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 Narębska, A. and Staniszewski, M.(1997) 'Separation of Fermentation Products by Membrane Techniques. I. Separation of Lactic Acid/Lactates by Diffusion Dialysis', Separation Science and Technology, 32: 10, 1669 — 1682
To link to this Article: DOI: 10.1080/01496399708000727
URL: http://dx.doi.org/10.1080/01496399708000727

SEPARATION SCIENCE AND TECHNOLOGY, 32(10), PP. 1669–1682, 1997

Separation of Fermentation Products by Membrane Techniques. I. Separation of Lactic Acid/Lactates by Diffusion Dialysis

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ABSTRACT

The results of the separation of lactic acid from sodium lactate by diffusion dialysis are presented in this paper. Neosepta AFN-7 and Selemion DSV membranes were used for the separation. The dialytic separation factor for lactic acid/sodium lactate was found to be ~20 for Neosepta AFN-7 and ~30 for Selemion DSV membranes. The fluxes inherent in the separation were up to ~1 mol/m^2·h for the acid and only up to ~0.07 mol/m^2·h for the salt. The effects that enable the separation, i.e., the differences in solubility and diffusivity of the acid and the salt, were estimated (single solute experiments). The partition coefficients for lactic acid were found close to or above unity whereas those for sodium lactate were much lower. On the contrary, the apparent diffusion coefficients of both solutes were comparable, being of the order of 10^{-11} m^2/s. It results that the separation of the weak acid and salt is based on differences in solubilities rather than in diffusivities, i.e., the phenomenon is different from those which enable separation of strong acids and salts. The results prove the diffusion dialysis technique is effective for separating lactic acid from lactates.

INTRODUCTION

The conventional fermentation of carbohydrates by microorganisms is a well-known technology for producing carboxylic acids for the food, pharmaceutical, and chemical industries. One of the acids is lactic acid—the metabolite of *Lactobacillus* bacteria, various strains. The an-

nual production of lactic acid reaches 30,000 t/a. From 50 to 60% of the production comes from fermentation.

The fermentation broths are complex suspensions of viable cells, untransformed nutrients, and the final products. The concentration of lactates in the products depends on the nature and the concentration of the carbohydrate used. It could be in a range of only a few percent if unconcentrated cheese whey with a natural content of lactose is fermented, or it may range up to 0.7 mol/dm^3 and more with glucose as a substrate.

To keep the microorganisms active during fermentation, the pH of the broth is maintained at 5–6, for which hydroxides or carbonates are used. This means, however, that there are mixtures of calcium, ammonium, or sodium lactates and lactic acid as the products to be recovered. The most efficient techniques are those in which recovery of lactate is combined with salt to acid conversion.

The complex content of the broth is also an economic problem. In spite of using productive microorganisms, the economy of fermentation deteriorates during elaborate operations for the isolation and purification of the products.

Membrane techniques have been evaluated since the 1980s in terms of their usefulness in solving this problem (1–9). Various membranes and membrane systems have been designed for application 1) to the demineralization of whey before fermentation, 2) to the recovery of lactate, and 3) to the salt to acid conversion combined with the concentration of pure lactic acid. Integrated systems of ultrafiltration and electrodialysis have turned out to be effective for separation. The broth is first micro- or ultrafiltered, and then the cell-free filtrate is electrodialyzed in order to recover lactate or to isolate the acid after conversion. Another electrodialysis-fermentation system for the semicontinuous production of lactic acid by immobilized growing cells entrapped in calcium alginate as a fermenter, integrated with a electrodialysis unit, has been designed (10–13). More membrane techniques are still being examined, including reverse osmosis and nanofiltration (14, 15).

In this paper the results of examining the diffusion dialysis technique (Dd) for the separation of lactic acid (LA) from sodium lactate (NaLA) are presented.

Diffusion dialysis has proved to be effective for the recovery of strong acids like: sulfuric, nitric, and hydrofluoric (16–22). The membranes required by this technique are produced by Tokuyama Co. and Asahi Glass Co. (Japan). It has not been clear, however, if the technique would be useful for the recovery of weak acids. The main difference is that weak acids appear predominantly in the form of undissociated molecules, which

implies differences both in acid sorption and permeation as well as in the fundamentals of separation.

To discuss the phenomenon, the permeation, solubility, and diffusivity of lactic acid and sodium lactate and the dialytic separation of LA/NaLA mixtures were evaluated.

EXPERIMENTAL

Membranes

Two anion-exchange diffusion dialysis membranes were used for the experiments: Neosepta AFN-7 by Tokuyama Co. Japan (24) and Selemion DSV by Asahi Glass Co., Japan. The characteristics of the membranes as determined by routine methods (23) are presented in Table 1.

Sorption Equilibria

Precautions were taken to differentiate between ion exchange and dissolution of the solutes within water swelling the membranes (another term for dissolution is "physical sorption").

To establish sorption equilibria for the acid, samples of the membranes in hydroxyl form were equilibrated with an excess of lactic acid solutions of 0.1–1 mol/dm^3 concentrations for 5 hours with constant stirring. Then the membranes were dried with filter paper and the dissolved acid was eluted with redistilled water. Because hydrolysis of the functional groups (R^+LA^-) might affect elution of the acid, this effect was checked by fitting the experimental data to the exponential equation

$$c_{t\to\infty} - c_t = c_d \exp(-k_d t) + c_h \exp(-k_h t) \quad (1)$$

Equation (1) represents the kinetics of the elution of the acid as composed

TABLE 1
Characteristics of the Diffusion Dialysis Membranes[a]

Properties	Neosepta AFN-7	Selemion DSV
Ion-exchange capacity: mmol/g	3.24	2.29
mmol/cm^3	2.23	1.77
Water content: %	34.5	26.4
g/g	0.527	0.359
Thickness, cm	0.016	0.011

[a] Chloride form.

of two first-order processes: washing out the acid dissolved in a membrane (k_d = the rate constant, c_d = acid concentration in the eluate after $t \rightarrow \infty$) and hydrolysis of the functional groups (k_h = the rate constant, c_h = acid concentration in the eluate due to hydrolysis in $t \rightarrow \infty$), $c_{t\rightarrow\infty} = c_d + c_h$; the symbol c_t is the acid concentration in the eluate after time t. The experimental data and the two constituent curves are shown in Fig. 1 (as an example). The constants found are $k_d = 0.012 \pm 0.0012$ (1/s) and $k_h = 0.0015 \pm 0.00011$ (1/s). Resolution of the experimental curves results in accuracies within the 4–5% range in determining the amount of dissolved acid in a membrane.

For sorption experiments with sodium lactate (c = 0.1–1.0 mol/dm^3), the membranes were prepared in the lactate form and the time of equilibration was 12 hours. Then the amount of eluted salt was determined. Capillary electrophoresis (EA-100, Villa Labeco, Slovakia), was used for analysis. The accuracy in determining the concentrations of LA and NaLA by this method was 5%. The amount of swelling water was determined for each equilibrium state. The sorption of solutes in moles per volume of a swollen membrane ($\bar{c}$), the molality ($\bar{m} = \bar{n}/\bar{w}$), and the partition coefficients ($k = \bar{c}/c$) are displayed in Table 2.

Transport Experiments (single component solutions)

The permeability of LA and NaLA was measured with an automatic set-up developed in our laboratory (20, 25, 26). The measured conductivity of a permeate in a receiver versus time was stored and processed automatically. The permeability coefficient was calculated on the basis of Fick's

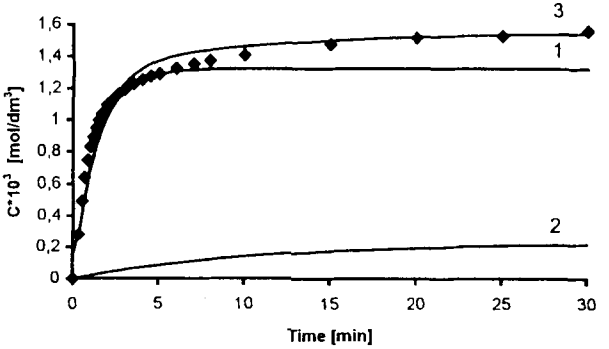

FIG. 1 Elution of lactic acid from Neosepta AFN-7 membrane. (◆) Experimental. Solid lines: (1) concentration of acid eluted from the membrane, (2) effect of hydrolysis, (3) combined curve.

TABLE 2
Sorption Equilibria. Concentration of Lactic Acid and Sodium Lactate in Neosepta AFN-7 and Selemion DSV Membranes and the Partition Coefficients (single solute experiments)

External solution (mol/dm³), c	Internal membrane solution (mol/dm³), $\bar{c}$	Swelling, g/g	Molality, $\bar{m}$	k
Neosepta AFN-7 Membrane				
		Lactic Acid		
0.07	0.10	0.406	0.39	1.43
0.23	0.30	0.407	0.78	1.30
0.48	0.60	0.409	1.50	1.25
0.75	0.91	0.411	2.14	1.21
1.03	1.07	0.414	2.79	1.04
		Sodium Lactate		
0.10	0.004	0.399	0.015	0.04
0.25	0.01	0.397	0.04	0.04
0.50	0.02	0.395	0.08	0.04
0.75	0.03	0.391	0.09	0.04
1.00	0.05	0.387	0.16	0.05
Selemion DSV Membrane				
		Lactic Acid		
0.08	0.07	0.316	0.33	0.88
0.24	0.18	0.317	0.64	0.75
0.48	0.32	0.319	1.17	0.66
0.75	0.46	0.321	1.59	0.61
1.03	0.59	0.322	1.91	0.57
		Sodium Lactate		
0.10	0.003	0.304	0.01	0.03
0.24	0.01	0.301	0.03	0.04
0.50	0.02	0.298	0.06	0.04
0.75	0.03	0.295	0.09	0.04
1.00	0.04	0.291	0.13	0.04

law adopted to the experimental findings:

$$\frac{l}{h}\ln\left[\frac{c_f^0 - c_s^t(1 + b) + bc_s^0}{c_f^0 - c_s^0}\right] = -Pt \qquad (2)$$

where l is a membrane's thickness, $b = V_s/V_f$, $h = [A(1 + b)]/V_s$, A is the surface area of a membrane, and P is a permeability coefficient. The

indexes at concentration (c) and volume (V) correspond with the feed (f) and permeate (s) solutions. In the end of the experiment the concentration of a solute in a permeate did not exceed 3% of the concentration in a feed.

Dialysis of Two Solutes

A schematic representation of an automatically controlled set-up for dialytic separation of LA/NaLA is presented in Fig. 2. The effective membrane area in the dialyzer was 50 cm^2. The solution and water were pumped in countercurrent flow using a MasterFlex pump (USA) at a rate of 60 mL/min. As the technique has been intended for isolation of LA from a broth containing lactate in excess of the acid, the experiments were carried out using a solution with a LA concentration of 0.05 mol/dm^3 and a NaLA concentration of 0.2 mol/dm^3. The concentration of the solutes in a permeate was controlled by conductometry and potentiometry (Elmetron CX-721, Zabrze-Mikulczyce, Poland). By measuring the pH and conductivity versus time, the concentrations of lactic acid (c_{LA}) and lactate (c_{NaLA}) in a permeate (forming a buffer) were found by solving the equations

$$pH = pK_{LA} + \log(c_{NaLA}/c_{LA}) \tag{3a}$$

$$\kappa = a_1 c_{NaLA} + a_2 c_{NaLA}^2 + b_1 c_{LA} + b_2 c_{LA}^2 + b_3 c_{LA}^3 \tag{3b}$$

Equation (3a) is for the pH of a buffer solution while Eq. (3b) is for the

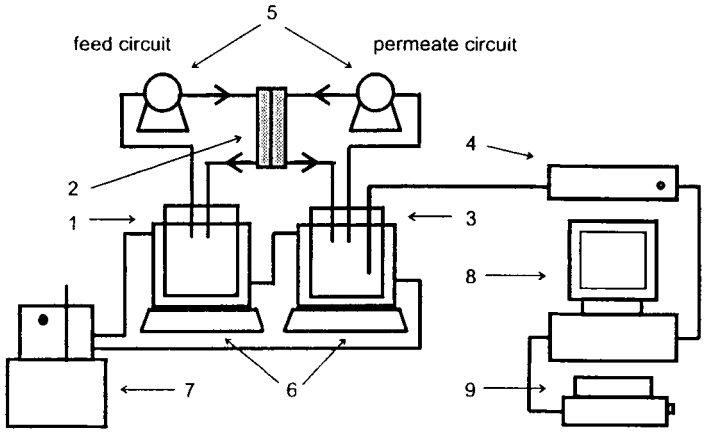

FIG. 2 Scheme of experimental arrangement for separation of acid and salt by diffusion dialysis: (1) feed tank, (2) diffusion dialyzer, (3) receiver, (4) pH and conductivity meter, (5) pump, (6) magnetic stirrers, (7) thermostat, (8) computer, (9) printer.

conductivity of the two solutes, with κ represented by polynomials: the second degree is for NaLA and the third degree is for LA. In the equations K_{LA} is the dissociation constant of lactic acid, and a_1, a_2, b_1, b_2, and b_3 are the constants of the corresponding polynomials. By measuring the pH and κ for model solutions with the anticipated concentration of both solutes in a permeate, the accuracy in determining the concentrations of LA and NaLA was predetermined. The error in the determined concentration was found to be 6% for the acid and 3% for the salt. At the end of each of the experiment the total concentration of both solutes (LA + NaLA) was checked by capillary electrophoresis. Having determined the acid and salt concentrations versus time, the separation factors $S_{LA/NaLA}$ were calculated:

$$S_{LA/NaLA} = \frac{U_{LA}}{U_{NaLA}} = \left(\frac{W_{LA}}{\Delta c_{LA}}\right) \times \left(\frac{W_{NaLA}}{\Delta c_{NaLA}}\right)^{-1} \quad (4)$$

where U is the dialysis coefficient (m/s), W is the molar transport rate (mol/s), and Δc is the concentration difference between the feed and the permeate solutions (mol/m^3).

RESULTS AND DISCUSSION

Sorption Equilibria

Sorption occurs in ion-exchange membranes by ion exchange and by dissolution of a solute within the internal water. Only a dissolved solute is free to diffuse, with $\Delta c_{ext} \neq 0$ acting as a driving force. Dissolution is highly restricted if a strong electrolyte of low molarity is in contact (Donnan exclusion effect). However, that is not the same when considering weak acids and neutral solutes. As for lactic acid (pK = 3.86), sorption of undissociated molecules is expected.

In Table 2 the concentrations of the solutes dissolved in a membrane (in mol/dm^3) the molalities, and the partition coefficients are displayed. The differences in k_{LA} and k_{NaLA} are extensive. Sodium lactate is excluded from the membranes, and the partition coefficients are low (within 0.04–0.05). It is different, however, for lactic acid. For the DSV membrane in a low molarity range, the partition coefficient for LA approaches unity. For the AFN membrane it exceeds unity in the whole concentration range. This means that both membranes concentrate the acid in the internal phase. The values for both $\bar{c}$ and $\bar{m}$ prove that the internal medium for diffusion of the acid is a concentrated, possibly structured solution with hydrated and associated acid molecules. Certainly the polymeric network may affect the molecular arrangements of the acid and water molecules

inside a membrane. Still, we know too little to comment on this. A detailed mechanism of acid permeation in this solution is an open question.

Transport Experiments (single permeant solutions)

In Fig. 3 the fluxes of lactic acid and sodium lactate across the Neosepta AFN and the Selemion DSV membranes are displayed. Each of the points in the curves was determined separately by measuring the permeation at a steady state for a definite feed concentration.

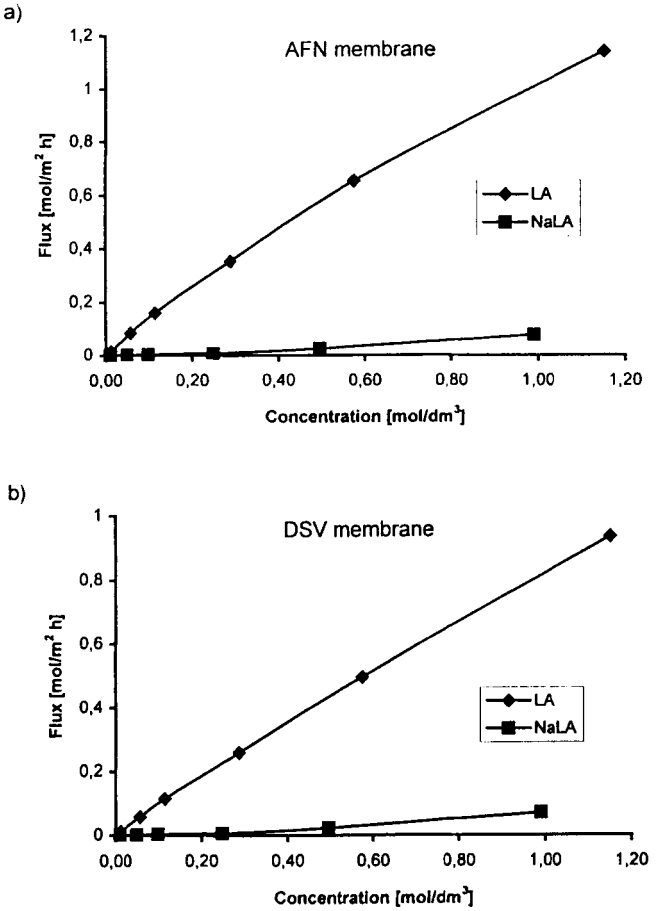

FIG. 3 Transport of lactic acid and sodium lactate across AFN (a) and DSV (b) membranes (single solute experiments).

The fluxes of lactic acid exceed the fluxes of sodium lactate in the whole concentration range. For both membranes the fluxes of the acid are up to ~1 mol/m²·h, and hence are 10 times higher than the fluxes of the salt. After determining the partition coefficients (k, Table 2) and the permeability coefficients (P, Eq. 2) for both solutes, the apparent diffusion coefficients $\bar{D}$ for LA and NaLA were computed: $P = \bar{D}\bar{c}/c$ (Table 3). Unlike sorption, the apparent diffusion coefficients for the acid and the salt are in $\sim 10^{-11}$ m²/s and are similar for both membranes. Therefore, the transport rates of lactic acid and lactate within the membranes are controlled by their solubilities rather than by their diffusivities. However, further examination of the dynamics of the system is needed.

Acid/Salt Separation by Diffusion Dialysis (ternary solution)

The kinetics of collecting lactic acid and sodium lactate in a permeate, found in experiments performed with ternary solutions, is seen in Fig. 4. With these results, the separation factors $S_{LA/NaLA}$ have been calculated (Eq. 4, Table 4). The results confirm easy permeation of the acid against the salt, as was found in single permeant experiments. The separation factor was ~20 with the Neosepta AFN-7 membrane and ~30 with the Selemion DSV membrane.

Data concerning the dialytic separation of hydrochloric acid/sodium chloride can be helpful for discussing the results of lactic acid/sodium lactate separation. In earlier experiments performed with the Neosepta AFN-7 membrane and HCl and NaCl solutions (16, 22), the separation factors $S_{HCl/NaCl}$ were found to be 11.8 and 18.3, respectively. Those experiments were performed with one-to-one acid and salt concentrations

TABLE 3
Apparent Diffusion Coefficients of Lactic Acid and Sodium Lactate within Neosepta AFN-7 and Selemion DSV Membranes (single solute experiments)

	$\bar{D} \times 10^{11}$ (m²/s)			
	Neosepta AFN-7		Selemion DSV	
c [mol/dm³]	LA	NaLA	LA	NaLA
0.1	4.39	3.54	3.39	3.21
0.25	4.17	3.44	3.87	3.01
0.5	4.03	5.21	4.06	4.11
1.0	4.25	7.27	4.57	5.80

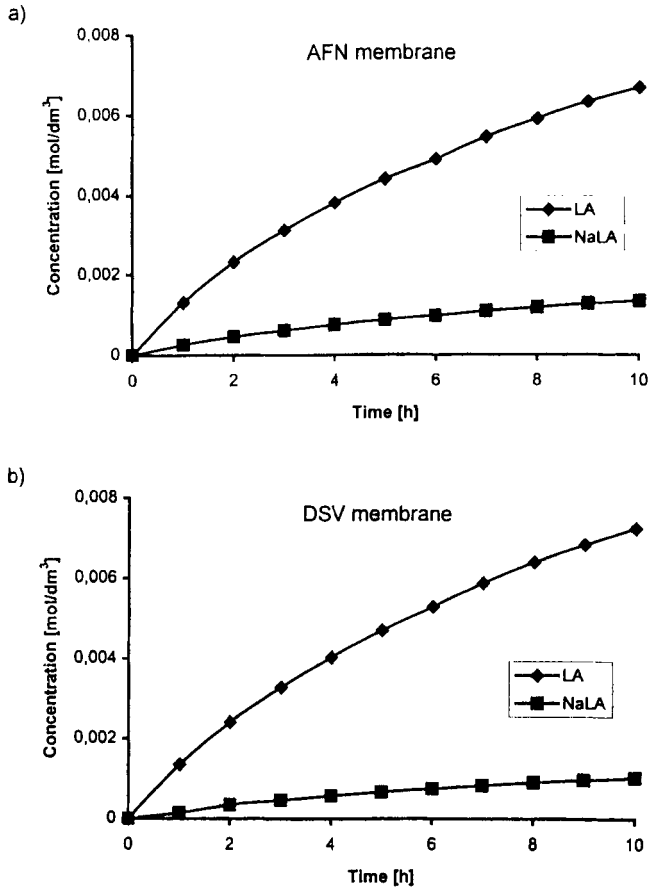

FIG. 4 Dialytic transport of lactic acid and sodium lactate from ternary solution across AFN (a) and DSV (b) membranes. Initial concentrations in feed: $c_{LA} = 0.05$ mol/dm^3, $c_{NaLA} = 0.2$ mol/dm^3.

TABLE 4
Dialysis Coefficients and Separation Factors for Lactic Acid/Sodium Lactate

	Neosepta AFN-7	Selemion DSV
Dialysis coefficient, m/s	$U_{LA} = 2.67 \times 10^{-8}$ $U_{NaLA} = 1.33 \times 10^{-9}$	$U_{LA} = 3.32 \times 10^{-8}$ $U_{NaLA} = 1.13 \times 10^{-9}$
Separation factor	20.1	29.4

TABLE 5
Solubility/Permeability Data and Dialytic Separation Factor for HCl/NaCl (20) and LA/NaLA with Neosepta AFN-7 Membrane at Low Molarities in Feed (acid ≈ 0.05 mol/dm³; salt ≈ 0.2 mol/dm³)

	$\bar{c}$, mol/dm³	$\bar{c}_{acid}/\bar{c}_{salt}$	Flux × 10^2 mol/m²·h	$\bar{D} \times 10^{11}$ m²/s	$U \times 10^9$ m/s	$S_{acid/salt}$
HCl	0.006[a]		4.2[a]	25.0	18.8	
NaCl	0.016	0.38	1.6	7.5	3.75	5.0
LA	0.30		3.0	4.5	26.7	
NaLA	0.03	10.0	0.6	3.4	1.33	20.1

[a] Interpolated (20).

or with an excess of the acid. Since solubility and diffusivity depend on concentrations, the results of the separation of LA/NaLA and HCl/NaCl at the same concentrations are displayed in Table 5 (some data were interpolated). The results indicate that different phenomena affect the separation of strong and weak acids from salts. These are a high diffusion rate for strong acids and a high sorption for weak acids.

To examine the isolation of lactic acid by dialysis in practice, an ultrafiltered broth containing LA, NaLA, phosphates, and other inorganic salts (Table 6, the broth and data kindly supplied by ATO-DLO Wageningen, The Netherlands) was dialyzed by using the Neosepta AFN-7 membrane. Dialysis continued for 30 hours and the concentration of lactic acid was measured repeatedly; the sodium and potassium salts concentrations were

TABLE 6
Content of the Ultrafiltered Fermentation Broth[a]

Compounds	g/dm³
Lactic acid and lactate	~45
M.R.S., solid components in the solution[b]	11.5
Na_2HPO_4	10.8
KH_2PO_4	1.4

[a] Supplied by ATO-DLO, Wageningen, The Netherlands. pH 4.2, dry mass content = 8.36%, density = 1.05 g/cm³, conductivity = 16.8 mS/cm.

[b] M.R.S. (de Man, Rogosa, Sharpe) solution contains: K_2HPO_4, sodium acetate, diammonium citrate, $MgSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, and the organic nutrients.

determined only at the end of the experiment. The concentrations of metal ions were determined by AAS spectroscopy. The integral fluxes (mol/m^2·h) are

$$J_{LA} = 0.043, \qquad J_{Na^+} = 0.006, \qquad J_{K^+} = 0.002$$

Because of the low content of LA in the broth, and thus the low concentration gradient, the flux of lactic acid was low. The fluxes of salts were much lower.

A method for making isolation of lactic acid from the broth more effective will be the subject of our next paper.

CONCLUSIONS

Diffusion dialysis membranes Neosepta AFN-7 and Selemion DSV were examined for the separation of lactic acid from sodium lactate. Experiments were carried out using single component and bicomponent solutions which approximated the content of acid and salt in fermentation broths.

The following conclusions can be drawn.

- Both membranes are effective for the separation of lactic acid from lactate in a wide concentration range including the concentrations found in fermentation broths.
- Both membranes concentrate lactic acid in their interior, with the partition coefficient value as high as unity for the Selemion DSV membrane and exceeding unity for the Neosepta AFN-7 membrane. On the other hand, sodium lactate is rejected by each of the membranes. The corresponding partition coefficients for NaLA are 0.04–0.05.
- Reflecting sorption, the fluxes are as high as ~1 mol/m^2·h for the acid and ~0.07 mol/m^2·h for the salt.
- The experimental dialytic separation factor found for lactic acid/sodium lactate is ~20 for the Neosepta AFN-7 membrane and up to ~30 for the Selemion DSV membrane.

Although the technique was checked for the separation of lactic acid and sodium lactate, it should be applicable for the separation of other carboxylic acids/carboxylates mixtures produced by fermentation.

ACKNOWLEDGMENT

This work was supported by Copernicus Project ERB-CIPA-CT92-3018.

SYMBOLS

a, b	constants of polynomials in Eq. (3) for the conductivity of a permeate (a for NaLA, b for LA)
c	molar concentration of a solute in an external solution
c_f^0, c_s^0, c_s^t	concentrations of the acid in feed (f) and strip solutions (s) at t_0 and after time t (Eq. 2)
c_d, c_h, c_t, $c_{t\to\infty}$	concentrations of lactic acid eluted from the membrane (d), formed by hydrolysis of the functional groups (h), and the total concentration of acid in eluate after time t and $t\to\infty$ (Eq. 1)
$\bar{c}$	molar concentration of a solute in a membrane in moles per dm^3 of a swollen membrane
$\bar{D}$	apparent diffusion coefficient of a solute within a membrane (m^2/s)
J	flux ($mol/m^2 \cdot h$)
K_{LA}	dissociation constant of lactic acid
k	partition coefficient (undimensional)
k_d, k_h	first-order rate constants (1/s) in the equation for the elution of dissolved acid (d) and hydrolysis (h) (Eq. 1)
l	thickness of a membrane (cm)
$\bar{m}$	molality of a solute in a membrane in moles per kg of internal water
$\bar{n}$	amount of a solute in a unit mass of a membrane (mol/kg)
P	permeability coefficient (m^2/s)
S	separation factor (undimensional)
U	dialysis coefficient (m/s)
W	molar transport rate (mol/s)
$\bar{w}$	mass of swelling water per unit mass of a membrane (kg/kg)

Greek Letter

κ	conductivity of a permeate [mS/cm]

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Received by editor July 24, 1996
Revision received November 1996