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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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Online publication date: 12 June 1999

To cite this Article Shah, B. G. , Trivedi, G. S. , Ray, P. and Adhikary, S. K.(1999) 'Separation of Sodium Formate and Pentaerythritol by Electrodialysis', Separation Science and Technology, 34: 16, 3243 — 3253

To link to this Article: DOI: 10.1081/SS-100100833

URL: http://dx.doi.org/10.1081/SS-100100833

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SEPARATION SCIENCE AND TECHNOLOGY, **34**(16), pp. 3243–3253, 1999

Separation of Sodium Formate and Pentaerythritol by Electrodialysis

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ABSTRACT

The electrodialysis (ED) process using ion-exchange membranes is mainly used for the desalination of brackish water and wheys and for the concentration of seawater. ED has of late become a unique operation for the separation of chemicals from a mixture of ionic and nonionic substances. During the manufacture of pentaerythritol, sodium formate is also formed, which is to be separated from the mixture. Since ED is used to separate electrolytes from nonelectrolytes, attempts were made to make use of this process for the separation of sodium formate and pentaerythritol from their mixture. In this paper we have discussed the experimental results obtained their separation under different experimental conditions.

INTRODUCTION

Electrodialysis (ED) using ion-exchange membranes was developed for the desalination of saline waters and the concentration of seawater. The most recent important industrial applications of ED are the production of fresh water from brackish water and brine solutions from seawater. ED is also used for the purification by demineralization of solutions of widely varying industrial fluids encountered in the food, chemicals, and pharmaceutical industries (1–3). ED has of late become a unit operation for the separation of chemicals from a mixture of ionic and nonionic substances, viz., separation of inorganic salts from cheese whey containing organics such as proteins and sugars; deacidification of fruit juices (4–8).

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Pentaerythritol (PET) (tetramethylal methane) is a polyhydric alcohol. The most important industrial use of pentraerythritol is in a wide variety of paints, coatings, and varnishes, where the crosslinking capability of the four hydroxyl groups is critical. Alkyd resins are produced by reaction of pentaerythritol with organic acids such as phthalic acid or maleic acid and natural oil species. Long-chain esters of pentaerythritol have been used as pour-point depressants for lubricant products, ranging from fuel oils and diesel fuels to the high performance lubricating oils required for such demanding outlets as aviation, power lubricants, and automobiles. Esters with inorganic acids, such as nitric acid (PETN), are used as explosives.

Pentaerythritol is used in self-extinguishing, nondripping, flame-retardant compositions with a variety of polymers, including olefins, vinyl acetate, and alcohol. Photocurable materials for photographic films contain pentaerythritol.

Pentaerythritol is produced by reaction of formaldehyde and acetaldehyde in the presence of a basic catalyst, generally an alkali or alkaline-earth hydroxide. Reaction proceeds by aldol addition to the carbon adjacent to the hydroxyl on the acetaldehyde. The pentaerythrose so produced is converted to pentaerythritol by a crossed Cannizzaro reaction using formaldehyde. The most common catalysts are sodium hydroxide and calcium hydroxide, generally used at a modest excess over the nominal stoichiometric amount to avoid formaldehyde—only addition reactions. Metal formate is also formed during the reaction (9). The metal formate may be recovered as hydroxide and/or formic acid by ion-exchange or used as is for deicing or other commercial applications.

Since a electrodialysis technique can be employed for the separation of chemicals from a mixture of ionic and nonionic substances, attempts have been made to separate sodium formate from the mixture of pentaerythritol and sodium formate. In this paper we describe the results of experiments to separate sodium formate and pentaerythritol from their mixtures.

EXPERIMENTAL

An electrodialysis stack was packed with 15 cell pairs of cation- and anion-exchange membranes prepared from interpolymer films based on high density polyethylene (HDPE)–linear low density polyethylene (LLDPE)–styrene–divinylbenzene. A parallel-cum-series flow in three equal stages was employed in the stack. The single effective membrane area of the stack is 80 cm^2. The salient features of the ED stack are given in Table 1, and the flow diagram of the experimental setup is presented in Fig. 1.

The solution of a mixture of pentaerythritol and sodium formate was circulated through the diluate (treated) compartments. At the same time distilled water was fed through the concentrate compartments. After the initial flush-

TABLE 1
Characteristics of the Electrodialysis Stack Employing Ion-Exchange Membranes

No. of cell pairs	15
Membranes:	
(a) cation exchange	Interpolymer type, sulfonic acid group
Areal resistance, $\Omega \cdot cm^2$	1–3
(b) Anion exchange	Intrerpolymer type, quarternary ammonium group
Areal resistance, $\Omega \cdot cm^2$	3–4
Effective cross-sectional area of each membrane, cm^2	80
Cell thickness, cm	0.2
Gaskets	Built-in flow arrangements and spacers
Electrodes:	
Anode	Expanded titanium metal coated with precious metal oxide
Cathode	SS 316 sheet
Housing for electrode	Rigid PVC with built-in flow distributor and Outlets
Pressing assembly	Threaded tie rods with nuts
Flow arrangements	Parallel-cum-series

ing of all the compartments with distilled water and the above mixture, the volumes of solution and water were measured. It was observed in preliminary experiments that the circulation flow rate of water and PET solution did not have significant effect on ED performance (7, 10). Hence, all the experiments were carried out at circulation flow rate of 7 L/h for both diluate and concentrate streams by using small dozing pumps. A dilute solution of sodium formate was recirculated through the two electrode compartments at the end of the experiments to remove the products of electrolysis. A predetermined DC electrical potential was applied between the two electrodes by means of an AC-DC rectifier having a variable current capacity of 0–15 A and a variable voltage of 0 to 150 V. The low initial current progressively increased in a few minutes and then gradually fell down to a minimum due to progressive reduction of sodium formate in the original mixture. The circulations of both treated and concentrate streams were continued throughout the experiments. Samples were drawn at regular intervals from each stream and analyzed for sodium formate and pentaerythritol.

Sodium formate present in the solution was estimated by employing an ion-exchange technique: The solution was passed through a column of strong acid cation-exchange resin in the H^+ form, and the eluate was collected and titrated with standard sodium hydroxide solution using thymol blue as indicator. Thus the concentration of sodium formate was estimated by

$$\text{Sodium formate concentration (g/L)} = \text{titre value in mL} \times \text{normality of NaOH} \times 68.01$$

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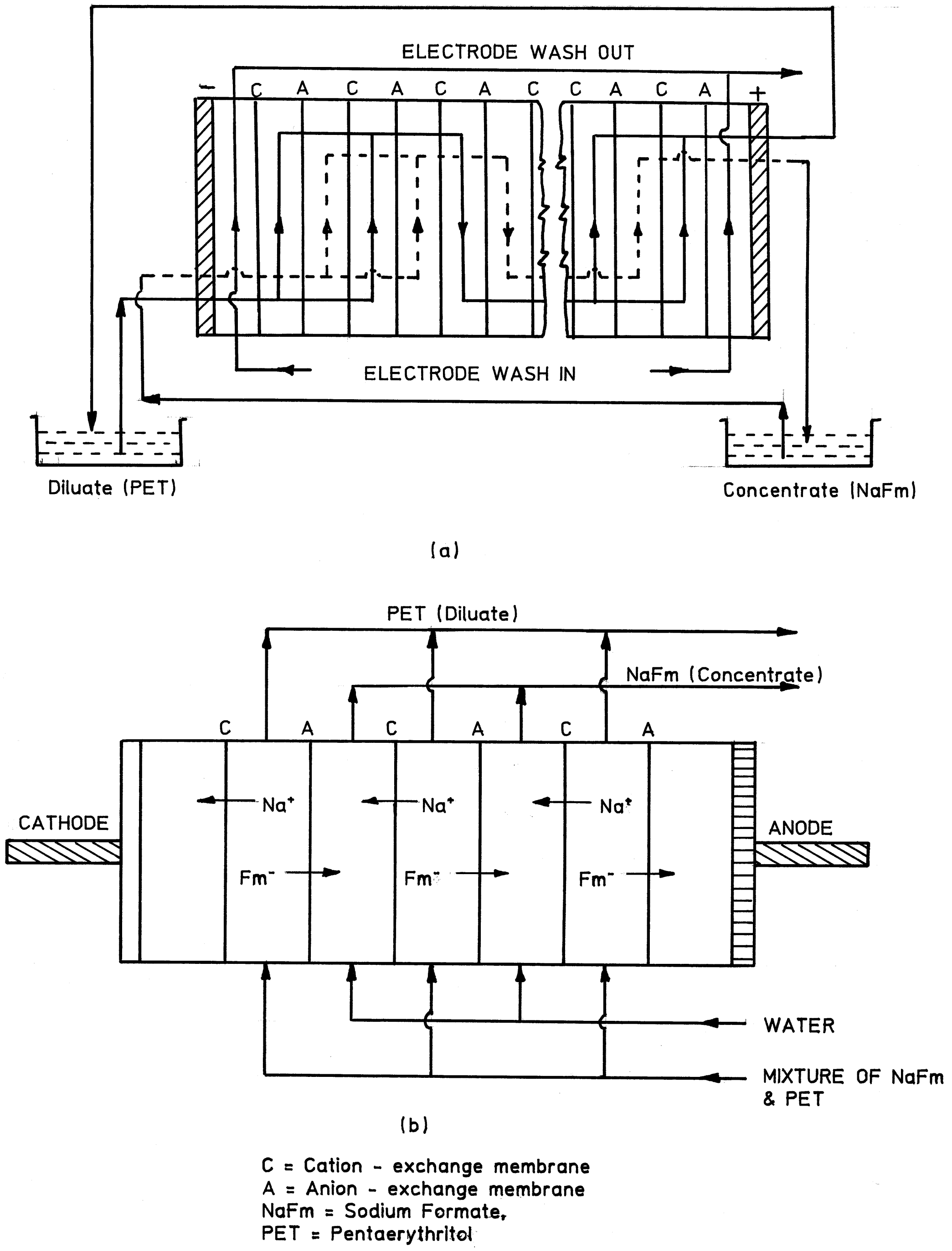

FIG. 1 (a) Schematic flow diagram. (b) Principle of separation of sodium formate (NaFm) and pentaerythritol (PET).

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Pentaerythritol was reacted with benzaldehyde to form dibenzyl which is crystalline and could be estimated gravimetrically (11). The percentage of monopentaerythritol was calculated by

$$P = 0.436 \times 100(w_2 + 0.0269)(1/w_1 y)$$

where w_1 = grams of sample
w_2 = grams of precipitate
y = aliquot fraction of sample
0.436 = gravimetric factor for pentaerythritol
0.0269 = emperical correction for slightly soluble precipitate

From the experimental data, the concentrations of sodium formate in the diluate stream, the current efficiency (C.E.), and the energy consumption (E) were calculated by

$$\text{C.E. } (\%) = (wF/MNQ) \times 100 \tag{1}$$

where w = weight of sodium formate (g)
F = Faraday = 26.8 A·h
M = molecular weight of sodium formate (g/mol)
N = number of cell pairs
Q = amount of electricity (A·h)

$$E\ (\text{kWh/m}^3) = \int (Vidt)/v \tag{2}$$

where V = voltage (V)
t = time
i = current at time t (A)
v = volume of solution taken (L)

The pentaerythritol solution used in this study was collected from a local industry. The solution, which was analyzed as per the methods described here, contained 9% (w/v) PET. and 5.4% (w/v) sodium formate (NaFm). The experiments were carried out under three different voltages, 20, 25, and 30 V, at ambient temperature (28–30)°C.

In the preliminary investigation, experiments which were carried out without changing any stream (diluate and concentrate), showed that reduction of NaFm in the diluate stream could not be achieved beyond 0.25% (w/v) from its original concentration of 5.4% (w/v). This might be due to backdiffusion of NaFm which would considerably nullified ion transport. It is known that salt diffusion takes place through an ion-exchange membrane under a concentration gradient in the absence of any applied electrical field. As the experiment was carried out in the continuous recirculation mode, after some time the concentration of NaFm in the concentrate reaches such a high value that the diffusion of NaFm from concentrate to diluate becomes the predominant factor compared to ion transport from diluate to concentrate because the current value is very low. Hence, backdiffusion becomes facile at this point. It was therefore decided to remove part of the solution from the concentrate stream and replace it with distilled water. It was observed that when the current dropped to nearly 0.5 A at 30 or 25 V, one time replacement of the concentrate stream (we refer this as C_1) with distilled water was sufficient to achieve the required level of NaFm reduction in the diluate stream.

When the final concentration of NaFm in the diluate stream became 0.1% (w/v), the experiment for batch processing was stopped.

RESULTS AND DISCUSSIONS

Experimental results of the separation of NaFm and PET from their mixture are presented in Figs. 2–5. The current vs time curves for three different voltages (20, 25, and 30 V), shown in Fig. 2, indicate that initially the current is

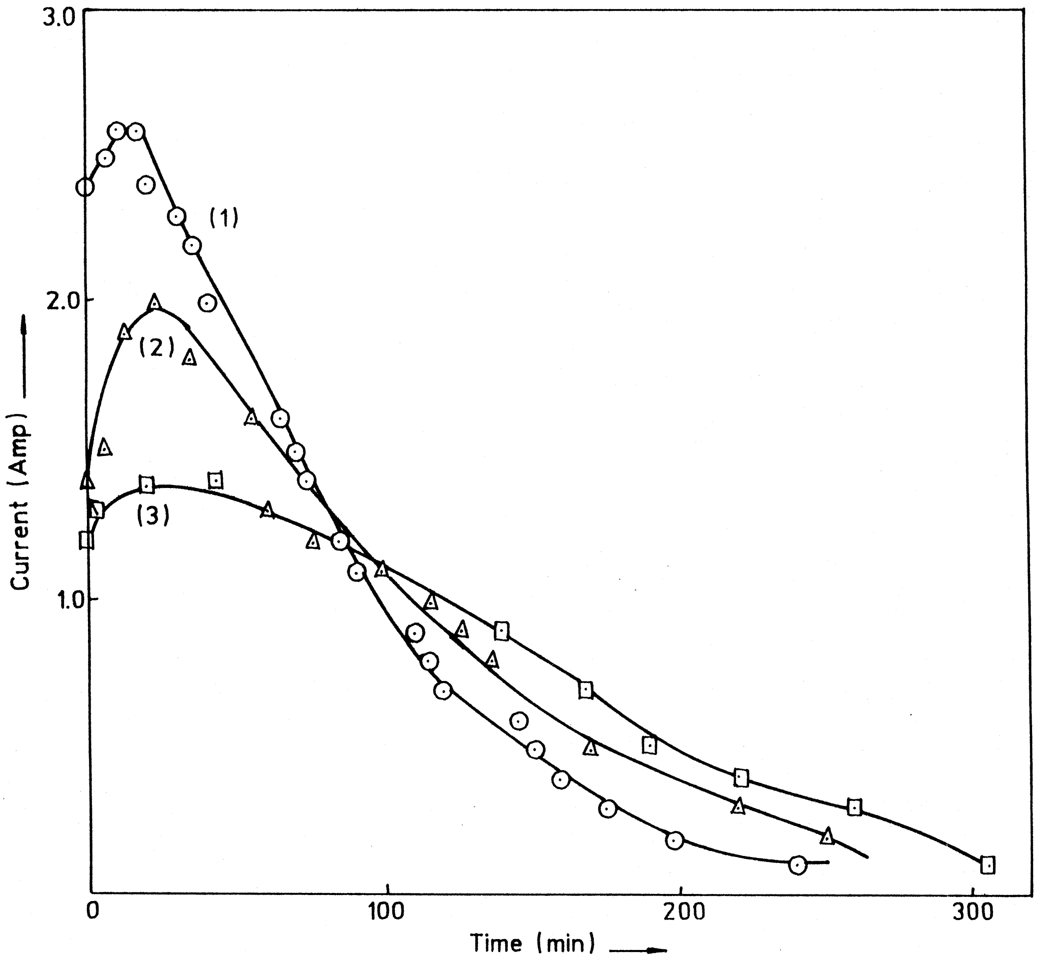

FIG. 2 Current vs time at different voltages: (1) 30 V, (2) 25 V, (3) 20 V.

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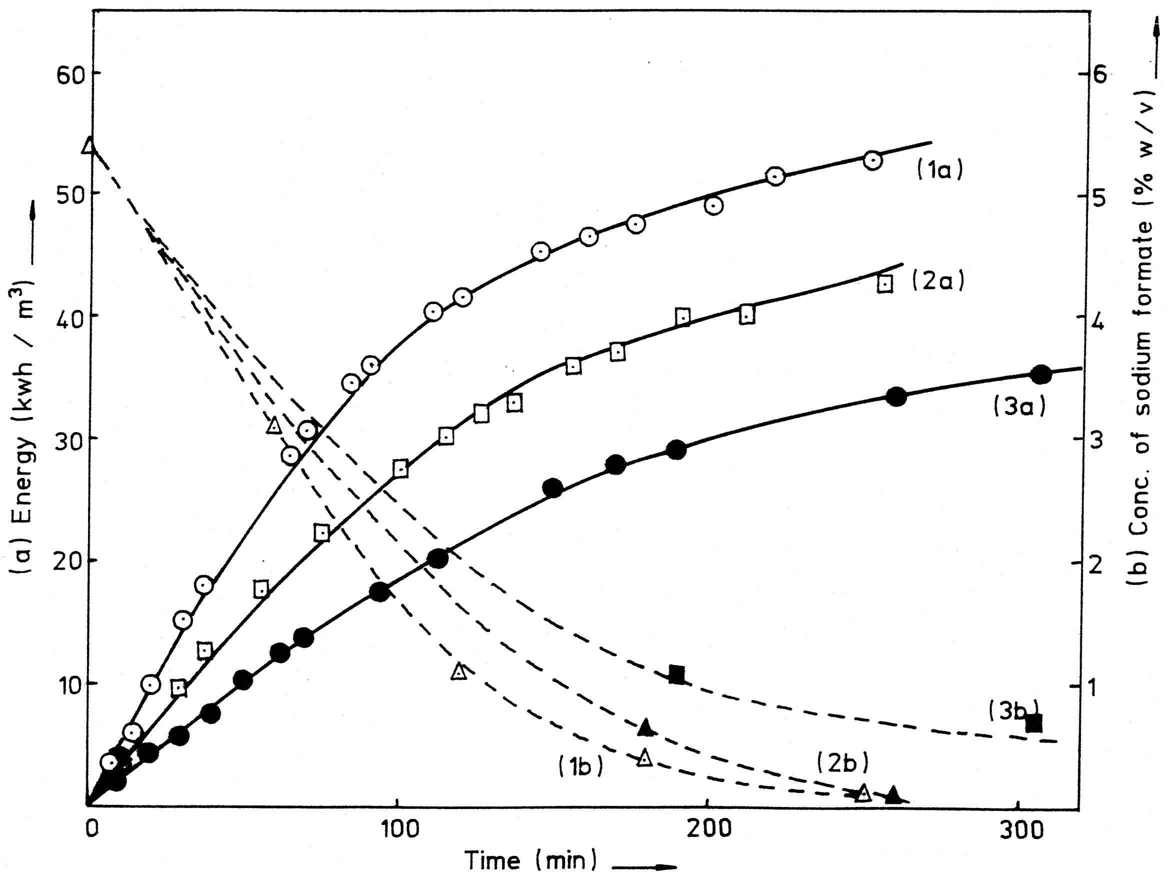

FIG. 3 (a) Energy vs time. (b) Concentration of NaFm vs time at different voltages: (1) 30 V, (2) 25 V, (3) 20 V.

low, progressively increases within a few minutes to a maximum, and then decreases for all three voltages. This variation of current with time can be explained as follows.

In the beginning of the experiments, the concentrate compartments through which distilled water is passed offer a high electrical resistance. With the onset of the migration of NaFm from the diluate compartments into the concentrate compartments (concentrate), the concentration of NaFm is built up in these compartments while that in the diluate compartments is reduced. As a result, the electric resistances offered by the diluate compartments are continuously being decreased and those offered by the concentrate compartments are increased. The net effect is that the overall electrical resistances of the ED stack decreases initially with time, causing an increase in current. After some time the concentration of NaFm in the diluate compartments become sufficiently low to cause an increase in the overall electrical resistance of the ED stack, and hence the current decreases.

Energy consumption (kWh/m^3) vs time graphs (Fig. 3) indicate that energy consumption increases with time (Curves a). For the same time period, energy

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consumption increases when the applied potential changes from 20 to 30 V (Curves 3a, 2a, 1a). Higher current is obtained by applying higher voltages, and hence higher energy is consumed. Both the rate of increase in energy consumption and the rate of decrease in NaFm concentration in the diluate compartments with time are initially sharp. Both rates become gradual after 140–150 minutes (Fig. 3, Curves a and b). The time taken to reach a concentration of NaFm in the dilute of ~0.1% (w/v) is lowest when 30 V is applied (Curve 1b) and highest when 20 V is applied (Curve 3b). Here, a higher current supplied by a higher voltage enhances the transport of ions through the membranes, and hence the time duration of the experiments is reduced.

The reduction of NaFm concentration is due to the transport of ions from the diluate compartments to the concentrate compartments. Some water and

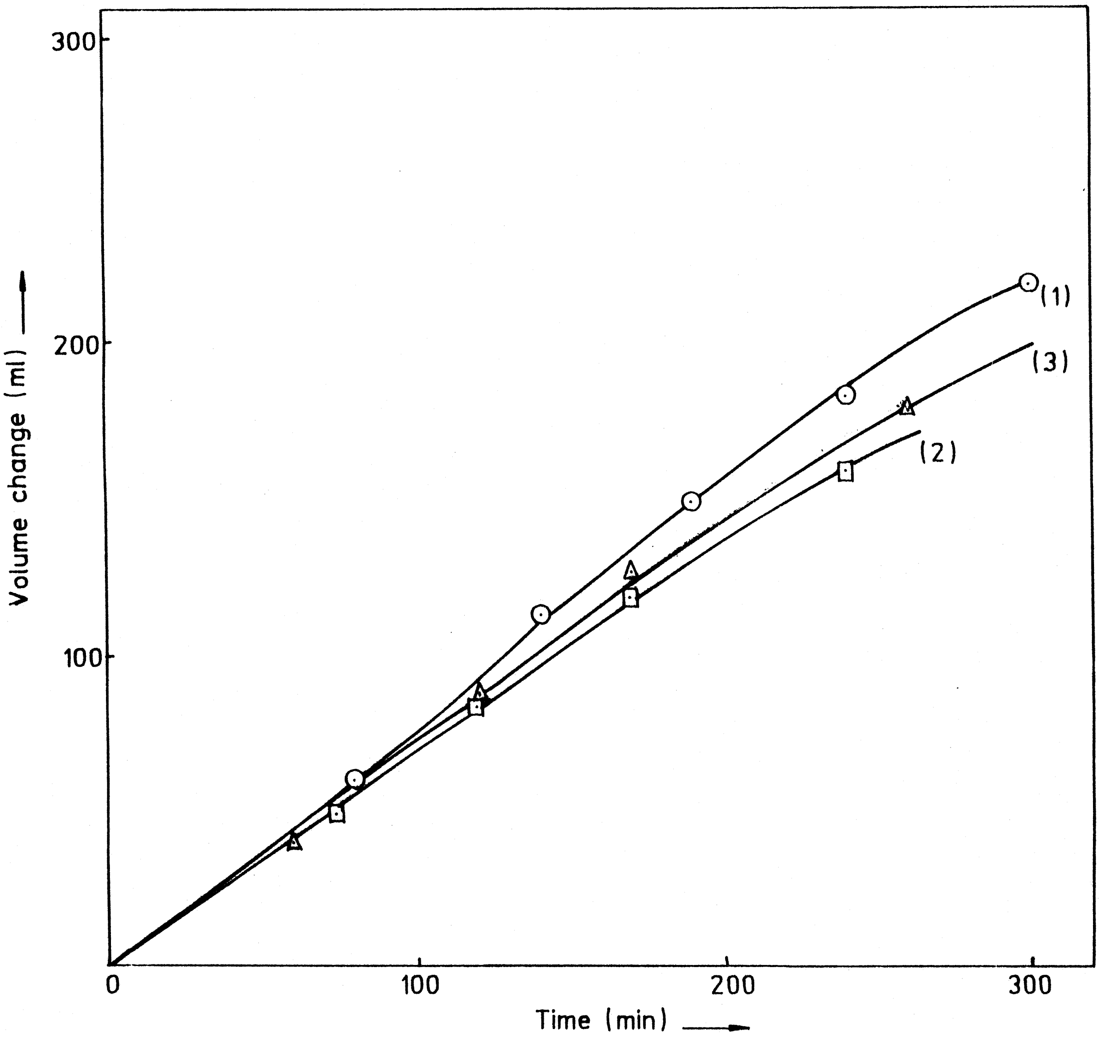

FIG. 4 Volume change vs time at different voltages: (1) 20 V, (2) 25 V, (3) 30 V.

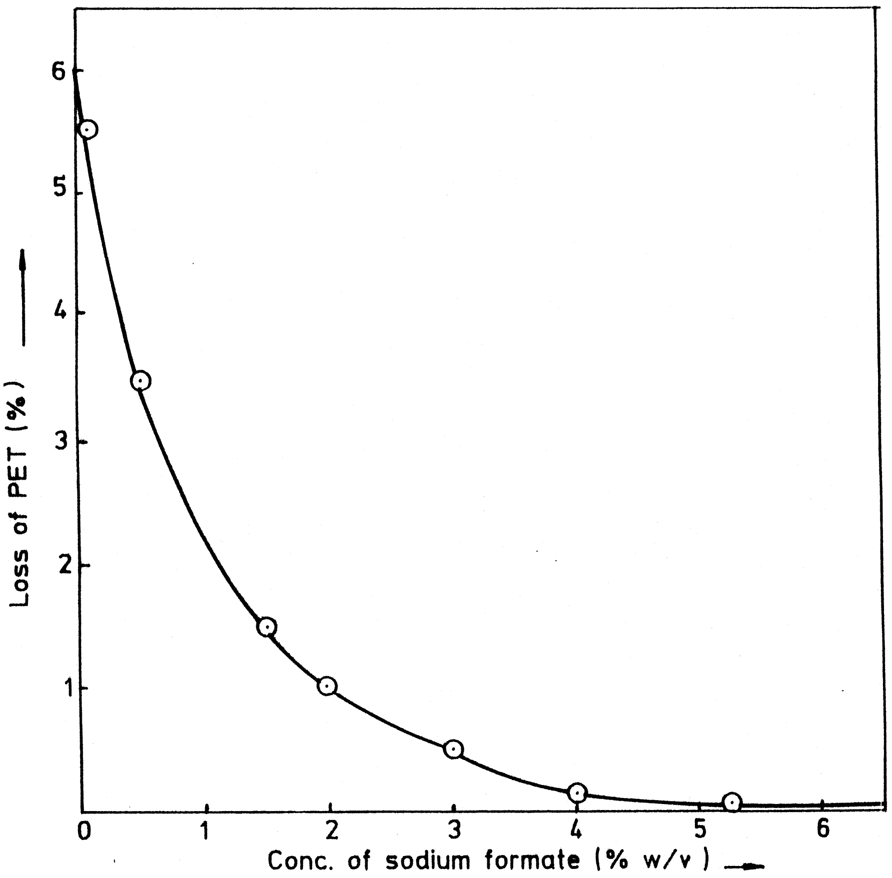

FIG. 5 Loss of PET vs concentration of NaFm.

possibly some PET are also transported with the transport of ions due to diffusion. Due to water and PET diffusion, the volume of the diluate stream is continuously reduced. This volume change with time is represented in Fig. 4. The volume change is minimum when 25 V is applied.

Loss of PET vs concentration of NaFm in the diluate stream is shown in Fig. 5. As the concentration of NaFm in the diluate stream decreases, the loss of PET in that stream increases. The loss of PET is <1% (w/w) when the NaFm concentration in the diluate is ~2% (w/v), after which a sharp loss of PET is observed in the diluate stream with any further reduction of NaFm concentration in the same stream.

The experimental data results are summarized in Table 2. The following trends can be seen:

(1) The best results are obtained with 25 V, where current efficiency was the highest, and water transport and PET loss were lowest. Although a higher voltage (30 V) favors the rate of ion transport, it also enhance polarization which affects C.E. and PET loss badly.

TABLE 2
Experimental Data of Separation of Sodium Formate (NaFm) and Pentaerythritol (PET)

Voltage (V)	Duration (min)	Volume (ml)		Concentration of NaFm (% w/v)		Concentration of PET (% w/v)		PET loss (%)	C.E. (%)
		Diluate	Concentrate[a]	Diluate	Concentrate	Diluate	Concentrate		
20	0	2300	2200	5.40	—	9.00	—	—	—
	190	2150	2120 (C_1)	1.10	4.10	—	0.60	—	76.1
	305	2080	1300 (Final)	0.72	2.62	8.67	0.41	10.2	65.2
25	0	2300	2200	5.40	—	9.00	—	—	—
	170	2230	2250 (C_1)	0.65	4.10	—	0.41	—	80.7
	260	2020	1470 (Final)	0.10	4.10	11.10	0.35	4.8	76.0
30	0	2300	2200	5.40	—	9.00	—	—	—
	180	2000	2200 (C_1)	0.40	4.40	—	0.70	—	74.4
	250	1900	1000 (Final)	0.10	2.00	10.50	0.80	6.2	70.7

[a] C_1 = Concentrate lot which was replaced with fresh distilled water.

(2) Concentrate-1 (C_1), containing 4.1% (w/v) NaFm and 0.41% (w/v) PET, was removed after 170 minutes and the experiment was continued with fresh distilled water. By this procedure the final concentration of NaFm in the diluate stream could be reduced to 0.1% (w/v) with minimum loss of PET (4.8%). The final lot concentrate also contained 4.1% (w/v) NaFm.

CONCLUSION

- An electrodialysis process using interpolymeric ion-exchange membranes prepared in this Institute can be conveniently used to separate sodium formate (NaFm) from pentaerythritol (PET).
- The reduction of NaFm in the final diluate stream can be lowered from 5.4% (w/v) to 0.1% (w/v) with a current efficiency of 76% by operating an ED stack containing 15 cell pairs of cation- and anion-exchange membranes (the effective cross-sectional area of a single membrane is 80 cm^2) at 25 V.
- At 25 V, when the concentration of NaFm in the diluate stream is 0.65% (w/v) and that in the concentrate stream is 4.1% (w/v) (i.e., after 170 minutes), the concentrate (C_1) is replaced by demineralized water before the experiment is continued.
- The loss of PET is only about 5%.
- Three solutions are obtained by this method. (1) A final diluate containing 11.1% (w/v) PET and only 0.1% (w/v) NaFm. (2) A concentrate-1 con-

taining 4.1% (w/v) NaFm and 0.41% (w/v) PET. (3) A final concentrate containing 4.1% (w/v) NaFm and 0.35% (w/v) PET.

- This investigation demonstrates the technical feasibility of separating NaFm from PET.

REFERENCES

1. Y. Hara, *Bull. Chem. Soc. Jpn.*, *36*(11), 1373 (1963).
2. F. Leitz, *Environ. Sci. Technol.*, *10*(2), 136 (1979).
3. R. Audinos, *Rev. Gen. Electr.*, *88*(1), 858 (1989).
4. R. W. Kilburn and H. P. Gregor, US Patents 3,165,415 (January 12, 1965) and 3,265,607 (August 9, 1966).
5. J. A. Zang, *Proceedings of the Symposium on Membrane Processes for Industry* (Birmingham, Alabama, USA, May 19–20, 1966), p. 35.
6. N. A. Gordona and M. J. Milan, *Desalination*, *35*, 317 (1980).
7. S. K. Adhikary, W. P. Harkare, K. P. Govindan, and A. M. Nanjundaswamy, *Indian J. Technol.*, *21*, 120 (1983).
8. S. K. Adhikary, W. P. Harkare, K. P. Govindan, K. C. Chikkappaji, S. Saroja, and A. M. Nanjuncdaswamy, *Ibid.*, *25*, 24 (1987).
9. J. D. Wagner, G. R. Lappin, and J. R. Zieth, in *Encyclopedia of Chemical Technology* (R. E. Kirk and D. F. Othmes, Ed, 4th ed., Vol. 1, Wiley, New York, NY, 1991, p. 913.
10. S. K. Thampy, P. K. Narayanan, D. K. Chauhan, S. K. Adhikary, and V. K. Indusekhar, *Water Treat.*, *6*, 385 (1991).
11. F. J. Welcher (Ed.), *Standard Methods of Chemical Analysis*, Vol. 2, Part B, Van Nostrand, NJ, 1963, p. 1655.

Received by editor November 17, 1998
Revision received February 1999

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