Thermally Enhanced Extraction of Citric Acid Through Supported Liquid Membrane

Joav T. Rockman, Ephraim Kehat, and Ram Lavie
Dept. of Chemical Engineering, Technion, Israel Institute of Technology, Haifa, Israel 32000.

A thermally driven liquid-liquid extraction process designed to purify and concentrate citric acid from a fermentation broth raw material was first developed at Israel Mining Industries (IMI) (Baniel et. al., 1973) over 20 years ago. The ingenious novel separation concept that served as a basis for this process has been widely acclaimed (NRC, 1987) as preceding its time in achieving objectives that were only formulated much later as, for example, waste products minimization. This is due to its ability to achieve uphill separation without reverting to the use of costly chemicals. Surprisingly, little was done since then to further this promising direction, although some work has followed on the modeling of equilibrium in similar systems (Wennersten, 1983; Kertes and King, 1986; Tamada et. al., 1990; Eyal et. al., 1991; Bízek et al., 1992).

Some time ago, while seeking ways to extend our own results concerning the combination of mass and heat exchange (HME) in gas-solid systems (Lavie, 1985) to liquid extraction, we came across this previous work which seemed to follow the same line of thinking but with a totally different motivation. Since liquid-liquid extraction is implemented mostly in batteries of mixer-settlers, requiring two such steps to transfer the solute to an organic solvent and back to an aqueous phase, we wondered if one could not devise a process that would intensify and compact the two steps into one. As it turned out, extraction through a supported liquid membrane as was studied in recent years (Cianetti and Danesi, 1983; Frank and Sirkar, 1986; Sengupta et. al., 1988; Basu and Sirkar, 1991; Deblay et. al., 1991; Friesen et. al., 1991; Molinari et. al., 1992) fitted well our objective. Evidently, this structure relies on the transport diffusional aspects of the mass transfer, rather than the equilibrium controlled situation in conventional liquid extraction, but this also fitted well the transient nature of HME. Having been warned about the difficulty of maintaining stable supported liquid membranes (SLM), where the organic solvent is impregnated into some porous solid matrix, we decided to embark in this direction.

The present work is a theoretical and experimental study of the potential of effecting simultaneous purification and concentration of an aqueous solution of citric acid by means of uphill extraction through a SLM subjected to a thermal gradient. An analytical solution is proposed to the mathematical model and its predictions are confronted with isothermal experimental results taken from published literature as well as with nonisothermal experimental results of our own.

Theoretical

An organic SLM separating two aqueous solutions can be pictured with the capacity of transporting a solute from one aqueous phase to the other as shown in Figure 1. The solute A in the left aqueous phase reacts quickly and reversibly with the complexing agent $\overline{B}$ in the membrane to form a complex $\overline{AB}$ at the SLM left boundary ($x = 0$). $\overline{AB}$ now diffuses across the SLM to its right boundary ($x = l$). The reaction that occurred at the inlet is now reversed causing $\overline{AB}$ to decompose, consequently expelling A into the right aqueous phase, leav-

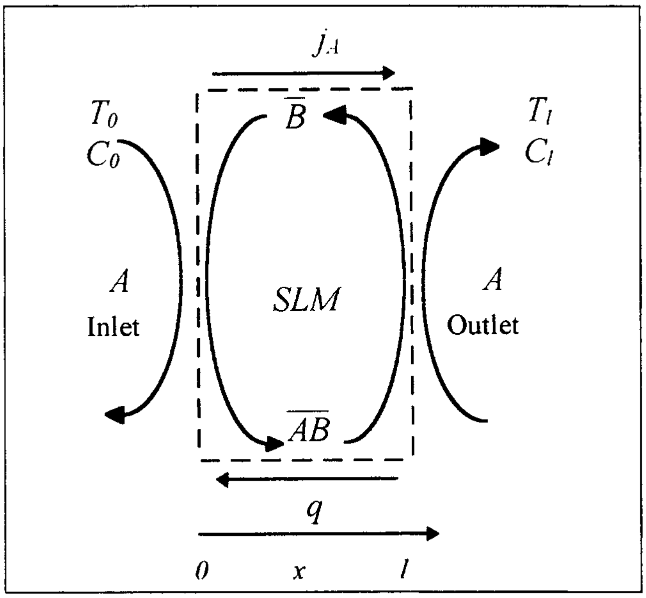

Figure 1. Transport of a solute from one phase to another via a flat unidimensional SLM.

ing free $\bar{B}$ to diffuse back from right to left, thus completing a full cycle.

We chose to assume: (a) Equilibrium prevails at the SLM interfaces (at $x = 0$ and $x = l$); (b) solubilization of the solute is negligible, namely A cannot exist on its own in the organic phase making up the SLM; (c) mass transport inside the SLM is driven by concentration gradients alone.

The mass flux j_A (grmol/(cm^2·s)) increases monotonously with the difference in complex concentrations prevailing at either ends ($x = 0$ and $x = l$). Maximizing this difference is therefore beneficial to mass transfer. This may be promoted by changing temperatures at the left and right boundaries, provided, of course, that the equilibrium between the reacting species is affected by temperature. The mathematical model developed by Rockman (1995) is an improvement on that described in Rockman et al. (1995) where the detailed assumptions along with the fundamental mass and energy balances are presented. The result of the model is an analytical solution that expresses explicitly the normalized mass flux $\tilde{j}_A$ as a function of the temperature and concentration boundary conditions prevalent at the SLM interfaces

$$\tilde{j}_A = -\phi \frac{\beta_0 C_0 - \beta_l C_l}{(1 + \phi \beta_l C_l)(1 + \beta_0 C_0) - (\beta_0 C_0 - \beta_l C_l)(1 - \phi)\gamma} \frac{1}{L} \tag{1}$$

where $\beta_0 = \beta(T_0)$ and $\beta_1 = \beta(T_1)$ are the equilibrium coefficients (dimensionless) of the 1:1 complexation reaction evaluated at the interfaces. (Although complexation reactions occur for a number of stoichiometries simultaneously (Tamada et al., 1990; Bízek et al., 1992), we neglect this for the sake of simplicity and in order to reduce the number of model parameters. Rockman (1995) develops the model further to allow for multi stoichiometric reactions.) Also

$$\beta = \beta(T) = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right). \tag{2}$$

The variables γ and L (dimensionless) are given respectively as

$$\gamma = -\frac{T_l e^{-B/T_l} - T_0 e^{-B/T_0} + (B - T_l)\left\{Ei\left(1, -\frac{B}{T_l}\right) - Ei\left(1, -\frac{B}{T_0}\right)\right\}}{(T_l - T_0)\left\{Ei\left(1, -\frac{B}{T_l}\right) - Ei\left(1, -\frac{B}{T_0}\right)\right\}} \tag{3}$$

and

$$L = \frac{T_{\text{ref}}}{T_l - T_0} \exp\left(-\frac{B}{T_{\text{ref}}}\right) \cdot \left\{Ei\left(1, -\frac{B}{T_l}\right) - Ei\left(1, -\frac{B}{T_0}\right)\right\}. \tag{4}$$

Ei is the exponential integral function defined as

$$Ei(1, x) = \int_1^\infty \frac{e^{-xt}}{t} dt. \tag{5}$$

In the following we first show that uphill separation utilizing a temperature shift is possible in a SLM configuration. Then, we attempt to validate the model by confrontation with our own experimental data and with data previously published in the literature. Validation will essentially consist of finding for a given set of materials used in the membrane, a set of parameter values (ΔH, ΔS, B and ϕ) that are thermodynamically plausible and that will best fit for a large number of experimental measurements.

Experimental Validation

An experimental apparatus was built to test steady-state operations with unidimensional heat and mass transfer in well mixed cells. The apparatus was constructed from two hollow perspex cylinders separated by a membrane with an active area for permeation of $A = 12.56$ cm^2. A total aqueous phase volume of 100 mL in each cell and its connecting piping was pumped vigorously through glass coils submerged in heating or cooling mediums with independent temperature regulation. The conductivities and temperatures in the solutions were continuously measured *in situ* and translated to concentrations. Further details of the apparatus and method of experimentation are given by Rockman (1995).

Citric acid and tricaprylyl amine (Alamine 336), a tertiary amine with C$_8$-C$_{10}$ aliphatic chains, were used in all experiments. The organic solvent consisted of a 90:10% v/v mixture of tetradecane and n-octanol. The membrane liquid was supported on a 140 μm thick PTFE microporous membrane having an average pore size of 0.2 μm leading to a relatively stable SLM.

Figure 2 depicts the results of a sample run indicating the molar deviation, n_d, (the change in the number of moles as compared to the beginning of an experiment) in both cells. The organic liquid membrane in this experiment consisted of 30% (v/v) Alamine 336, 63% Tetradecane, and 7% *n*-octanol. Boundary temperatures were maintained at $T_0 = 10$°C and $T_l = 80$°C for the duration of the experiment. Initial boundary concentrations (grmol/liter) were $C_0 = C_l = 0.01$ M on either side of the SLM. Note how molar concentrations change linearly in time, rising in the hot cell and decreasing in the cold one clearly indicating the uphill migration of citric acid. The measured rates of accumulation/depletion were 7.74×10^{-6} mol/h in the hot cell and -7.32×10^{-6} mol/h in the cold one. The 3.9% mismatch in mass balance is apparently due to experimental error. We chose to define a "suc-

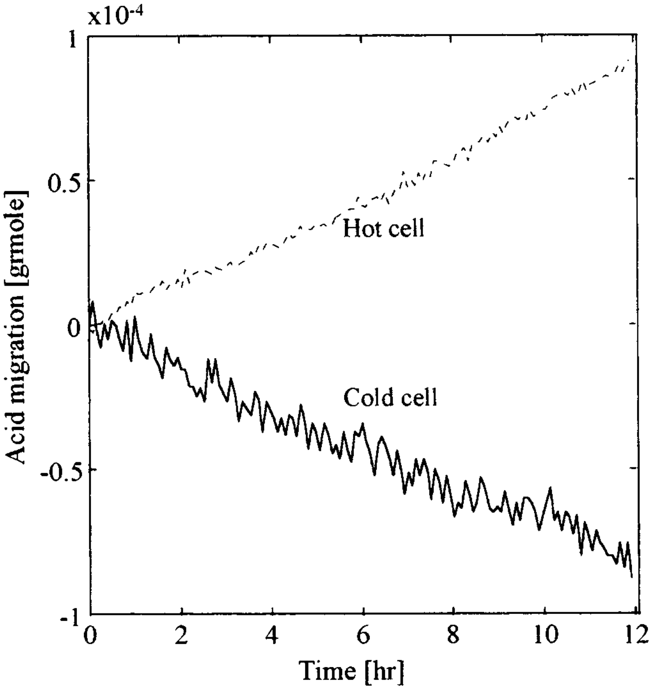

Figure 2. Molar deviations for a typical experimental run, $C_0 = C_l = 0.01$ M, $T_0 = 10°C$, $T_l = 80°C$.

cessful" run as one yielding less than 5% mass balance mismatch.

Repeated experimental runs were carried out at various aqueous phase concentrations and temperatures for several organic phase compositions. Comparison of dimensionless calculated values to measured dimensional fluxes necessitates a conversion coefficient

$$\tilde{j}_A = \tilde{D}_{AB}\frac{d\tilde{C}_{AB}}{d\tilde{x}} = \frac{D_{AB}}{D_B(T_{\rm ref})}\,\frac{d\left[\dfrac{C_{AB}}{C_T}\right]}{d\left[\dfrac{x}{l}\right]}$$

$$= \frac{l}{C_T D_B(T_{\rm ref})}\left[D_{AB}\frac{dC_{AB}}{dx}\right] \equiv \frac{l}{C_T D_B(T_{\rm ref})}j_A. \quad (6)$$

or

$$j_A = \vartheta \tilde{j}_A, \quad (7)$$

where ϑ is the required conversion coefficient given as

$$\vartheta = \frac{C_T D_B(T_{\rm ref})}{l}. \quad (8)$$

Parameter values of $\phi = 1$, $\Delta H = -20.27\times10^3$ J/grmol and $\Delta S = -45.33$ J/grmol·K gave the best fit, while maintaining the B parameter at a constant value of 2,000 K (evaluated by an independent set of experiments), with a correlation coefficient of 0.983 and a slope of $\vartheta = 3.19\times10^{-5}$ grmol/h. All subsequent plots of the experimental data also include calculated data using that same value of ϑ.

Given the membrane thickness (m) $l = 140$ μm, and total amine concentration $C_T = 0.6$ M, an effective diffusion coefficient of $D_{\rm ref}$ @ 20°C, is evaluated therefrom as

$$D_B(T_{\rm ref}) = \frac{\vartheta\cdot l}{C_T}$$

$$= \frac{3.19\times10^{-5}\,[\text{mol/h}]\times140\times10^{-4}\,[\text{cm}]}{12.6\,[\text{cm}^2]\times3{,}600\,[\text{s/h}]\times0.6\times10^{-3}\,[\text{mol/cm}^3]}$$

$$= 1.64\times10^{-8}\ \text{cm}^2/\text{s} \quad (9)$$

The effect of the cell temperatures on the flux through the membrane is illustrated in Figure 3 showing that the flux rises with temperature difference. Predicted and experimental data coincide well.

The effect of boundary concentrations was analyzed using a constant concentration ratio of $\alpha = C_l/C_0 = 0.15$ between inlet and outlet concentrations allowing its evaluation over a wide range. The result is plotted in Figure 4. The predicted flux passes through a maximum (which is proven by Rockman, 1995). The experimental results seem to support this with a relatively wide margin of error, which is due to a low accuracy of the conductivity measuring the instrument at high concentrations.

Isothermal Model Validation

The same validation method was also applied to data of Friesen et al. (1991), who for isothermal conditions relates

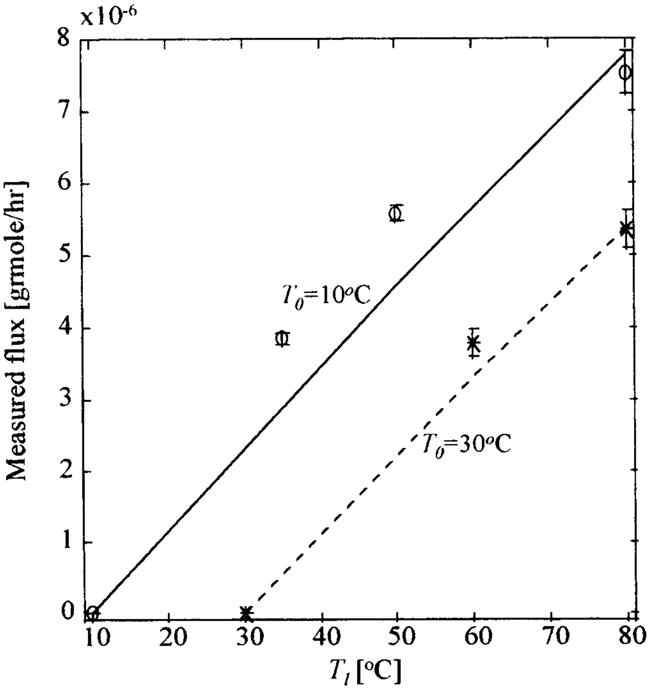

Figure 3. Effect of boundary temperatures T_0 and T_l on the flux ($C_0 = C_l = 0.01$ M).

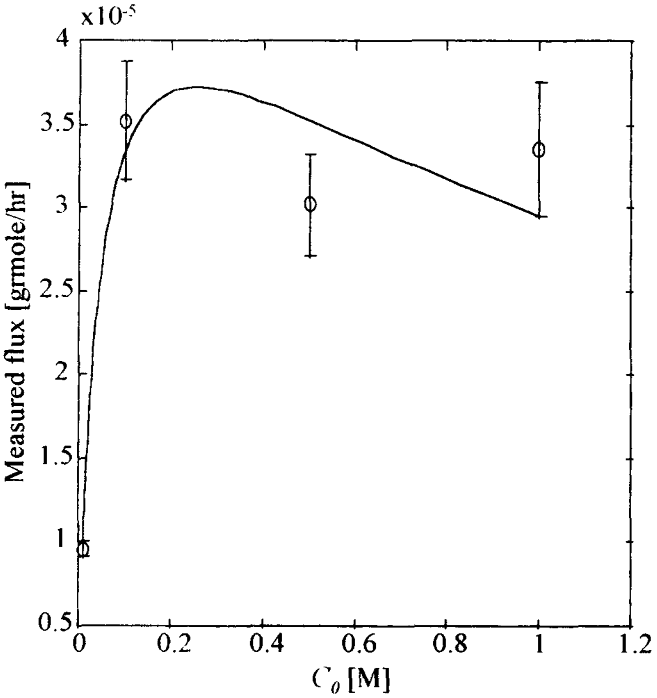

Figure 4. Effect of inlet concentration on the flux for constant concentration ratio of $\alpha \equiv C_l/C_0 = 0.15$ ($T_0 = 10°C$, $T_l = 80°C$).

"facilitated transport" of citric acid through a microporous polypropylene membrane (Celgard 2400) using an organic solvent consisting of a paraffin (Shell-Sol 75), a modifier (n-octanol), and a long chain tertiary amine (Trilaurylamine) as the carrier.

Here, the best fit was obtained with $\phi = 1$, $B = 2{,}000$ K, $\Delta H = -20.15 \times 10^3$ J/grmol and $\Delta S = -56.65$ J/grmol·K. Linear regression derives a straight line crossing the origin with a correlation coefficient of $r = 0.993$. Those values turn out to be close to those obtained when fitting our own data. The conversion factor is $\vartheta = 41.53 \times 10^{-6}$ gr./(cm²min) indicating, for a PP membrane with thickness $l = 25$ μm and an amine concentration of 38% [v/v] Trilaurylamine (~ 0.76 M), a reference diffusion coefficient of

$$D_B(T_{\mathrm{ref}}) = \frac{\vartheta \cdot l}{C_T}$$

$$= \frac{41.53 \times 10^{-6}\ [\mathrm{g/cm^2 min}] \times 25 \times 10^{-4}\ [\mathrm{cm}]}{192.13\ [\mathrm{g/mol}] \times 60\ [\mathrm{s/min}] \times 0.76 \times 10^{-3}\ [\mathrm{mol/cm^3}]}$$

$$= 1.18 \times 10^{-8}\ \mathrm{cm^2/s}.$$

This compares favorably with the value obtained from our data (1.64×10^{-8} cm²/s). Considering the differences between the two systems in terms of the solid support and the organic phase composition, this fit is remarkable, suggesting perhaps that the SLM acts more as a continuous liquid rather than a solid supported film with porosity and tortuosity effects.

Heat Transfer in the SLM

Evidently, the transport of the acid uphill from the dilute solution to the more concentrated one occurs by virtue of the temperature gradient across the membrane. By the second law of thermodynamics, the process is only made possible because some heat is also transferred from the hot boundary to the cold one thereby generating the work necessary to drive the mass transfer uphill. The efficiency of the process may then be measured in terms of the amount of heat expended (transport from the hot source to the cold sink) per unit mass (acid) transferred uphill. While the apparatus used in this work is not ideally suited to measure the thermal efficiency of the process, an experiment was devised to estimate the amount of heat transferred. The experimental system was modified slightly so that cooling of the cold cell could be started or stopped at will while the hot cell temperature was kept constant. Heat flowing from the hot cell to the cold cell was now registered as a temperature rise in the cold cell and, by a simple energy balance, heat fluxes could thereby be estimated.

As an example, with boundary conditions specified as $T_0 = 10°C$, $T_l = 80°C$, $C_0 = C_l = 0.01$ M (corresponding to a mass flow of 7.53×10^{-6} mol/h), the heat flow through the SLM module was estimated at 175 kJ/h. Therefore, the ratio between heat and mass transfer, η was

$$\eta = \frac{175\ \mathrm{kJ/h}}{7.53 \times 10^{-6}\ \mathrm{mol/h}} = 2.33 \times 10^7\ \mathrm{KJ/mol\ transfered}. \tag{10}$$

Evidently, this high value reflects the combined effect of a low mass-transfer rate coupled with a substantial heat leak. As yet, we do not know if and to what extent this situation may be improved by an appropriate design of an apparatus. The issue of mass-transfer efficiency enhancement merits a separate investigation, now underway.

Conclusions

This study set out to explore the feasibility of thermally assisted liquid-liquid extraction in which the two steps of extraction of citric acid from an aqueous solution into an organic phase and its back extraction into a second more concentrated aqueous solution, are combined into a single step of mass transfer through the SLM.

A simple and intuitive mathematical model was developed relying on four fundamental parameters defining sensitivity to boundary conditions.

It was shown experimentally that uphill transport of citric acid from a dilute source to a concentrated sink is feasible by means of a supported liquid membrane subjected to a temperature gradient. The effect of the boundary conditions turns out to be similar to that observed in the classical extraction implementation: flux increases with temperature difference and decreases with rising outlet concentration.

Experimental and predicted data coincide to a large degree with the mathematical model generally predicting experimentally observed behavior. Prediction excelled for data taken from the literature and were not as good with regards to our own experimental data. Evidently, our model does not include the full details of the conditions prevailing in our own apparatus. In particular, thermal boundary layers were not taken into account. Nevertheless, this model can serve our understanding of the process and will help refine the method.

A procedure enabling the evaluation of the basic system parameters and of the effective mass-transfer rates has been defined, thereby providing the means to evaluate the efficiency of the process.

Acknowledgments

This work was supported by a grant of the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities and by the fund for the promotion of research at the Technion, I.I.T. We also wish to thank IMI for making available to us relevant data and advice.

Notation

D = diffusion coefficient, cm^2/s
ΔH = enthalpy of reaction/complexation, J/mol
R = gas constant, J/(mol·K)
ΔS = entropy of reaction/complexation, J/mol·K
x = length, m
B = temperature sensitivity of viscosity, K
ϕ = ratio between complex and carrier diffusion coefficients, dimensionless

Subscripts

A = acid solute
B = amine carrier
AB = complex formed
o = property at membrane inlet
l = property at membrane outlet
ref = reference temperature
T = total carrier concentration

Special symbols

$\sim$ = relates to a dimensionless variable
$-$ = relates to species in SLM or organic phase

Literature Cited

Baniel, A. M., R. Blumberg, and K. Hajdu, "Recovery of Acids from Aqueous Solutions," British Patent 1,426,018 (1973).

Basu, R., and K. K. Sirkar, "Hollow Fiber Contained Liquid Membrane Separation of Citric Acid," *AIChE J.*, **37**, 383 (1991).

Bìzek, V., J. Horacek, R. Rericha, and M. Kousova, "Amine Extraction of Hydroxycarboxylic Acids: 1. Extraction of Citric Acid with 1-Octanol/*n*-Heptane Solutions of Trialkylamine," *Ind. Eng. Chem. Res.*, **31**, 1554 (1992).

Cianetti, C., and P. R. Danesi, "Facilitated Transport of HNO_3 Through a Supported Liquid Membrane Containing a Tertiary Amine as Carrier," *Solvent. Extr. & Ion Exch.*, **1**, 565 (1983).

Deblay, P., M. Delepine, M. Minier, and H. Renon, "Selection of Organic Phases for Optimal Efficiency of Flat-Sheet Supported Liquid Membranes, *Sep. Sci. Tech.*, **26**, 97 (1991).

Eyal, A. M., and A. M. Baniel, "Recovery and Concentration of Strong Mineral Acids From Dilute Solutions Through LLX. I: Review of Parameters for Adjusting Extractant Properties and Analysis of Process Options," *Solv. Ext & Ion Exch.*, **9**, 195 (1991).

Frank, G T., and K. K. Sirkar, "An Integrated Bioreactor-Separator: In Situ Recovery of Fermentation Products by a Novel Membrane-Based Dispersion-Free Solvent Extraction Technique," *Biotech. Bioeng. Symp.*, **17**, 303 (1986).

Friesen, D. T., W. C. Babcock, D. J. Brose, and A. R. Chambers, "Recovery of Citric Acid From Fermentation Beer Using Supported-Liquid Memb," *J. Memb. Sci.*, **56**, 127 (1991).

Lavie, R., "An Optimal Interaction of Heat and Mass Exchange for the Improvement of Separation Efficiency," *Chem. Eng. Sci.*, **40**, 2019 (1985).

Molinari, R., L. De Bartolo, and E. Drioli, "Coupled Transport of Amino Acids Through a Supported Liquid Membrane," *J. Memb. Sci.*, **73**, 203 (1992).

"NRC Separation and Purification Needs and Opportunities," Report of the committee on separation science and technology of the NRC, National Academy Press, Washington, DC (1987)..

Rockman, J. T., "Thermally Driven Liquid Liquid Extraction," D.Sc. Diss., The Technion, Israel Inst. of Technol. (1995).

Rockman, J. T, E. Kehat, and R. Lavie, "Mathematical Model for Thermally Enhanced Facilitated Transport," *Ind. Eng. Chem. Res.*, **34**, 2455 (1995).

Sengupta, A., R. Basu, and K. K. Sirkar, "Separations of Solutes from Aqueous Solutions by Contained Liquid Membranes," *AIChE J.*, **34**, 1698 (1988).

Tamada, J. A., A. S. Kertes, and C. J. King, "Extraction of Carboxylic Acids with Amine Extractants: 1–3," *Ind. Eng. Chem. Res.*, **29**, 131 (1990).

Wennersten, R., "The Extraction of Citric Acid from Fermentation Broth Using a Solution of a Tertiary Amine," *J. Chem. Technol. & Biotechnol. B.*, **33**, 85 (1983).

Manuscript received Sept. 17, 1996, and revision received May 23, 1997.