pair	NRTL			UNIQUAC	
ij	A_{ij}/K	A_{ji}/K	α	A_{ij}/K	A_{ji}/K
12	294.85	4100.2	0.377 02	−81.928	13.554
13	886.48	156.50	0.470 00	137.99	67.401
14	1613.9	−349.87	0.200 00	216.71	55.281
15	1653.4	4.2485	0.470 00	−162.36	3491.4
23	−404.94	2216.5	0.204 36	−13.852	−9.7416
24	7.5967	3367.6	0.202 96	779.09	−261.55
25	122.72	2022.0	0.470 00	−332.81	3204.3
35	6000.0	−1190.4	0.393 91	−210.09	−11.947
45	147.60	−1410.7	0.200 00	−370.41	3389.8

Table 7. Mean Deviations in the Phase Compositions

	Δw (%)	
system	NRTL	UNIQUAC
water + citric acid + 2-butanol	0.85	1.35
water + citric acid + 1-butanol	0.53	0.47
water + citric acid + 2-butanol + 5% tricaprylin	1.25	1.28
water + citric acid + 1-butanol + 5% tricaprylin	0.74	0.68
water + citric acid + 2-butanol + 10% tricaprylin	0.97	0.96

the experimental data, the addition of the salt causes a slight decrease of the citric acid distribution coefficient but a significant increase in the selectivity.

Modeling

This work is a part of a complete study of separation of citric acid using a liquid−liquid extraction process. In a previous work,[8] liquid−liquid equilibrium data for the system water + citric acid + 2-butanol + NaCl were determined and also correlated using the NRTL and UNIQUAC models. In the modeling of the whole set of experimental data the binary parameters common to all systems (water + citric acid, water + 2-butanol, and citric acid + 2-butanol) were kept constant. The citric acid was considered as a single component, so that the phenomenon of partial dissociation was not considered in the adjustment.

The experimental equilibrium data were used to adjust parameters for the NRTL and UNIQUAC models. Due to the difference of molecular weights of the components, mass fractions were used as unity of concentration.[9]

The values of r_i' and q_i' for the UNIQUAC model were calculated using eq 3. The parameters R_k and Q_k were obtained from Magnussen et al.[10] and Macedo et al.[11]

$$r_i' = \frac{1}{M_i}\sum_k^G \nu_k^{(i)} R_k$$

$$q_i' = \frac{1}{M_i}\sum_k^G \nu_k^{(i)} Q_k \tag{3}$$

where M_i is the molecular weight and G is the total number of groups in the molecule of component i.

The parameter estimation procedure is based on the minimization of the objective function of composition, according to Stragevitch and d'Avila:[12]

$$S = \sum_m^D \sum_n^N \sum_i^{C-1} \left[\left(\frac{w_{inm}^{\mathrm{I,ex}} - w_{inm}^{\mathrm{I,calc}}}{\sigma_{w_{inm}^{\mathrm{I}}}} \right)^2 + \left(\frac{w_{inm}^{\mathrm{II,ex}} - w_{inm}^{\mathrm{II,calc}}}{\sigma_{w_{inm}^{\mathrm{II}}}} \right)^2 \right] \tag{4}$$

where D is the total number of groups of data, N is the total number of tie lines, and C is the total number of components in the group of data m. w is the mass fraction, the subscripts i, n, and m are component, tie line, and group number, respectively, and the superscripts I and II are the phases; ex and calc refer to experimental and calculated concentrations. $\sigma_{w_{inm}^{\mathrm{I}}}$ and $\sigma_{w_{inm}^{\mathrm{II}}}$ are the standard deviations observed in the compositions of the two liquid phases.

For all ternary and quaternary systems, estimation of the NRTL and UNIQUAC thermodynamic model parameters was carried out, and they are shown in Table 6.

With the calculated parameters, the compositions for both phases were estimated by performing liquid−liquid flash calculations. The results, expressed as mean deviations between experimental and calculated compositions in both phases, are given in Table 7. These deviations are calculated according to eq 5:

$$\Delta w = 100\sqrt{\frac{\sum_n^N \sum_i^C [(w_{i,n}^{\mathrm{I,ex}} - w_{i,n}^{\mathrm{I,calc}})^2 + (w_{i,n}^{\mathrm{II,ex}} - w_{i,n}^{\mathrm{II,calc}})^2]}{2NC}} \tag{5}$$

The equilibrium diagrams were plotted in rectangular coordinates. Some papers usually represent quaternary systems as pseudoternary systems. Only with the objective of improving the visualization of those systems was their representation done supposing that the solvent would include both the alcohol and tricaprylin. It is very important to emphasize, however, that they should not be considered as pseudoternary systems.

Figures 1−6 represent the experimental and the calculated tie lines and the calculated binodal curve. For the quaternary systems, 2-butanol + tricaprylin or 1-butanol + tricaprylin was admitted as solvent.

Figures 5 and 6 represent the experimental data for each system in tricaprylin free basis concentrations with the objective of emphasizing this effect upon the equilibrium. The tricaprylin free basis concentrations were calculated using the following equation.

$$w_i^* = \frac{w_i}{1 - w_4} \tag{6}$$

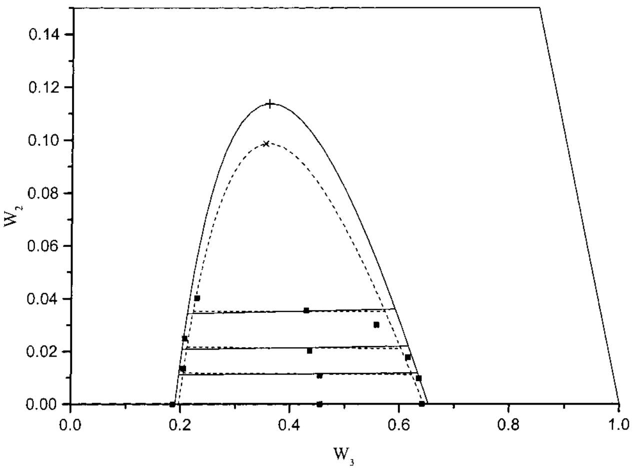

Figure 1. Ternary system water (1) + citric acid (2) + 2-butanol (3) at 298.15 K: (■) experimental; (· · ·) NRTL; (—) UNIQUAC; (×) plait point (NRTL); (+) plait point (UNIQUAC).[1,8]

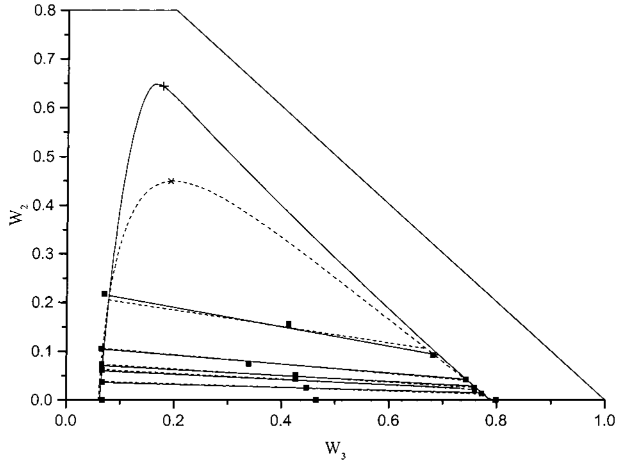

Figure 2. Ternary system water (1) + citric acid (2) + 1-butanol (3) at 298.15 K: (■) experimental; (· · ·) NRTL; (—) UNIQUAC; (×) plait point (NRTL); (+) plait point (UNIQUAC).

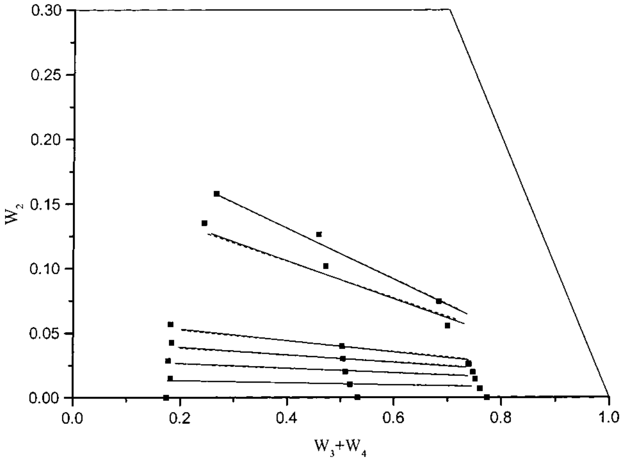

Figure 3. Quaternary system water (1) + citric acid (2) + 2-butanol (3) + 5% tricaprylin (4) at 298.15 K: (■) experimental; (· · ·) NRTL; (—) UNIQUAC.

where w_i^* is the mass fraction of the component i on a tricaprylin free basis and w_4 is the tricaprylin mass fraction

It was verified that the water + citric acid + 2-butanol system presented a distribution coefficient around unity, although it showed a very narrow two-phase region (Figure 1), as also reported in previous work by Grinberg et al.[13] The system constituted by water + citric acid + 1-butanol (Figure 2) showed a large two-phase region when compared with the water + citric acid + 2-butanol system, but its

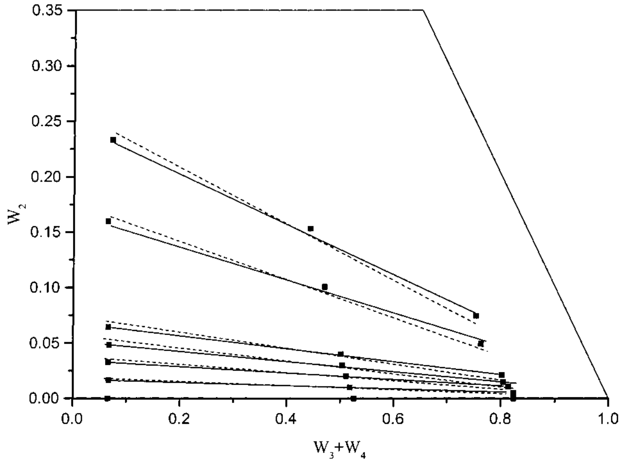

Figure 4. Quaternary system water (1) + citric acid (2) + 1-butanol (3) + 5% tricaprylin (4) at 298.15 K: (■) experimental; (· · ·) NRTL; (—) UNIQUAC.

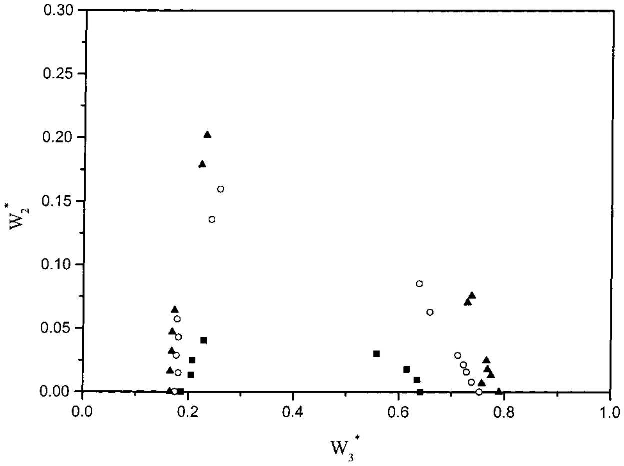

Figure 5. Comparison of the ternary system with 2-butanol (3) and the quaternary system on a tricaprylin free basis with 2-butanol (3) + 5 and 10% tricaprylin (4): (■) ternary system; (○) 5% tricaprylin; (▲) 10% tricaprylin.

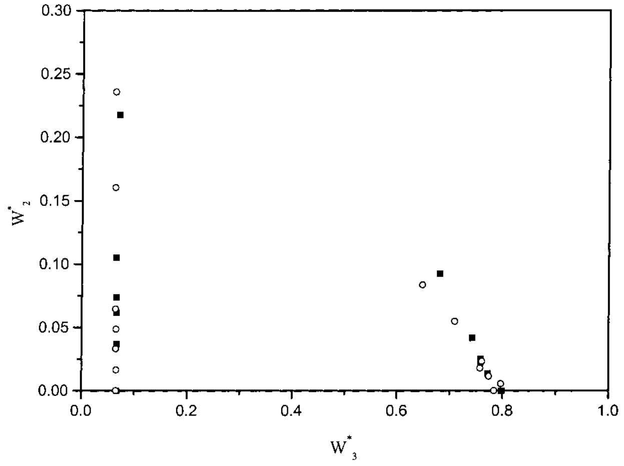

Figure 6. Comparison of the ternary system with 1-butanol (3) and the quaternary system on a tricaprylin free basis with 1-butanol (3) + 5% tricaprylin (4): (■) ternary system; (○) 5% tricaprylin.

distribution coefficient is lower than the corresponding one for the system constituted by 2-butanol.

The aim of adding another component (tricaprylin) to those ternary systems was to obtain an increase of the two-phase region without a significant decrease in the distribution coefficient of citric acid. It can be seen that, for the systems with tricaprylin, an increase in the two-phase region was achieved (Figures 3 and 4). This increase was more significant for the system with 2-butanol as solvent (Figure 5) than for the system with 1-butanol (Figure 6). It can be observed that for all the systems investigated a decrease of the distribution coefficient and an increase in the citric acid selectivity have occurred.

Concluding Remarks

The estimated parameters for the NRTL and UNIQUAC thermodynamic models seem to be representative, since the description of the liquid−liquid equilibria for all the studied systems had presented mean deviations lower than 1.28% with relation to experimental data. It is important to emphasize that no work on these estimations was found in the open literature.

Equilibrium data for systems containing water + citric acid + short chain alcohols + tricaprylin were experimentally determinate at 298.15 K. This verifies the importance of the present work, since these parameters enable the modeling and simulation of liquid−liquid extractors using the proposed mixed solvents.

The consideration of the partial dissociation of citric acid should improve the physical meaning of the binary parameters and, as a consequence, may allow a better extrapolation of such parameters to systems containing some of the compounds included in the present work. This study is being developed by the authors.

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Received for review July 28, 2000. Accepted January 3, 2001. This work was supported financially by research grants from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP−Proc. no. 97/07384-4, 00/00406-7, and 97/10630-7) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq−Proc. no. 46.6680/00-7 and 521011/95-7).

JE000226H