Liquid−Liquid Equilibrium of the Water + Citric Acid + 2-Butanol + Sodium Chloride 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

Liquid−liquid equilibrium data for water + citric acid + 2-butanol + NaCl at three different salt concentrations (5, 10, and 15 mass %) and at 298.15 K were determined. The parameters for the NRTL and UNIQUAC models were obtained by fitting the thermodynamic models to the experimental data.

Introduction

When a salt is added to an aqueous solution of a nonelectrolyte component, the activity coefficient of the nonelectrolyte changes. The increase in the activity coefficient is called a salting out effect, while the decrease in this coefficient is called a salting in effect.[1−2] A search of the published literature indicates that few studies have been performed on the salting out effect in systems with organic acids. These phenomena may be explained by various theories such as the hydration theory, the electrostatic theory, and the internal pressure concept. The salting out effect in ternary systems causes an increase in the heterogeneous region[3] and, in many cases, an increase in the distribution coefficient and selectivity.

Nowadays, the interest in extraction of fermentation products is increasing, especially of organic acids such as lactic, malic, and citric acids.[4−5] To develop a solvent extraction process as an alternative to the classical precipitation process for recovery of organic acids, a number of liquid−liquid systems have been investigated.[3,6−7] However, studies on the salting out effect on systems containing citric acid have not been reported in the open literature.

The aim of this work is to determine liquid−liquid equilibrium data for the system water + citric acid + 2-butanol + sodium chloride at 298.15 K. The salting out effect was studied by using NaCl at three different concentrations, (5, 10, and 15) mass %. On the basis of the experimental data, parameters for the UNIQUAC and NRTL models were determined.

Experimental Section

Citric acid monohydrate (99.5 mass % purity), sodium chloride (99.5 mass % purity), and 2-butanol (99.5 vol % purity) were purchased from Merck and were used without further purification. Distilled water was used in all experiments. For the determination of liquid−liquid equilibrium data, an equilibrium cell was used.[8] With the objective of allowing the visualization of the two liquid phases, the cell was built of Pyrex glass with a 60 mL internal volume and two lateral exits for the collection of the two-phase samples and a jacket for circulating water coming from the thermostatic bath, that has the purpose of maintaining the temperature constant inside the cell. Tie lines were obtained by preparing ternary and quaternary mixtures of known overall composition lying within the heterogeneous region. The amount of each component in the overall composition was calculated in order to obtain approximately the same volume for both phases, allowing the collection of the samples without disturbance of the equilibrium. The overall mass of each mixture was approximately 50 g.

The equilibrium cell temperature was kept at (298.15 ± 0.1) K by a thermostatic bath (Paar Physica, Viscoterm VT2). The components were weighed using an analytical electronic balance (Sartorius, A200 S model, with precision of ±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.

The citric acid concentration was determined by potentiometric titration of samples of known mass against 0.1 M sodium hydroxide,[9] with an automatic buret (Metrohm, Dosimat 715 model, with a precision of ±0.002 mL); these measurements were performed at least in duplicate. The total part of volatile (water + alcohol) was determined by evaporation in an oven at 60 °C until constant weight in triplicate measurements. Later, water and alcohol concentrations were determined by gas chromatography using Varian CG 3400 equipment 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 sodium chloride concentration was obtained by difference. The standard deviations (σ) were ±0.11 mass % for citric acid, ±0.03 mass % for the alcohol, ±0.03 mass % for water, and ±0.10

---

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

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

[‡] Food Engineering School/Physical Separation Laboratory.

10.1021/je000111d CCC: $19.00

Table 1. Experimental Tie Lines at 298.15 K for the System Water (1) + Citric Acid (2) + 2-Butanol (3) + 5 mass % NaCl (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
0.4750	0.0000	0.4739	0.0511	0.7991	0.0000	0.0921	0.1088	0.1639	0.0000	0.8339	0.0022
0.4632	0.0303	0.4558	0.0507	0.7590	0.0410	0.0900	0.1100	0.1782	0.0219	0.7982	0.0017
0.4482	0.0610	0.4398	0.0510	0.7226	0.0825	0.0869	0.1080	0.1878	0.0367	0.7648	0.0107
0.4371	0.0888	0.4252	0.0489	0.6970	0.1186	0.0869	0.0975	0.2041	0.0528	0.7285	0.0146
0.4167	0.1187	0.4143	0.0503	0.6594	0.1582	0.0839	0.0985	0.2159	0.0762	0.6865	0.0214

Table 2. Experimental Tie Lines at 298.15 K for the System Water (1) + Citric Acid (2) + 2-Butanol (3) + 10 mass % NaCl (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
0.4502	0.0000	0.4494	0.1004	0.7381	0.0000	0.0659	0.1960	0.0995	0.0000	0.8992	0.0013
0.4512	0.0302	0.4205	0.0981	0.7015	0.0389	0.0647	0.1949	0.1147	0.0187	0.8627	0.0039
0.4243	0.0606	0.4160	0.0991	0.6646	0.0789	0.0610	0.1955	0.1179	0.0359	0.8379	0.0083
0.4077	0.0909	0.4001	0.1013	0.6196	0.1172	0.0585	0.2047	0.1265	0.0531	0.8057	0.0147
0.3963	0.1218	0.3825	0.0994	0.6039	0.1513	0.0576	0.1872	0.1369	0.0634	0.7742	0.0255

Table 3. Experimental Tie Lines at 298.15 K for the System Water (1) + Citric Acid (2) + 2-Butanol (3) + 15 mass % NaCl (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
0.4262	0.0000	0.4231	0.1507	0.6871	0.0000	0.0549	0.2580	0.0658	0.0000	0.9331	0.0011
0.4100	0.0304	0.4076	0.1520	0.6535	0.0398	0.0535	0.2532	0.0789	0.0187	0.8976	0.0048
0.3968	0.0606	0.3919	0.1507	0.6254	0.0790	0.0525	0.2431	0.0903	0.0348	0.8634	0.0115
0.3840	0.0909	0.3742	0.1509	0.5969	0.1184	0.0525	0.2322	0.1036	0.0543	0.8270	0.0151
0.3700	0.1204	0.3590	0.1506	0.5636	0.1588	0.0512	0.2264	0.1201	0.0688	0.7859	0.0252

mass % for NaCl.

Results and Discussion

Tables 1−3 give the experimental tie lines. All the concentrations are expressed in mass fraction (w).

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 faction and the superscript I denotes the aqueous phase and 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 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 part of a broad study of liquid−liquid equilibrium data for ternary and quaternary systems containing citric acid. In a previous work,[10] the liquid−liquid equilibrium data for ternary and quaternary systems with 2-butanol + tricaprilyn were determined, that were also correlated using the NRTL and UNIQUAC models.

In the modeling of the systems containing NaCl, the previously determined binary parameters[10] (water−citric acid, water−2-butanol, and citric acid−2-butanol) were kept constant. Therefore, only the interaction parameters with NaCl were adjusted. The salt and the citric acid were considered as single components, so that the phenomena of total and partial dissociations were 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.[11]

The values of r_i' and q_i' for the UNIQUAC model were calculated using eq 3. The parameters R_i and Q_i were obtained from Magnussen et al.[12] and Macedo et al.[13]

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

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

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

The parameter estimation procedure is based on the minimization of the objective function of composition, according to Stragevitch and d'Ávila:[14]

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

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 represent experimental and calculated values. $\sigma_{w_{inm}^{\mathrm{I}}}$ and $\sigma_{w_{inm}^{\mathrm{II}}}$ are the standard deviations observed in the compositions of the two liquid phases.

Table 4. NRTL and UNIQUAC Parameters at 298.15 K: Water (1) + Citric Acid (2) + 2-Butanol (3) + NaCl (4)

	NRTL			UNIQUAC	
pair *ij*	A_{ij}/K	A_{ji}/K	α	A_{ij}/K	A_{ji}/K
12	294.85	4100.20	0.377 02	−81.93	13.55
13	886.48	156.50	0.470 00	137.99	67.40
14	−5524.10	−1440.90	0.224 07	353.60	−477.95
23	−404.94	2216.50	0.204 36	−13.85	−9.74
24	−3422.90	442.30	0.387 68	−169.26	3357.40
34	2712.20	2306.20	0.233 64	52.34	3405.50

Table 5. Mean Deviations in the Phase Compositions

	Δ*w* (%)	
system	NRTL	UNIQUAC
water + citric acid + 2-butanol + 5% NaCl	1.6096	1.4309
water + citric acid + 2-butanol + 10% NaCl	1.1671	1.2067
water + citric acid + 2-butanol + 15% NaCl	1.2456	1.3690

The parameters for the NRTL and UNIQUAC thermodynamic models are given in Table 4. The experimental data were compared to the calculated values by liquid−liquid flash[14,15] using the adjusted parameters. The percent of deviation of experimental mass fractions from the calculated ones can be found in Table 5. These deviations were calculated according to eq 5:

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

Figures 1−4 represent the experimental data and the calculated tie lines for each system. These figures are represented in salt free basis concentrations with the objective of emphasizing the salting out effect upon the equilibrium. The salt free basis concentrations were calculated using eq 6.

$$w_i^* = \frac{w_i}{1 - w_4} \qquad (6)$$

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

Figure 1 shows that the ternary system water + citric acid + 2-butanol presents a very narrow heterogeneous region, making it difficult to use pure 2-butanol as solvent in the extraction process, as already reported by Grinberg et al.[5] The addition of the salt increases remarkably the heterogeneous region. Although the distribution coefficient for citric acid decreases, the selectivity increases because the water concentration in the alcoholic phase decreases significantly by adding NaCl (Tables 1−3).

In Figures 2−4, the points on the right represent the concentrations obtained for the components of the alcoholic phase while the points on the left represent the aqueous phase. The points in the center of the diagram represent the overall mass compositions of the system. The very good alignment of these three points proves the good quality of the data and that the mass balance was obeyed in our experiments.

Both thermodynamic models presented a similar behavior, with approximately the same deviations between calculated and experimental concentrations (Table 5), except for the system with 5 mass % NaCl, where the equilibrium was better represented by the UNIQUAC model (Figure 2). In all systems (Figures 2−4), it can be noted that, with the increase of citric acid concentration and of the corresponding electrolyte concentrations, a larger deviation between the experimental and calculated tie lines is observed. However, for lower concentrations of citric acid in the systems (≤10 mass %) the models describe well the two-phase equilibrium, although the dissociation of the electrolytes was not taken into account. According to Wennersten,[16] the maximum concentration of citric acid in the fermentation broth is approximately 10 mass %.

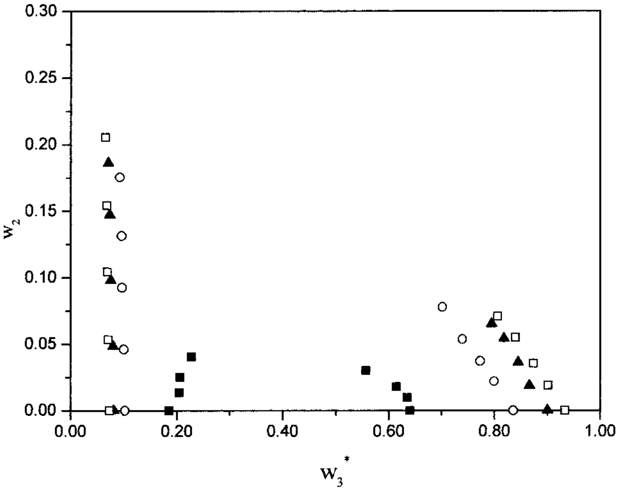

Figure 1. Comparison of the ternary system with citric acid (2) + 2-butanol (3) and the quaternary systems on a salt free basis with 5, 10, or 15 mass % NaCl at 298.15 K: (■) ternary system (Lintomen et al., 2000); (○) 5 mass % NaCl; (▲) 10 mass % NaCl; (□) 15 mass % NaCl.

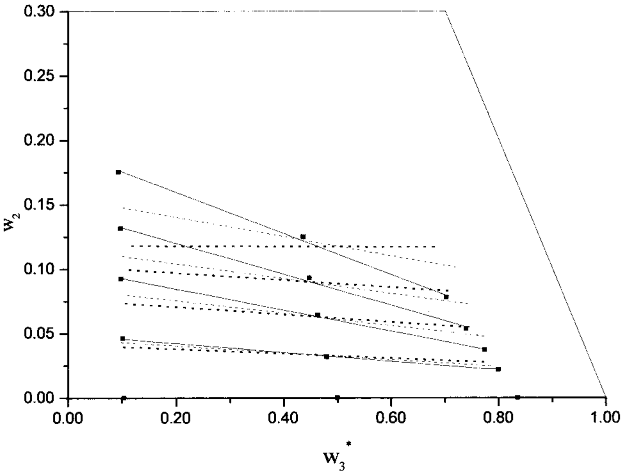

Figure 2. Equilibrium data on a salt free basis: water (1) + citric acid (2) + 2-butanol (3) + 5 mass % NaCl at 298.15 K: (■) experimental; (···) NRTL; (- - -) UNIQUAC.

In the quaternary system with 15 mass % NaCl, precipitation of a small amount of salt was observed in the experiments, with the formation of a cloud. This precipitation was very small and did not affect significantly the mass balance, as it can be observed in the tie-line alignment in Figure 4.

An approach similar to the present one was reported by Escudero et al.[17] They considered the quaternary system composed of 2,3-butanediol + 2-butoxyethanol + water + potassium chloride as a pseudoternary one, assuming as solvent the aqueous solution of KCl, and the dissociation of the electrolytes was not taken into account. The authors correlated the experimental data for this pseudoternary system using the UNIQUAC and NRTL models with good

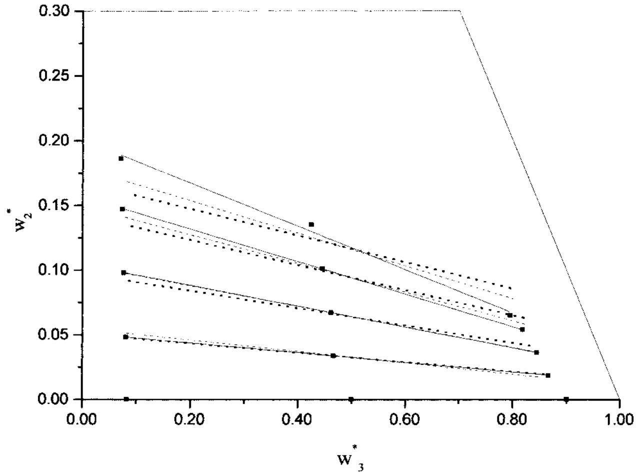

Figure 3. Equilibrium data on a salt free basis: water (1) + citric acid (2) + 2-butanol (3) + 10 mass % NaCl at 298.15 K: (■) experimental; (···) NRTL; (- - -) UNIQUAC.

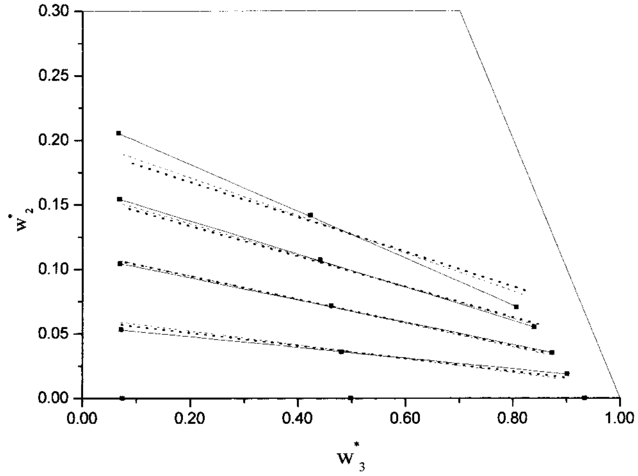

Figure 4. Equilibrium data on s salt free basis: water (1) + citric acid (2) + 2-butanol (3) + 15 mass % NaCl at 298.15 K: (■) experimental; (···) NRTL; (- - -) UNIQUAC.

results in both cases. In the present work, the dissociation of the electrolytes was not also considered, but the system was treated as a quaternary one.

Concluding Remarks

It can be concluded that, by adding NaCl to the water + citric acid + 2-butanol system, there is a large increase in the heterogeneous region and on the selectivity, without a significant decrease of the citric acid distribution coefficient.

The estimated parameters of the NRTL and UNIQUAC models seem to be representative, since the description of the liquid−liquid equilibrium in most cases has presented mean deviations lower than 1.4%. It is important to emphasize that no work on these estimations was found in the open literature. With these parameters, the modeling and the simulation of liquid−liquid extractors using the salting out effect for citric acid recovery are possible.

The consideration of the electrolyte dissociation should improve the physical meaning of the binary parameters and, as 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.

Literature Cited

(1) Al-Sahhaf, T. A.; Kapetanovic, E. Salt Effects of Lithium Chloride, Sodium Bromide, or Potassium Iodide on Liquid−Liquid Equilibrium in the Systems Water + 1-Butanol. *J. Chem. Eng. Data* **1997**, *42*, 74−77.

(2) Shah, D. J.; Tiwari, K. K. Effect of Salt on the Distribution of Acetic Acid between Water and Organic Solvent. *J. Chem. Eng. Data* **1981**, *26*, 375−379.

(3) Sólimo, H. N.; Bonatti, C. M.; Zurita, J. L.; Gramajo, M. B. Liquid−Liquid Equilibria for the System Water + Propionic Acid + 1-Butanol at 303.2K. Effect of Addition of Sodium Chloride. *Fluid Phase Equilib.* **1997**, *137*, 163−172.

(4) Kertes, A. S.; King, C. J. Extraction Chemistry of Fermentation Product Carboxylic Acids. *Biotechnol. Bioeng.* **1986**, *28*, 269−282.

(5) Grinberg, A.; Povimonski, D.; Apelblat, A. Liquid−Liquid Distribution in the Ternary System: Citric Acid- 2-Butanol- Water at 298.15 K. *Solvent Extr. Ion Exch.* **1991**, *9*, 127−135.

(6) Marcilla, A.; Ruíz, F.; Olaya, M. M. Liquid−Liquid-solid equilibria of quaternary system water-ethanol-1-butanol-sodium choride at 25 °C. *Fluid Phase Equilib.* **1995**, *105*, 71−91.

(7) Saravanan, G.; Srinivasan, D. Liquid−Liquid Equilibria for the System Ethyl Acetate−Acetic Acid−Water in the Presence of Dissolved Inorganic Salts. *J. Chem. Eng. Data* **1985**, *30*, 166−171.

(8) Silva, L. H. M.; Coimbra, J. S.; Meirelles, A. J. A. Equilibrium Phase Behavior of Poly(ethylene glycol) + Potassium Phosphate + Water Two Phase Systems at Various pH and Temperatures. *J. Chem. Eng. Data* **1997**, *42*, 398−401.

(9) Tiwari, R. D.; Sharma, J. P. *The Determination of Carboxylic Functional Groups*; Pergamon Press: New York, 1970.

(10) Lintomen, L.; Pinto, R. T. P.; Batista E.; Meirelles, A. J. A.; Maciel, M. R. W. *New Solvent Alternatives for Citric Acid Recovery by Liquid−Liquid Extraction. XIII Congresso Brasileiro de Engenharia Química*; in press.

(11) Batista, E.; Monnerat, S.; Kato, K.; Stragevitch, L.; Meirelles, A. J. A. Liquid−Liquid Equilibrium for Systems of Canola Oil, Oleic Acid and Short-Chain Alcohols. *J. Chem. Eng. Data* **1999**, *44*, 1360−1364.

(12) Magnussen, T.; Rasmussen, P.; Fredenslund, A. Unifac Parameter Table for Prediction of Liquid−Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331−339.

(13) Macedo, E. A.; Skovborg, P.; Rasmussen, P. Calculation of Phase Equilibria for Solutions of Strong Electrolytes in Solvent−Water Mixtures. *Chem. Eng. Sci.* **1990**, *45*, 875−882.

(14) Stragevitch, L.; d'Ávila, S. G. Application of a Generalised Maximum Likelihood Method in the Reduction of Multicomponent Liquid−Liquid Equilibrium Data. *Braz. J. Chem. Eng.* **1997**, *14*, 41−52.

(15) Shaw, J. M.; de Loos, Th. W.; Swaan Arons, J. Prediction of Unusual Retrograde Condensation in Model Reservoir Fluids. *Fluid Phase Equilib.* **1993**, *84*, 251−266.

(16) Wennersten, R. The Extraction of Citric Acid from Fermentation Broth Using a Solution of a Ternary Amine. *J. Chem. Technol. Biotechnol.* **1983**, *33B*, 85−94.

(17) Escudero, I.; Cabezas, J. L.; Coca, J. Liquid−Liquid Equilibria in (2,3-Butanediol + 2-Butoxyethanol + Water + Potassium Chloride) at 70 °C. *J. Chem. Eng. Data* **1996**, *41*, 1383−1387.

Received for review April 13, 2000. Accepted September 11, 2000. 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 1997/10630-7) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq−Proc. no. 521011/95-7).

JE000111D