CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124119

Extractant Screening for Liquid-Liquid Extraction in Environmentally Benign Production Routes

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Fermentation processes offer a promising alternative for the production of chemicals by more environmentally benign routes. However, a major challenge in applying this technology remains the recovery of typically highly hydrophilic products from the complex broth.
Here, we report the results of a study with the aim to enhance the separation of organic acids from fermentation broths by liquid-liquid extraction by improved design of the extractant.
Based on extensive literature research supported by molecular modeling and isothermal titration calorimetry (ITC) experiments, different groups of extractants were evaluated, including amines, amides, superbases, guanidines and N-oxides. Octanol, 2-octyl-1-dodecanol and heptane were used as solvents. After extraction, a sample of the aqueous phase was analyzed with high performance liquid chromatography (HPLC) and the distribution coefficients were calculated.
The obtained results showed that tertiary amines remain the state-of-the-art extractants for the recovery of organic acids. Highly basic compounds, like guanidines or superbases, as well as the N-oxides, were not able to outperform the tertiary amines.
The performed work demonstrated that the applied molecular modeling tools were not sufficient to adequately assess the interactions observed between amines and organic acids.

Introduction

A sharp increase in petroleum costs in the recent decennia has shifted the attention to fermentative processes and possibilities within (Joglekar et al. 2006). Lactic acid (a basic component of biodegradable plastics) can be produced through fermentation, but its recovery requires significant costs (Joglekar et al. 2006). A more cost-efficient and environmentally friendly method needs to be developed to enable in-situ removal of lactic acid, resulting in higher final concentration levels and that avoids excessive production of salts (Wasewar et al. 2004).

Please cite this article as: Krzyzaniak A., Schuur B., Sukumaran M., Zuilhof H. and De Haan A., 2011, Extractant screening for liquid-liquid extraction in environmentally benign production routes, Chemical Engineering Transactions, 24, 709-714
DOI: 10.3303/CET1124119

Recent studies show increased interest in liquid-liquid reactive extraction (Wasewar et al. 2004). It allows for direct removal of lactic acid from the fermentation broth, hence preventing the decrease in pH.

Liquid-liquid reactive extraction of carboxylic acids has been broadly described in the literature, addressing its dependence on i.e. properties of solvent (extractant and diluent), pH, temperature and acid concentration (Joglekar et al. 2006). The relative basicity of extractant has been identified as a crucial characteristic determining the effectiveness of acid recovery (Shan et al. 2006).

Here we describe the results of a study with the aim of enhancing the recovery of lactic acid from a fermentation broth by liquid-liquid reactive extraction with improved extractants. The design of improved extractants focuses on increasing the basicity of the molecule. Molecular modeling calculations are used to predict the strength of extractant-acid complexation.

Materials and Methods

Materials

Lactic acid crystals were kindly provided by Purac. Heptane (99%), 2-octyl-1-dodecanol (97%), octanol (>99.5%), trioctylamine (98%) and N,N,N′,N′-Tetramethyl-1,8-naphthalenediamine (proton sponge, 99%) were obtained from Sigma Aldrich. N,N – diethyl – m- toluamide was obtained from Acros Organics (98%) and Alfa Aesar (97%). LIX 7950 (guanidine) was kindly provided by Cognis. Bis-N-oxide (Figure 1) was custom synthesized by Syncom BV.

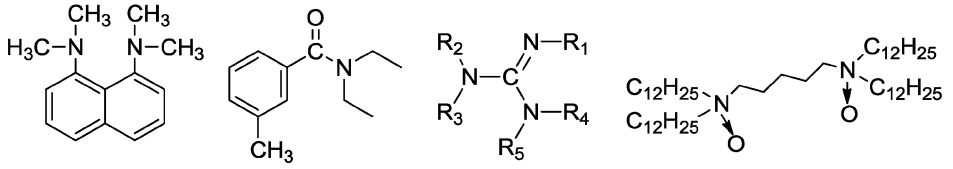

Figure 1 Structure of applied extractants, from left: proton sponge, N,N-diethyl-m-toluamide, LIX 7950 (guanidine), tetradodecyl-bis-N-oxide

Methods

Solutions of the extractants in heptane, octanol or 2-octyl-1-dodecanol were prepared at different weight ratios (20-100%wt extractant). 5-10 grams of aqueous acid solution (0.13M in MiliQ water) was contacted in 100ml glass bottles with an equal mass of organic phase and incubated for 17 hours at the temperature of 25°C or 55°C. After phase separation, the pH of the aqueous phase was measured. The lactic acid concentrations in the aqueous phase were determined with an HPLC system consisting of a pump, an autosampler and a UV-

detector (all from Varian ProStar). The column used was Aminex HPX-87H (Bio-Rad) and 0.005M H_2SO_4 solution was used as mobile phase, at a flow rate of 0.6ml/min. The lactic acid concentration in the organic phase was calculated by mass balance. Distribution coefficients (K_D) were calculated as the ratio of the concentration in the organic phase over the concentration in the aqueous phase.

Results and Discussion

Molecular modeling predictions

The hydrogen-bonding interaction between lactic acid and potential extractants was screened using density functional theory (DFT), with the application of B3LYP/6-311G(d,p) and M06/6-311G(d,p) calculations. The larger the negative value of ΔH, the stronger interaction between solute and extractant was expected. The obtained results are displayed in Figure 2. According to the predictions toluamide should provide results comparable to trioctylamine (TOA) and the tetradodecyl-bis-N-oxide is expected to outperform the tertiary amine. These predictions were verified experimentally.

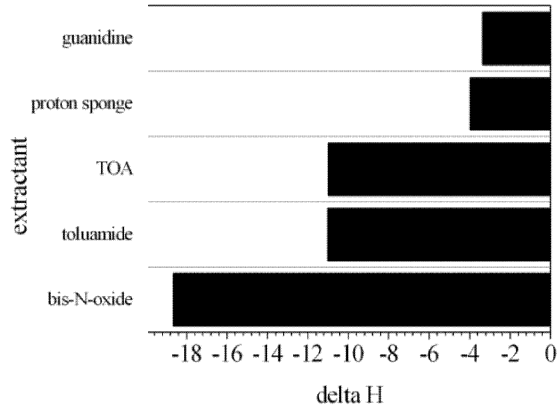

Figure 2 Molecular modelling predictions based on calculation of ΔH

Extraction with amines

The extraction of lactic acid from aqueous solutions was studied as function of the mass fraction of TOA in the solvent at two different temperatures (T=25°C, T=55°C). The highest K_D were obtained in all cases for 20%wt TOA at T=25°C. This optimum could be explained by the complex stabilizing action of the diluent. Extraction in octanol was more effective than with the highly branched alcohol, since the last one displayed lower solvating power for the amine-acid complex. At higher temperatures the entropy of the system increases

which results in decreased distributions. The obtained results, displayed in Figure 3, were used as a reference to assess the performance of the selected extractants.

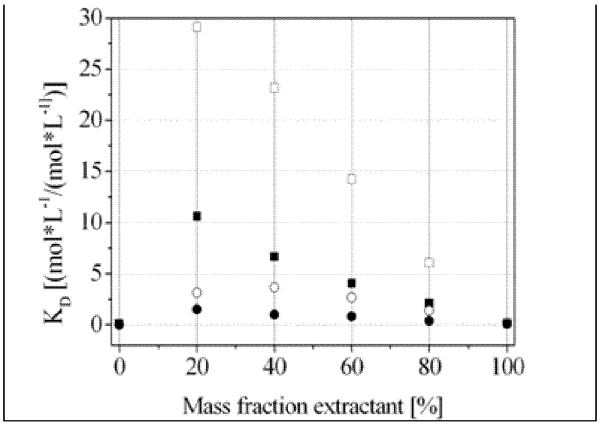

Figure 3 Extraction of lactic acid with TOA. LA $_{\text{initial concentration}}$ = 0.13M, TOA in octanol at T=25° (□) and T=55° (■), TOA in 2-octyl-1-dodecanol at T=25° (○) and T=55° (●).

Extraction with amides

Extraction with amides was performed according to the procedure described for amines. A maximum K_D of 10 was observed with pure toluamide, which is lower than for TOA, and in line with the molecular modeling predictions. Next to the less effective extraction, the toluamide is less favored compared to TOA because of significant leaching of the extractant to aqueous phase.

Extraction with superbases

Due to the solubility limit, extraction studies with the proton sponge were performed only at 20wt% and 40wt% of extractant. Heptane was the diluent of choice, since superbasic compounds are to be used in non-polar solvents. No extraction was observed in all performed experiments. A high increase in pH and a strong coloring of aqueous phase suggest that severe leaching of extractant into the aqueous phase took place.

Extraction with guanidines

Extraction with guanidines was as well performed according to the procedure described for amines. The obtained results (Figure 4) show that performance of the guanidine is lower when compared with the results obtained for TOA. This is in agreement with molecular modeling expectations. The optimal concentration of the extractant is 80wt% and the temperature does not influence the outcome significantly. The pH of the aqueous phase after

the extraction was higher than 7, which indicated that some leaching of extractant to water took place.

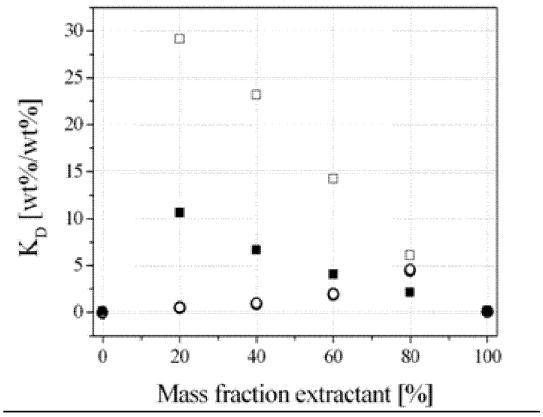

Figure 4 Comparison of lactic acid extraction efficiency for TOA and LIX 7950 (guanidine). LAinitial concentration = 0.13M, TOA in octanol at T=25° (□) and T=55° (■), LIX 7950 in octanol at T=25° (○) and T=55° (●).

Extraction with bis-N-oxide

The molecule of bis-N-oxide was designed based entirely on the molecular modeling calculations. Long alkyl chains were added to prevent the leaching of extractant to the aqueous phase. As a consequence, its molecular weight was very high, and solubility in the examined solvents low. The extraction studies were performed at 5wt% N-oxide, in all three diluents. Other conditions remained unchanged. In all cases obtained distributions were in the range $0.3<K_D<0.7$. Contrary to the expectations, proton exchange between acid and the nitrogen atoms of the N-oxide was not possible, because of the presence of the oxygen atom. Instead, the formation of hydrogen bonds with water molecules was preferred as predicted by the molecular modeling results. Apparently, this is not the most important interaction in the extraction of acids by bases.

Comparison of molecular modeling predictions with experimental results

In Table 1 a comparison between calculated ΔH values and experimentally obtained distributions is displayed. The experimental values follow a different trend than suggested by molecular modeling calculations. In two cases (toluamide, proton sponge) the underperformance is caused by extractant leaching. The difference between expectation and actual result is remarkable in the case of bis-N-oxide. It appears that the applied tools were not sufficient to describe the interaction between bis-N-oxide and lactic acid. The used

model is limited to predictions involving hydrogen bonding, and for these compounds protonation is the main complexation mechanism.

Table 1 Comparison of calculated H values and K_D values obtained experimentally (at T=25, in octanol)

Type of extractant	Calculated ΔH (Kcal/mol)	KD obtained experimentally
Guanidine	-3.35	4.5
Proton sponge	-3.97	<0.1
Trioctylamine (TOA)	-10.99	29
Toluamide	-11.01	<10
Bis-N-oxide	-18.66	0.3<KD<0.7

Conclusions

The results obtained in this study show that amines remain the state-of-art extractants for the recovery of lactic acid from fermentation broths. The examined compounds were not able to outperform amines, and in some cases (proton sponge and toluamide) severe leaching of the extractant was observed. N-oxides showed a preference for hydrogen bonding with water, and an unfavorable conformation hindered proton exchange with acid. The results obtained from the experimental study differ significantly from the predictions provided by molecular modeling. The applied tools were not sufficient to adequately assess interactions observed between amines and organic acids.

Acknowledgements

This is a DSTI project.

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