

## Evaluation of Liquid–Liquid Extraction Process for Separating Acrylic Acid Produced From Renewable Sugars

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### Abstract

In this article, the separation and the purification of the acrylic acid produced from renewable sugars were studied using the liquid–liquid extraction process. Nonrandom two-liquids and universal *quasi*-chemical models and the prediction method universal *quasi*-chemical functional activity coefficients were used for generating liquid–liquid equilibrium diagrams for systems made up of acrylic acid, water, and solvents (diisopropyl ether, isopropyl acetate, 2-ethyl hexanol, and methyl isobutyl ketone) and the results were compared with available liquid–liquid equilibrium experimental data. Aspen Plus (Aspen Technology, Inc., version 2004.1) software was used for equilibrium and process calculations. High concentration of acrylic acid was obtained in this article using diisopropyl ether as solvent.

**Index Entries:** Acrylic acid recovery; liquid–liquid extraction; separation; simulation; thermodynamic characterization; renewable sugars.

### Introduction

Renewable sugars, as can be derived from sugar cane, are interesting as alternative carbon sources for the production of chemicals, especially considering the power of modern biotechnological methods. One of the possible routes for obtaining acrylic acid (2-propenoic acid) is through dehydration of lactic acid, which can be obtained through anaerobic fermentation of sugars from biomass. The liquid–liquid extraction process is one option for the separation of acrylic acid from the mixture formed after the dehydration reaction, because it is suitable for dilute systems and is carried out in such a way that avoids thermal degradation of the materials being separated.

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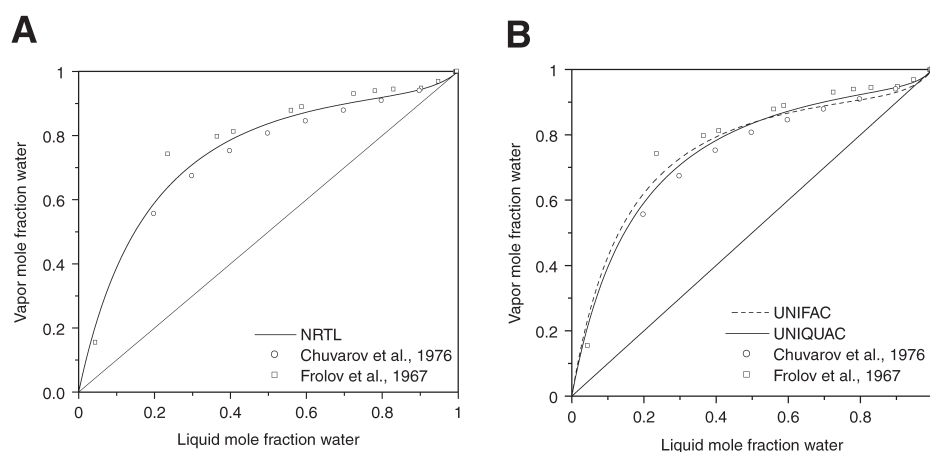
Acrylic acid is a commodity chemical that is produced by partial oxidation of propene. This acid could be produced from sugars on bulk industrial scale, as an alternative to its current production from petrochemical feedstocks (1). The major use of acrylic acid and its salts and esters, is in polymeric flocculants, dispersants, coatings, paints, adhesives, and binders for leather, paper, and textiles.

Some authors have been studying possible biotechnology routes to obtain acrylic acid from renewable sugars (1,2). This article will not focus on the conversion of sugars to lactic acid or the dehydration step required to produce acrylic acid; instead, we will focus on the separation of acrylic acid from water, according to data reported by Straathof (1). For this, it is necessary to devise a separation process to obtain acrylic acid with high purity and yield. We thus defined the experiment to consider a dilute stream made up of 3 mol% of acrylic acid and 97 mol% of water, near to the azeotropic point at one atm. The liquid–liquid extraction process being considered in this article was tested under these conditions using several solvents to obtain pure acrylic acid through this process.

Liquid–liquid extraction is an efficient, economical, and environmentally friendly method for separation of organic acids. Extractive recovery of carboxylic acids from dilute aqueous solutions has received attention in recent years because it can be conducted at low temperatures, avoiding material thermal composition. Liquid–liquid extraction is a diffusional separation process, wherein a feed flow is brought into contact with a selected solvent. This solvent will remove a particular chemical compound (the solute) from the feed flow. Two streams leave the column; the solute stream is named extract, and the other stream is named raffinate.

In the open literature, several solvents can be found to extract acrylic acid from aqueous solution through liquid–liquid equilibria (LLE) data. These solvents include diisopropyl ether, 2-ethylhexanol, isopropyl acetate, methyl isobutyl ketone (3), caproic acid, enanthic acid, caprylic acid, pelargonic acid, methyl caproate, methyl enanthate, methyl caprylate, methyl pelargonate (4), and trialkylphosphine oxide (5).

One of the objectives of this article is the characterization of the acrylic acid + water system in order to show the azeotropic point present in this system and, then, include the solvents in the characterization, because of the difficulty associated with separating this mixture through conventional distillation. The solvents must have proper characteristics in terms of solubility with the acid and in terms of facilities of separation from the acid for recycling. The methodology followed here will provide better understanding of the system behavior and will enable evaluation of a liquid–liquid extraction process to obtain pure acrylic acid from dilute aqueous solution. Finally, a liquid–liquid extractor was simulated and optimized to show the robustness of the separation.



**Fig. 1.** VLE diagram for the system acrylic acid + water (A) NRTL and (B) UNIQUAC and UNIFAC at 1 atm.

### Characterization of the Systems Acrylic Acid + Water and Acrylic Acid + Water + Solvents

A methodology for characterizing the two systems under consideration, acrylic acid + water and acrylic acid + water + solvents, was developed. The thermodynamic models used were universal *quasi*-chemical (UNIQUAC) and nonrandom two-liquids (NRTL) and the group contribution method UNIQUAC functional activity coefficients (UNIFAC) was used for equilibrium prediction. To evaluate the azeotropic points with the thermodynamic models used for the binary systems involved, the available parameters of vapor-liquid equilibria (VLE) were used. The calculations were made using Aspen Plus simulator; it was possible to find in the Aspen Plus Data Bank both VLE-ideal gas (VLE-IG) and VLE-Hayden-O'Connell data for calculations of activity and fugacity coefficients, respectively. When VLE data were not available for a given system, parameters predicted using UNIFAC activity coefficient method were used. They are called UNIFAC-IG, meaning UNIFAC for predicting activity coefficient and IG model for calculating the vapor phase.

In Fig. 1, the data obtained through simulations were compared with experimental data reported in the literature (6,7). These authors have reported these experimental data in Deutsche Gesellschaft für Chemisches Apparatewesen (DECHEMA), but their data were not ideal for this experiment because both thermodynamic consistency tests are negative. In Fig. 1, the liquid-vapor equilibrium diagram is shown for the acrylic acid + water system. The presence of an azeotrope can be observed at the composition of 2 mol% acrylic acid and 98 mol% water. This behavior indicates that, through a conventional distillation, it is not possible to obtain pure acrylic acid. UNIFAC was also used to predict VLE, as shown in the figure. The

close relationship between UNIFAC and UNIQUAC results indicate that the group contribution method is a powerful method to predict the equilibrium data. Considering this, and as it is a dilute stream, the liquid–liquid extraction process can be used.

According to a search made in the open literature as described, it was found that various solvents are available to extract acrylic acid from dilute aqueous solution. In this article, the following solvents, among the ones listed earlier, will be considered: diisopropyl ether, isopropyl acetate, 2-ethylhexanol, and methyl isobutyl ketone.

### LLE Data, Distribution Coefficient, and Heterogeneous Region

LLE data are essential for the design and development of extraction processes (8,9). First, a literature search was carried out to find LLE experimental data to guide the simulation and/or to validate it. In order to model the LLE, a number of models are available, including NRTL (10) and UNIQUAC (11), as well as a prediction method based on group contributions called UNIFAC (and their modifications) (12–14). In this article, the NRTL and UNIQUAC models were used to generate LLE diagrams, and the results were compared with available LLE experimental data. Aspen Plus software was used for these calculations. Group contribution methods as the UNIFAC method for liquid-liquid systems (UNIFAC-LL) can be applied to predict the LLE model parameters if no experimental data are available. The plant size is directly related to the selected solvent used in the liquid–liquid extraction unit, because their characteristics, such as distribution coefficient and selectivity, determine the composition of the raffinate and the extract streams, which will also determine the downstream processing requirements (8).

To evaluate the distribution coefficients and the heterogeneous region, a study was carried out with the unique experimental data reported (3). The outcomes of this study can be seen in Figs. 2 and 3. The distribution coefficient for liquid–liquid extractions involving an aqueous solution is simply equal to the concentration of the solute in the solvent phase divided by its equilibrium concentration in the aqueous phase. This is one of the main parameters used to establish the minimum solvent/feed ratio that must be manipulated in an extraction process. It is necessary that the acrylic acid remains in the organic phase (as indicated in Fig. 2). The heterogeneous region is very wide, avoiding problems in the extremes, wherein partial miscibility could occur, making the posterior recovery of the solvent difficult. The larger that region is, the better the separation through liquid–liquid extraction process will be. In Fig. 3, this region is represented by the binodal curves.

Figure 2 reports that all the solvents studied present higher acrylic acid distribution coefficient between the organic and the aqueous phases, distinguished among them the diisopropyl ether and 2-ethyl hexanol. From the data reported by Linek (3) shown in Fig. 3, the solvents present

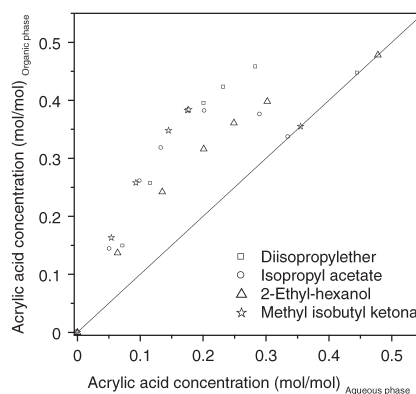


Fig. 2. Distribution coefficients of the solvents reported by Linek et al. (3).

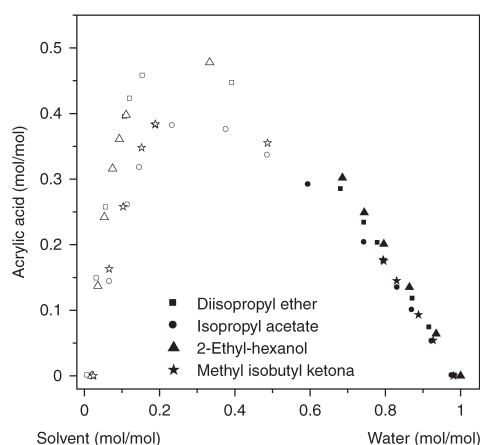
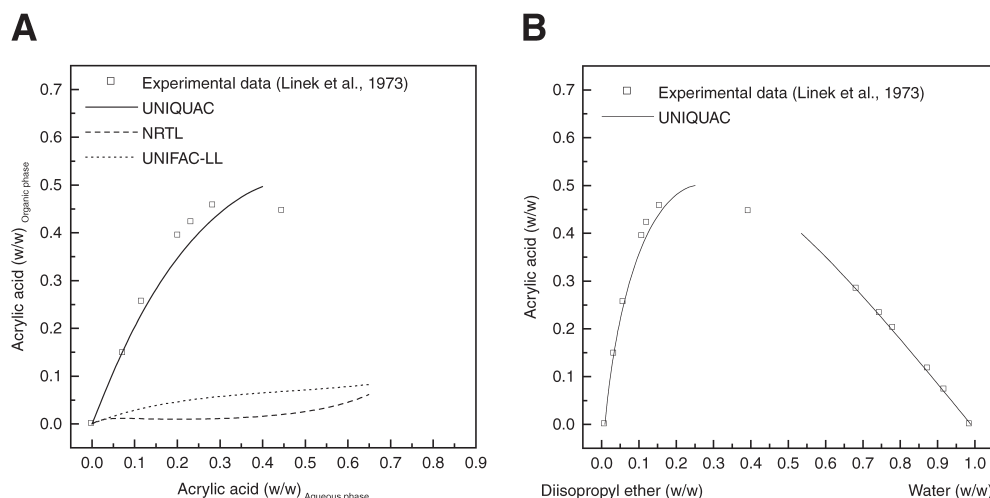


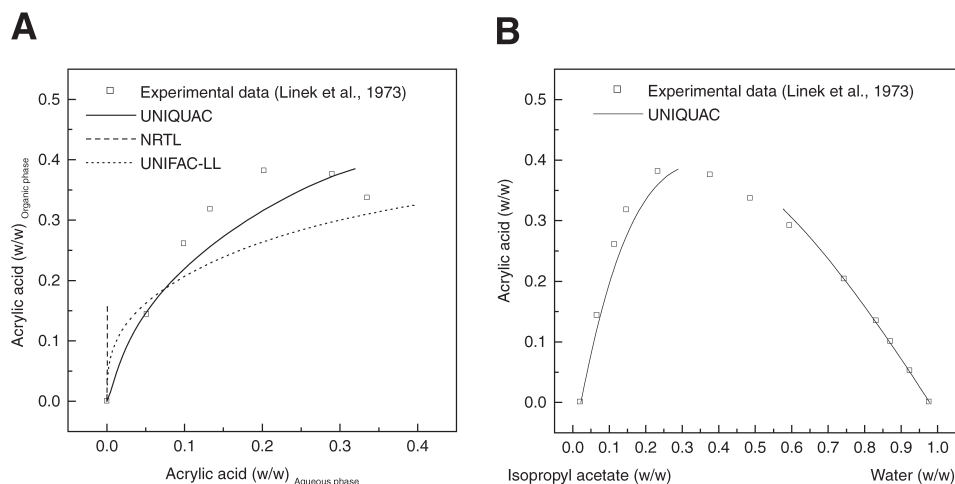
Fig. 3. Heterogeneous region of the solvents reported by Linek et al. (3), where closed symbols mean aqueous phase and open symbols mean organic phase.

low water solubility (water mass fraction equal to 0.009 for diisopropyl ether, 0.020 for 2-ethyl hexanol, 0.022 for isopropyl ether, and 0.024 for methyl isobutyl ketone) in the organic phase (heterogeneous region), which can introduce complications when the extract stream is to be treated, or even when the raffinate stream has to be pure water. With this behavior, the azeotropes formed among water + solvents do not affect the separation, because pure water tends to be obtained as raffinate and only a small amount of water goes to the extract phase.

Among the solvents studied, diisopropyl ether and the 2-ethyl hexanol perform better in terms of distribution coefficients and the range of the heterogeneous region. Thus, these solvents can be chosen for carrying out the extraction process simulations. These solvents were examined using two thermodynamic models for activity coefficients (NRTL and UNIQUAC) as well as the prediction through group contribution method



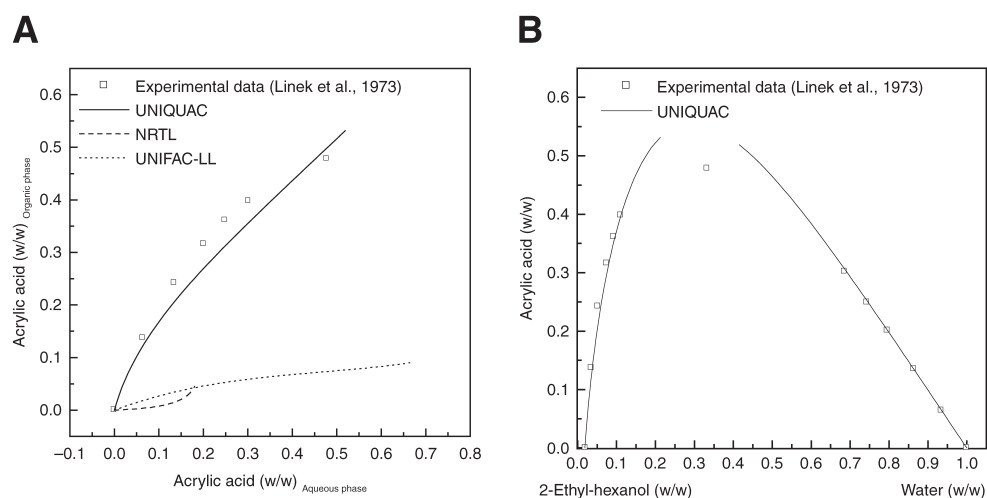
**Fig. 4.** System acrylic acid + water + diisopropyl ether: **(A)** distribution coefficient; **(B)** heterogeneous region.



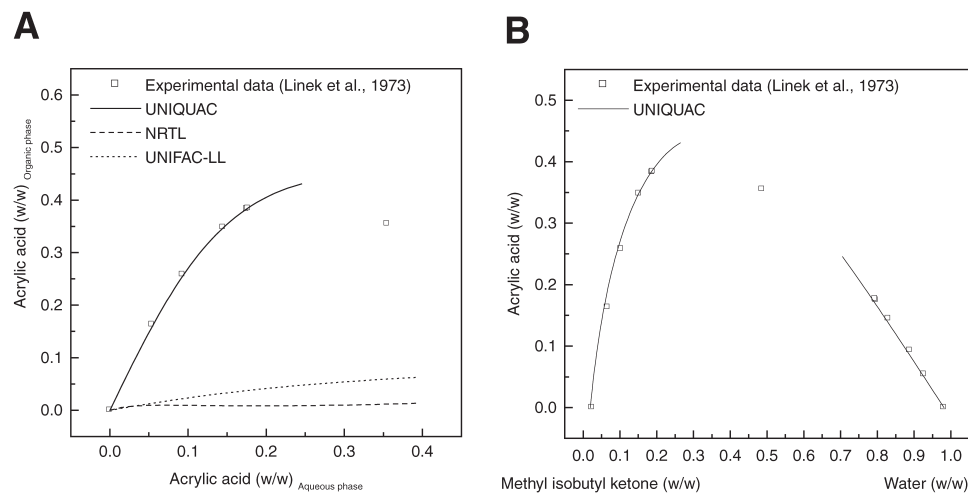
**Fig. 5.** System acrylic acid + water + isopropyl acetate: **(A)** distribution coefficient; **(B)** heterogeneous region.

(UNIFAC-LL), in order to evaluate the representative model of the distribution coefficient and heterogeneous region (Figs. 4–7).

According to the figures, it can be observed that the UNIQUAC model better represents the experimental equilibrium data. The NRTL and UNIFAC-LL models do not approximate the behavior reported in the experimental data. This is likely because of the different inputs that these models use. In the UNIQUAC model, all LLE binary interaction parameters are reported. In the NRTL model just one pair is reported, whereas the other LLE binary interaction parameters are predicted using UNIFAC-LL method. Using the prediction method (UNIFAC-LL), the simulation does



**Fig. 6.** System acrylic acid + water + 2-ethylhexanol: **(A)** distribution coefficient; **(B)** heterogeneous region.



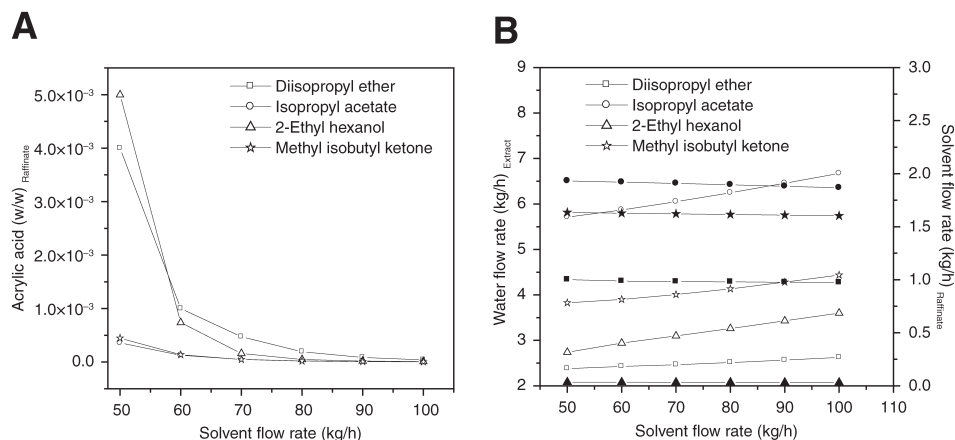
**Fig. 7.** System acrylic acid + water + methyl isobutyl ketone: **(A)** distribution coefficient; **(B)** heterogeneous region.

not represent well the experimental data because it is predictive, and so, more general. It is, indeed, good, when no information on the necessary data are available and evaluations must be made. Based on these results, the most appropriate model to be used is UNIQAC.

### Simulation of the Liquid–Liquid Extractor—Results and Discussion

Density was used to determine the entrance position of the feed (acrylic acid and water) and of the solvent. In this case, the feed stream enters at the





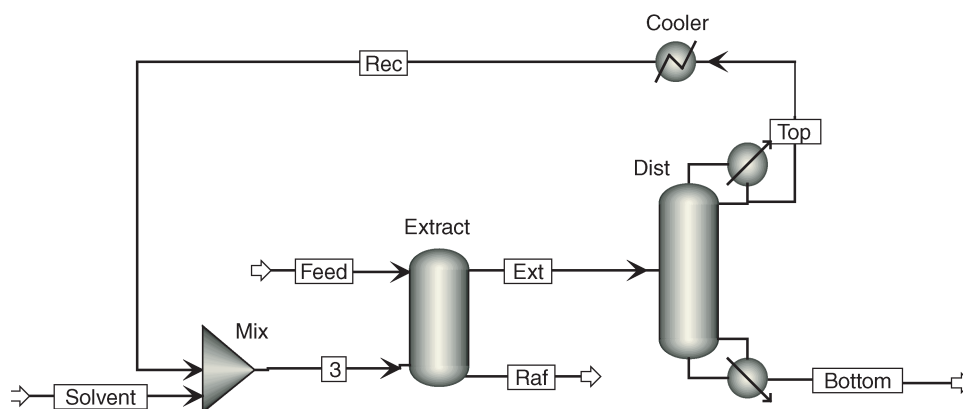
**Fig. 8.** (A) Acrylic acid (w/w) in the raffinate and (B) water flow rate (kg/h) in the extract (open symbols) in function of solvent flow rate (kg/h) and solvent flow rate (kg/h) in the raffinate (closed symbols) as a function of solvent flow rate (kg/h).

top and the solvent stream enters at the bottom of the extractor. As stated before, the solute-rich stream is labeled “extract” and the other stream is labeled “raffinate.” An Aspen Plus simulator was used for the liquid–liquid extraction process calculations. As stated earlier, the UNIQUAC activity coefficient model was used as it was established as the best in the previous part of the study. The simulation was made in order to analyze the ability of the solvents to extract acrylic acid from a dilute stream.

For all solvents, eight theoretical stages were used; conditions in the extraction column were set at 1 atm and 25°C. The temperature of the feed is 25°C and the mass flow rate is 100 kg/h. The temperature of the solvent is 25°C and its mass flow rate varied from 50 to 100 kg/h. The composition of the feed is 3 mol% of acrylic acid and 97 mol% of water (a composition below the azeotrope). Acrylic acid concentration (w/w) in the raffinate as well as water flow rate (kg/h) and solvent flow rate (kg/h) in the extract stream were determined as a function of the solvent flow rate (kg/h). These results are presented in Fig. 8.

According to Fig. 8A, it can be observed that practically no acrylic acid goes to the raffinate stream when the solvent flow rate is equal to 90 kg/h, for all solvents studied. When Fig. 8B (open symbols) is analyzed, it can be verified that when diisopropyl ether was used, a smaller amount of water goes to the extract stream, which is not desired because water + solvents form azeotropes. This introduces complications when the solvent is to be recovered. In Fig. 8B (closed symbols), the behavior of the solvent flow rate (kg/h) in the raffinate stream is displayed as a function of the variation in the solvent flow rate (kg/h). In this figure, it can be verified that, in terms of the amount in the raffinate stream, the best performance is associated with 2-ethyl hexanol. The extraction column was





**Fig. 9.** Whole plant for recovering acrylic acid from aqueous stream, including extraction column, distillation column, and solvent recycle.

simulated, with eight theoretical stages for diisopropyl ether, because it is the solvent that present the largest heterogeneous region. The solvent flow rate was set at 90 kg/h (the ratio of solvent to feed, 0.9), based on what was observed in Fig. 8A. With these conditions, it is possible to carry out the complete simulation of the extraction and purification of the acrylic acid.

### Complete Extraction Process—Results and Discussion

The compositions of each stream of the liquid–liquid extraction process (extract or raffinate) determine the next separation units to be used. If high solvent concentrations are found in the raffinate stream, another unit operation (downstream processing) is necessary to remove this component. On the other hand, the presence of water in the extract stream causes further problems for acrylic acid recovery and solvent recycle. These problems have been minimized by the choice of solvent. Calculations for the whole plant, including recycling and distillation column, were made using the NRTL model for representing the activity coefficient with binary interaction parameters from Aspen Databank. For the vapor phase, IG and Hayden-O’Connell models were used. The impact of solvent selection is evident when the complete extraction process is examined. Two separation units are used to recover acrylic acid coming from aqueous stream: extraction- and distillation column (Fig. 9).

The distillation column was used to recover the solvent from the extract stream, to recycle it, and to recover the solute. The simulation conditions were defined for a distillation column with 25 theoretical stages, and extract flow rate was set at 99.232 kg/h (made up of 11.009 kg/h of acrylic acid, 2.551 kg/h of water, and 85.672 kg/h of diisopropyl ether). This column was set to operate at 25°C and 1 atm. The feed stage of this column is 17th and the reflux ratio (mole basis) is equal to three. Table 1 shows the stream

Table 1  
Stream Compositions for the System Acrylic Acid + Water + Diisopropyl Ether

Component	Feed	Solvent	Ext	Raf	Top/rec	Bottom
Component mass fraction in each stream						
Water	0.890	–	0.026	0.989	0.029	11 ppb
Acrylic acid	0.110	–	0.111	5 ppm	Trace	1
Diisopropyl ether	–	1	0.863	0.011	0.971	117 ppm
Component mole fraction in each stream						
Water	0.970	–	0.125	0.998	0.144	42 ppb
Acrylic acid	0.030	–	0.135	1 ppm	Trace	1
Diisopropyl ether	–	1	0.740	0.002	0.856	82 ppm

compositions of the process. It is verified that for the solvent studied, it was possible to produce a raffinate stream of nearly pure water. At the bottom of the distillation column pure acrylic acid can be obtained. The solvent is recovered for recycle at the top of the distillation column.

## Conclusions

The recovery of acrylic acid from water using liquid–liquid extraction process has been presented. A thermodynamic evaluation of the systems involved indicates that UNIQUAC model better represents the LLE experimental data reported in the literature. The complete extraction process was considered (including the extraction column, the distillation column, and recycle). Four solvents for separating acrylic acid from water were examined. Among them, diisopropyl ether was found to be the most suitable in terms of smaller amount of water recovered in the extract stream and in terms of avoiding the problem of azeotrope formation with water and solvent, harming the solvent recovery and recycle.

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