Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Fröschl, F. , Mayerhofer, A. , Siebenhofer, M. and Marr, R.(1995) 'Enhanced Acid Extraction Using Amine-Loaded Compressed Carbon Dioxide', Separation Science and Technology, 30: 7, 1917 — 1929
To link to this Article: DOI: 10.1080/01496399508010384
URL: http://dx.doi.org/10.1080/01496399508010384

SEPARATION SCIENCE AND TECHNOLOGY, 30(7-9), pp. 1917-1929, 1995

ENHANCED ACID EXTRACTION USING AMINE-LOADED COMPRESSED CARBON DIOXIDE

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ABSTRACT

Compressed carbon dioxide, doped with secondary and tertiary amine entrainers, was used for the separation of acetic and lactic acid. The solubility of the amines in liquid and supercritical CO_2 was tested, and the partition of the acids between the aqueous and the amine-loaded gas phase was investigated. A model for the description of the phase equilibria based on the acid loading of the amine in the carbon dioxide phase was used. By performing semi-batch experiments, the rate-determining step of the separation was found to be the interphase reaction. The applicability of this separation process was tested and found to be feasible in a continuously operated countercurrent lab-scale extraction plant

INTRODUCTION

Supercritical fluid extraction (SFE) is well known to be a process for the separation of low-volatility, non- or low-polar substances from natural products. Long-chain organic acids already have been extracted by SFE. Tests with acetic or lactic acid have been carried out rarely. For that purpose, a research program for extractive separation techniques was established to investigate the extractive separation of these acids from aqueous broth.

Pure acetic acid is highly soluble in carbon dioxide, but the phase equilibrium of the acid between its aqueous solution and a CO_2-phase shows that CO_2 is not suitable for the separation of acetic acid from its aqueous solution. This already was determined by Francis 1954 (1) and confirmed by Briones et al. (2). Another attempt to extract acetic acid from aqueous solutions was made by using nearly supercritical and propane for extraction (3). From these results, it was concluded that propane is a weak solvent for the extraction of acetic acid from aqueous solutions as well. Shimshick (4,5) tried to enhance extraction by using the entrainer dimethyl ether. The ratio of the partition coefficients for the dimethyl ether-loaded CO_2, compared to that of pure CO_2 was 2.3.

The solubility of lactic acid in CO_2 was found to be less than 0.5 wt % (1). A similar extraction behavior in comparison with acetic acid may be expected.

As the use of pure CO_2 and the application of physical entrainers for the extraction of acetic acid and lactic acid proved to be inefficient, reactive entrainers were used. While physical entrainers are used for correcting the properties of the solvent phase, reactive entrainers form an extractable compound with the solute.

THEORETICAL CONSIDERATIONS

When using inert diluents (e.g., kerosene) for extraction, the acid loading of the amine in the solvent phase depends on the acid concentration of the aqueous phase only (6). At equilibrium, the acid concentration in the solvent phase is linearly dependent on the amine content of the diluent.

The model applied for the description of the phase equilibrium is based on these boundaries, with Z being the acid loading of the amine:

$$Z = \frac{c^*_{A,d}}{c_{B,d}} = f\,(c^*_{A,c}) \tag{1}$$

Z is derived from experimental tests. Then, the phase equilibrium can be predicted for different amine contents in the solvent phase.

The rate of separation and the rate determining step were evaluated for different amine loadings of the solvent (CO_2) phase.

The transport of the acid in the aqueous phase was evaluated by Eq. (2), the transport of the amine and the transport of the extraction product in the solvent phase were determined by equations of the same type for the CO_2 phase. The interphase reaction with A considering the acid, B the amine, and C the product was described by Eq. (3).

$$\dot{N}_A = -\frac{d(V_c \cdot c_{A,c})}{dt} = k_c \cdot A \cdot (c_{A,c} - c^*_{A,c}) \cong -V_c \cdot \frac{dc_{A,c}}{dt} \tag{2}$$

$$\dot{N}_A = -\frac{d(V_c \cdot c_{A,c})}{dt} = k_+ \cdot A \cdot c^a_{A,c} \cdot c^b_{B,d} \cong -V_c \cdot \frac{dc_{A,c}}{dt} \tag{3}$$

Equation 3 does not consider the reverse reaction as the solvent loading during the semi-batch experiments was kept below 15% of the loading capacity at equilibrium by using freshly prepared solvent.

EXPERIMENTAL

The solubility tests and the evaluation of the phase equilibria were carrried out in a 350-mL static cell, designed for an operating pressure of 400 bar and a maximum operation temperature of 100°C. Solubility tests were performed at 25 and 40°C and up to a pressure of 170 bar. Phase equilibrium data were measured for the same temperature span and at an operating pressure of 130 and 175 bar.

Figure 1 shows the set up of the semi-batch extraction unit, which was designed for operating conditions up to 350 bar and 200°C. The semi-batch experiments were worked out in a 500-mL extractor, considering an operation pressure up to 250 bar and an operating temperature between 20 and 50°C. Solvent flow varied from 7 to 15 kg/h.

The setup of the continuously operating plant is shown in Figure 2. It consists of an extraction column with a 2-m active height and is equipped with Sulzer DX packings. It was designed for a maximum operating pressure of 180 bar at 100°C. Experiments were performed at pressures of 130 and 175 bar, and at temperatures of 25 and 40°C. The phase ratio was varied from 10 to 60 kg of solvent per kg of feed.

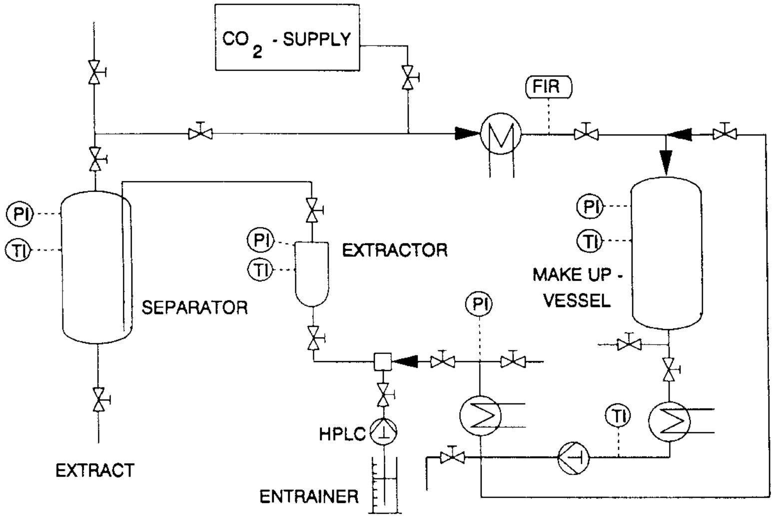

FIGURE 1. Semi-batch extraction plant.

Secondary and tertiary amines of technical grade show an increased solubility in water. The solubility is mainly caused by primary and secondary short-chain amines (7). Therefore, the amine entrainers had to be purified by scrubbing.

RESULTS

The solubility of the secondary amine Amberlite LA-2 (LA-2), a di-dodecyl/tridecylamine, and trihexylamine (THA) in carbon dioxide was tested. As shown by Figure 3, the maximum loading capacity of THA in CO_2 is 25% within the considered operation conditions. In comparison, the loading capacity for LA-2 is less than 6%. When the solubility of different amines (e.g., triethylamine) was investigated (8), it was found that the amine solubility decreases with increasing length of the hydrocarbon group.

Phase equilibria between aqueous acid phases and amine-loaded CO_2 phases showed that carbon dioxide does not affect the distribution ratio. Figure 4 represents the

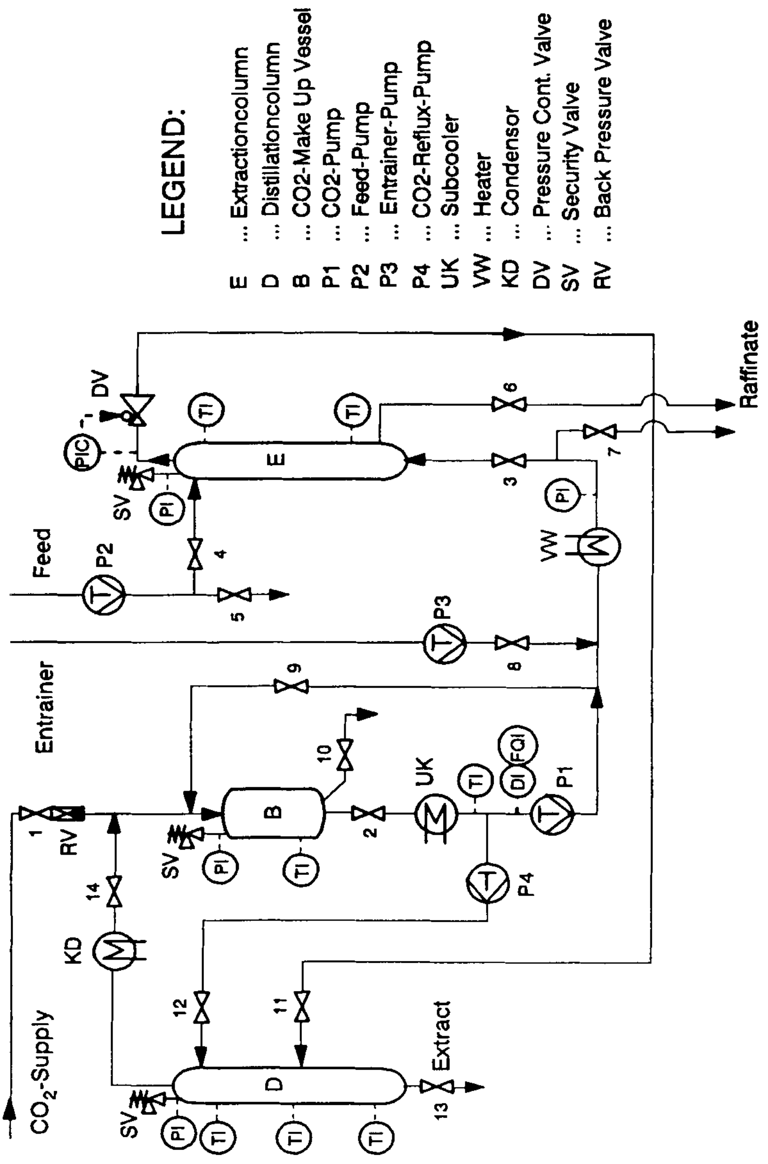

FIGURE 2. Continuously operated lab-scale extraction unit.

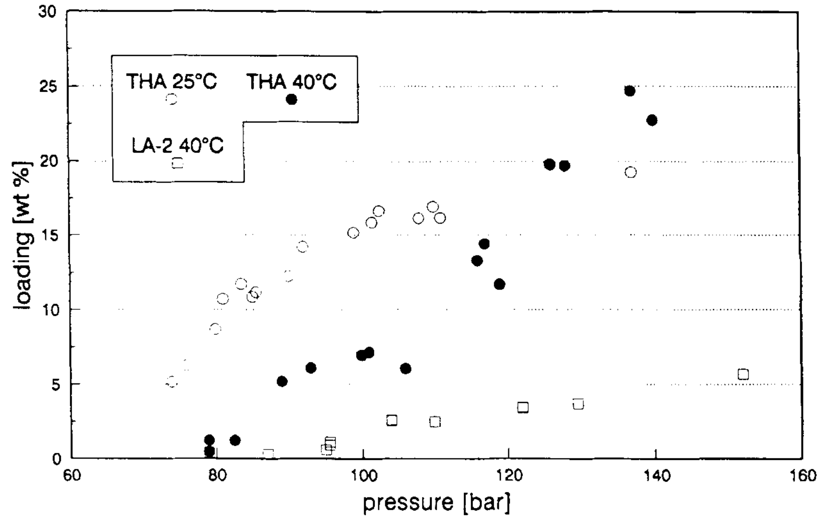

FIGURE 3. Solubility of THA and LA-2 in carbon dioxide.

loading ratio Z, when using the entrainer THA for the extraction of acetic acid. The correlation of Z and the acid content of the aqueous phase was possible for both acids and the secondary and the tertiary amine (9). Figure 4 shows a representative correlation. The comparison of test results and calculated equilibrium data for the system $H_2O/HLac-CO_2/LA-2$ is demonstrated in Figure 5. The model used for the description of the equilibria was tested for acid concentrations in the aqueous phase up to 0.25 mol/L.

The temperature, the phase ratio, and the amine content of the CO_2 phase were found to be the separation determining parameters. Figure 6 shows the separation graphs for acetic acid when varying the amine content of the solvent phase. The experiments were performed in the plant shown in Figure 1. With regard to the acid in the aqueous phase, the best fit of the experimentally obtained results was achieved by a reaction order of 1 for the aqueous acid concentration.

Further data interpretion pointed out that the mass transfer cannot be the rate determining step, as the mass transfer coefficient is not constant during the experiment. A set of seven different experiments confirmed this result. When testing for reaction

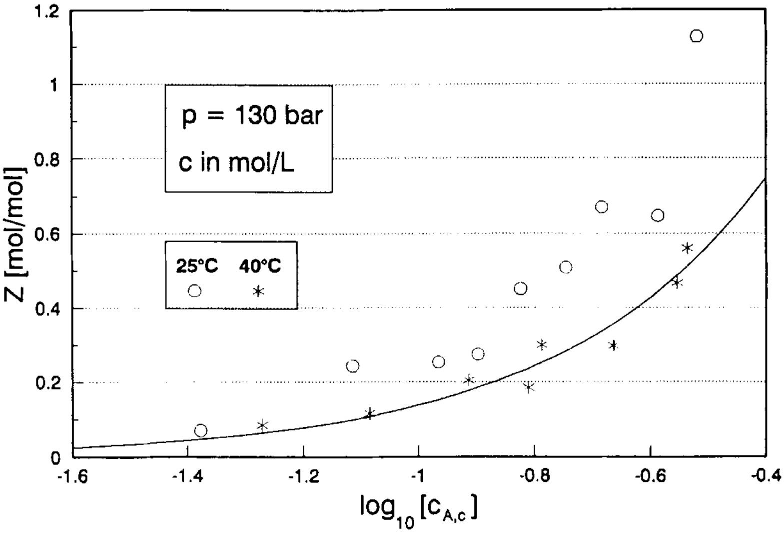

FIGURE 4. Acetic acid loading of trihexylamine.

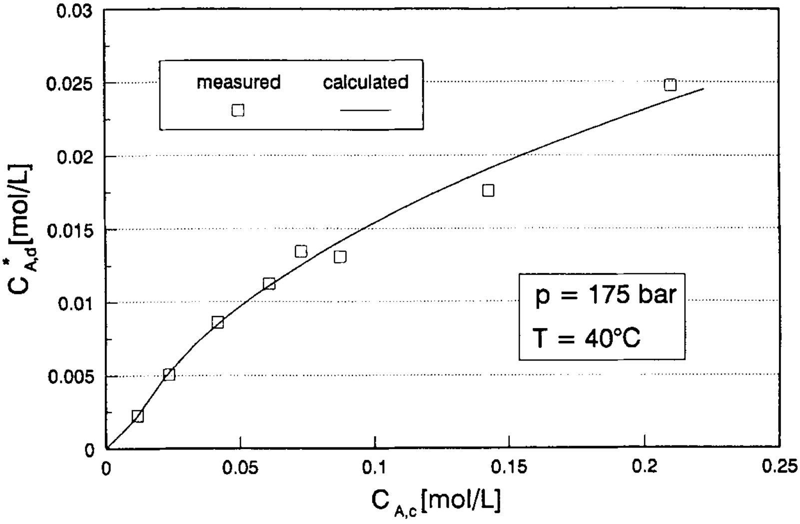

FIGURE 5. Comparison of calculated and measured equilibrium data.

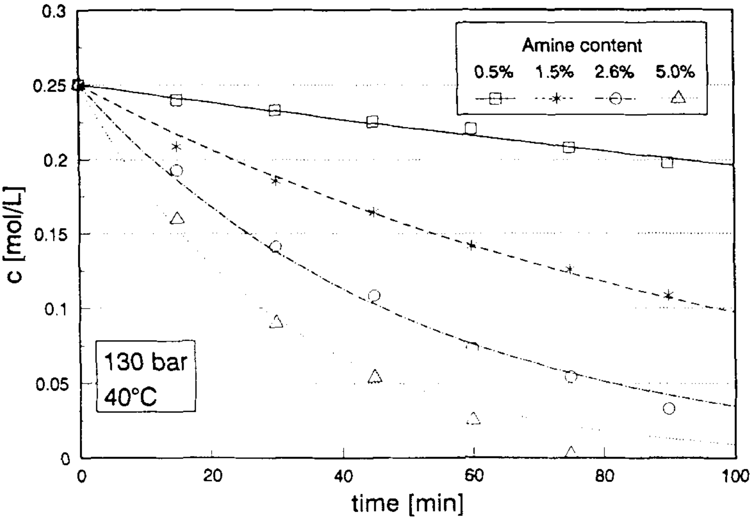

FIGURE 6. Separation of acetic acid using THA entrainer.

control applying Eq. (4), the rate constant did not vary during the experiment. Based on these experiments, the rate determining step of the separation was therefore found to be the interphase reaction.

$$c_{A,c,t} = c_{A,c,t=0} \cdot e^{-\frac{k_+ \cdot A \cdot c_{B,d}^{b} \cdot t}{V_c}} = c_{A,c,t=0} \cdot e^{-k^* \cdot t} \qquad \textbf{(4)}$$

With the order of reaction n=a=1 for the acid, Eq. (4) can be derived from Eq. (3). Then, it is possible to calculate the order of reaction n=b for the amine by evaluating k* for different amine contents of the solvent phase $c_{B,d}$. As shown by Figure 7, the order of reaction for the amine, n=b, is 1 also.

The product $k_+ . A$ can then be calculated. Table 1 shows the results of the $k_+ . A$ product for the investigated substances. Figure 8 shows the comparison of the test results and the calculated separation values, when extracting acetic acid with the entrainer THA.

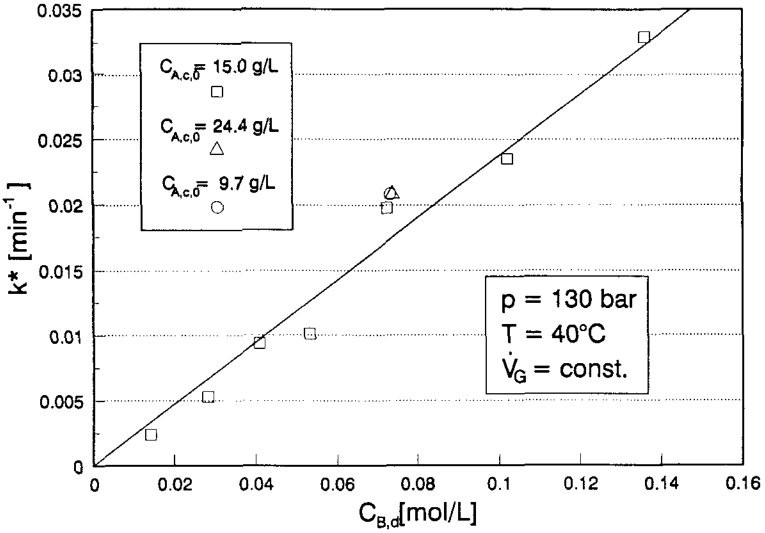

FIGURE 7. Evaluation of the order of reaction; system HAc/THA.

TABLE 1.

VALUES OF k_+.A FOR BOTH ACIDS USING THE INVESTIGATED AMINES.

Acid	Entrainer	p [bar] / T [°C]	k_+.A [$l^2.mol^{-1}.min^{-1}$]
lactic	THA	130 / 40	0.0076
acetic	LA-2	175 / 40	0.175
lactic	LA-2	175 / 40	0.280

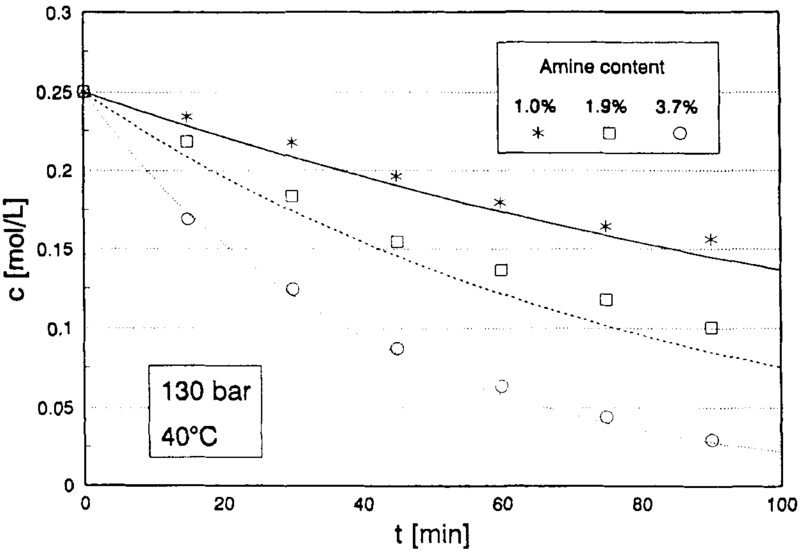

FIGURE 8. Comparison of experimental data and calculated graphs.

The practical applicability of this separation process was tested in a continuously working countercurrently operated lab-scale extraction plant as shown by Figure 2.

Acetic acid could be extracted from the aqueous phase with an efficiency of 80% when using THA and with an efficiency of 95% when using LA-2. In the CO_2-free THA phase, a mean acid content of 80-100 g/L was measured when using an aqueous feed content of 15 g/L. The recovery of the acid from the amine by distillation resulted in an acid concentration of the distilled phase of 65 wt %. Figure 9 shows the concentration profile of acetic acid along the fractional height of the column in stationary operation during a period of 2 hours when using 1.3 wt % of the LA-2 entrainer in the gas phase at an operating pressure of 175 bar, and at a temperature of 25°C. The gas-free LA-2 phase contained 70-80 g/L acid when using the same feed concentration. As demonstrated by Figure 9, the data show a high reproducibility.

Lactic acid was extracted by LA-2 loaded carbon dioxide only. A maximum extraction yield of 98 to 99% was achieved at an operating temperature of 25°C. These experiments were also performed by using clarified fermentation broth as a feed

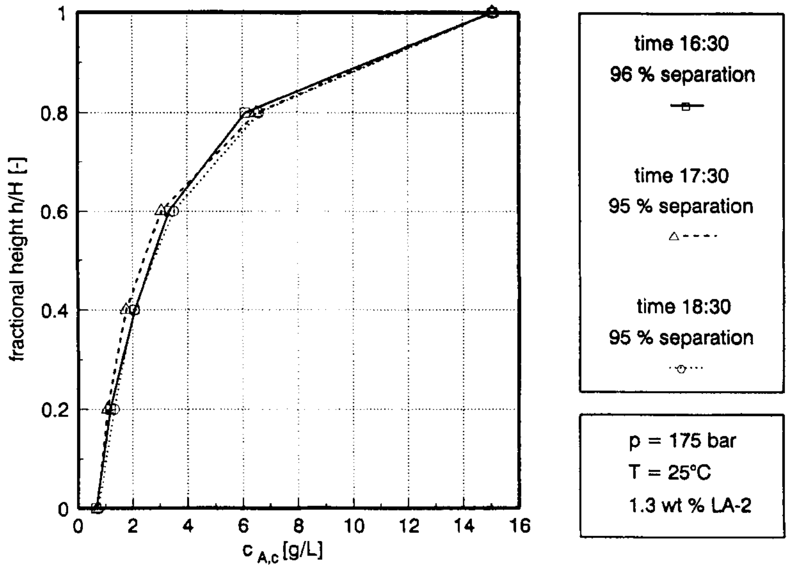

FIGURE 9. Continuous acetic acid extraction using LA-2 entrainer.

solution. The extraction yield of the fermentation broth and the synthetic feed solution did not differ. Acid concentrations of 100-130 g/L in the CO_2-free amine phase were found. These results show a significant advantage of supercritical fluid extraction over liquid-liquid extraction.

During fermentation, the pH-value must be kept constant by buffering. For the separation of lactic acid by liquid-liquid extraction, the fermentation broth must be acidified continuously. When extracting lactic acid by supercritical fluid extraction, continuous addition of acid is not necessary as the ph-value is kept constant by the solvent carbon dioxide. In liquid-liquid extraction, Hauer's results (10) show mineral acids have to be added to the fermentation broth to reach optimum extraction pH.

DISCUSSION

The extraction of acetic and lactic acid with carbon dioxide can be enhanced by adding secondary and tertiary amine entrainers to the extraction gas. For technical application, the solubility of trihexylamine and Amberlite LA-2 in carbon dioxide have a sufficient magnitude.

The acid content in the solvent phase correlates with the entrainer content of the gaseous solvent phase. By performing tests in a countercurrently operated high-pressure extraction column, it was demonstrated that this process can be operated under technical conditions.

With the example of lactic acid extraction, it was demonstrated that there is no difference in the extraction efficiency when comparing the extraction of synthetic solutions and fermentation broth.

NOMENCLATURE

A	interphase area
c	concentration
k_c	mass transfer coefficient
k_+	rate constant of the formation reaction
t	time
V	volume
Z	acid loading of the amine

Subscripts

A	acid
B	amine
c	continuous phase
d	dispersed phase
t	at the time t

Superscripts

a,b	reaction orders
$*$	at equilibrium

ACKNOWLEDGEMENT

This project was supported by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung.

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