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Separation of Calcium and Cadmium by Electrodialysis in the Presence of Ethylenediaminetetraacetic Acid

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ABSTRACT

The separation of calcium and cadmium ions in a system containing ethylenediaminetetraacetic (EDTA) as the complexing agent has been studied using a laboratory-scale batch electrodialyzer. The theoretical distribution diagram constructed for the Ca–Cd–EDTA system suggested that cadmium preferably formed negatively charged complexes while calcium remained in the positively charged uncomplexed form. The experimental results confirmed that under the influence of an electric field, calcium was exclusively transported to the cathode while more than 90% of cadmium totally removed from the middle compartment of the batch electrodialyzer migrated toward the anode. The separation effect resulting from EDTA complexation was studied within the 1.5–4.0 pH range.

Key Words. Calcium; Cadmium; Electrodialysis; EDTA

INTRODUCTION

The ion-exchange electrodialysis process is a membrane separation technique widely used to separate different charged ions. Electrodialysis is used today for the production of potable water by desalination (1–3), the recovery of water and valuable metal ions from industrial effluents (1, 2, 4), the removal

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of salts and acids from pharmaceutical solutions and in food processing (1, 5, 6), and for the production of salts from seawater (2). When an electrodialysis separation technique is applied to a multicomponent system, the transfer direction and transfer rate for each ion depend on its charge and mobility, solution conductivity, relative concentrations, applied voltage, etc. Because ions of the same charge move to the same electrode, their separation is closely related to the characteristics of the ion-exchange membrane, especially its permselectivity in the system being used (2).
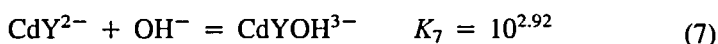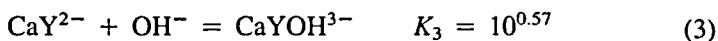
Several papers have been published on the preferential transport of ions through an ion-exchange membrane with electrodialysis in the absence of a complexing agent in which the permselectivities of both cation-exchange membranes and anion-exchange membranes were studied (7–11). A metal ion separation process which combines the electrodialysis technique and complexing reactions has recently received attention. This process is characterized by its high selectivity for one metal in a two-metal system, resulting basically from different stabilities of the two or more complexes involved. For example, by using citric acid or glycine as the complexing agents in electrodialysis of the Cu–Ni system, the transport of Ni ions through cation-exchange membrane was preferred (12). However, employing complexing agents in the electrodialysis process may influence not only the permselectivity of the membrane but also the transport behavior of metal ions in the bulk solution, as shown in the separation of silver from zinc and copper using ethylenediaminetetraacetic acid (EDTA) as a complexing agent (13). As the charges of the complexes formed exhibited different signs, silver was obtained with an acceptable yield in the cathode section whereas the copper and zinc were obtained in the anode section.

THEORETICAL CONSIDERATIONS

Consider an aqueous solution containing equimolar concentrations of calcium and cadmium. When EDTA is added to the solution, it is distributed between the two metals in a ratio whose value depends on many conditions. The complex equilibrium established is mainly influenced by the reactants' concentrations, ionic strength of the solution, pH value, temperature, etc. In this work, simplified complex equlibrium diagrams including calcium, cadmium, and EDTA were calculated in the 0–12 pH range at a temperature of 25°C.

The presence of four different Ca–EDTA complexes were experimentally proved when a system containing calcium and EDTA at different pH values was studied. Likewise, three different Cd–EDTA complexes were defined in a system containing cadmium and EDTA. By using Eqs. (1)–(7), the thermo-

dynamic equilibrium constants K_1-K_7 were defined (14) as shown in the following (H_4Y represents EDTA):

$$Ca^{2+} + HY^{3-} = CaYH^- \qquad K_1 = 10^{3.51} \qquad (1)$$

$$Ca^{2+} + Y^{4-} = CaY^{2-} \qquad K_2 = 10^{10.77} \qquad (2)$$

$$CaY^{2-} + OH^- = CaYOH^{3-} \qquad K_3 = 10^{0.57} \qquad (3)$$

$$2Ca^{2+} + Y^{4-} = Ca_2Y \qquad K_4 = 10^{12.52} \qquad (4)$$

$$Cd^{2+} + HY^{3-} = CdHY^- \qquad K_5 = 10^{9.10} \qquad (5)$$

$$Cd^{2+} + Y^{4-} = CdY^{2-} \qquad K_6 = 10^{16.50} \qquad (6)$$

$$CdY^{2-} + OH^- = CdYOH^{3-} \qquad K_7 = 10^{2.92} \qquad (7)$$

Additional balance equations can be derived for the sum of the total calcium species (Ca_t), the sum of the total cadmium species (Cd_t), and the sum of the total EDTA species $(EDTA_t)$. To simplify the calculations, molar concentration are used instead of activities.

$$(Ca_t) = (Ca^{2+}) + 2(Ca_2Y) + (CaYH^-) + (CaY^{2-}) + (CaYOH^{3-})$$
$$(8)$$

$$(Cd_t) = (Cd^{2+}) + (CdYH^-) + (CdY^{2-}) + (CdYOH^{3-}) \qquad (9)$$

$$(EDTA_t) = (H_4Y) + (H_3Y^-) + (H_2Y^{2-}) + (HY^{3-}) + (Y^{4-})$$
$$+ (Ca_2Y) + (CaYH^-) + (CaY^{2-}) + (CaYOH^{3-}) \quad (10)$$
$$+ (CdYH^-) + (CdY^{2-}) + (CaYOH^{3-})$$

By solving Eqs. (1)–(10) the equilibrium distribution diagram of the system Ca-Cd-EDTA was calculated assuming $(Ca_t) = 0.01$ M, $(Cd_t) = 0.01$ M, and $(EDTA_t) = 0.01$ M. To reflect the very unequal complexation of the two metals studied, the resulting distribution diagram is presented in Fig. 1a using a linear scale y-axis and in Fig. 1b using a logarithmic scale y-axis.

As can be seen from both Figs. 1a and 1b, the Ca^{2+} ion is the dominant calcium ion in the whole pH range studied. Under the conditions given, the calcium complexation is practically negligible within pH 0–12 and the concentration of the Ca^{2+} ions is equal or very close to 0.01 M. Cadmium, on the other hand, remains in the form of the Cd^{2+} ions only in the low pH region of the distribution diagram, and from a pH of about 0.5 the Cd^{2+} ions start to be converted into the negatively charged $CdYH^-$ complex. At about pH 2.0 approximately 90% of cadmium is in the form of the $CdYH^-$ complexed ion and at the pH about 3.0 less then 1% of cadmium remains in the form of uncomplexed Cd^{2+} ion. It follows from the distribution diagram that
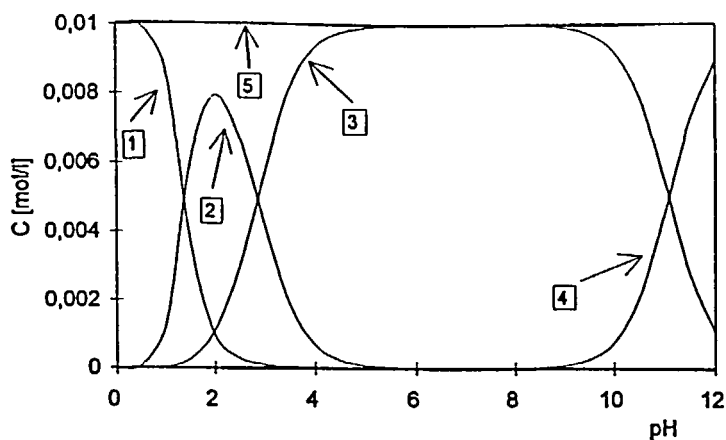
FIG. 1a   The equilibrium distribution diagram for the Ca–Cd–EDTA system (Ca_t = 0.01 M, Cd_t = 0.01 M, $EDTA_t$ = 0.01 M) with a linear scale y-axis: (1) Cd^{2+}, (2) $CdHY^-$, (3) CdY^{2-}, (4) $CdYOH^{3-}$, (5) Ca^{2+}.
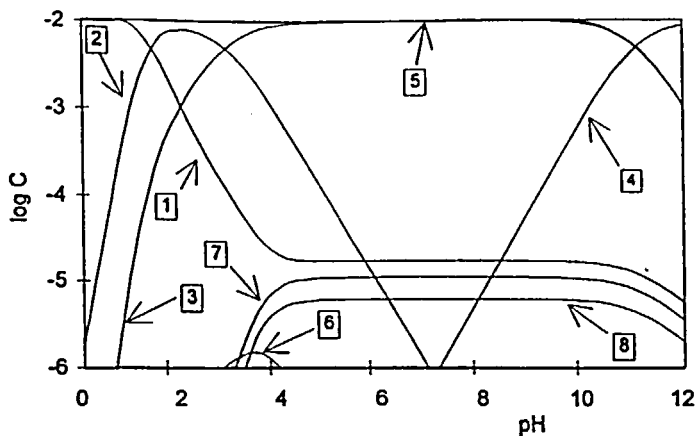
FIG. 1b   The equilibrium distribution diagram for the Ca–Cd–EDTA system (Ca_t = 0.01 M, Cd_t = 0.01 M, $EDTA_t$ = 0.01 M) with a logarithmic scale y-axis: (1) Cd^{2+}, (2) $CdHY^-$, (3) CdY^{2-}, (4) $CdYOH^{3-}$, (5) Ca^{2+}, (6) $CaHY^-$, (7) CaY^{2-}, (8) Ca_2Y.

starting from approximately pH 3.0, cadmium is almost fully complexed in the form of negatively charged ions while calcium remains in the form of positively charged Ca^{2+} ions. Ca^{2+} ions should migrate toward the cathode when introduced into the electric field, while the negatively charged cadmium complexes should migrate toward the anode.

The distribution diagram of the Ca–Cd–EDTA system also predicts the existence of a Ca_2Y calcium complex which formally is uncharged and consequently immobile in the electric field. However, it follows from Fig. 1b that the participation of this complexed calcium form is negligible within the total calcium content considered.

It should be noted that the assumptions following from the theoretical distribution diagram are of limited value when applied to a real solution containing other types of ions besides those included in the diagram. Depending on its ionic strength, the distribution lines in a real solution may be shifted when compared with the theoretical diagram. To prove the validity of the theoretical considerations, experiments were carried out in the most interesting pH range.

EXPERIMENTAL

In this work a laboratory-scale electrodialysis glass cell, cylindrical in shape, was used as schematically shown in the Fig. 2. The middle compartment was 10 cm long, 4 cm in diameter, and it was separated from the two electrode compartments of the same diameter by a heterogeneous cation-exchange membrane (RALEX C) and a heterogeneous anion-exchange membrane (RALEX A) produced by MEGA a. s. in Stráž p. Ralskem, Czech Republic. The basic characteristics of the membranes used are summarized in Table 1.

Each electrode compartment was connected to the glass bottle using silicone tubes through which the electrolytes circulated. At the beginning of each experiment 125 mL of the feed solution [0.01 M $Ca(NO_3)_2$ + 0.01 M $Cd(NO_3)_2$; 0.01 M $Ca(NO_3)_2$ + 0.01 M $Cd(NO_3)_2$ + 0.01 M Na_2EDTA, respectively] were introduced into the middle compartment while 2000 mL of 0.01 M $NaNO_3$ was circulating through each electrode compartment. The electrolyte in the middle compartment was not circulated. The pH values in both the anode and cathode compartments were set at 2.5 and kept constant by the automatic titration of nitric acid and sodium hydroxide, respectively. The pH value in the middle compartment was measured periodically through a special tube connected to the glass wall of the middle compartment. If the pH changed more than 0.05 in the middle compartment, it was set again by using a nitric acid addition after which the electrolyte was mixed. The experiments were carried out under galvanostatic conditions with 50 mA (3.98 mA/cm^2) passing through the electrodialysis cell for 5 hours at a constant temperature of 25°C. Practically no calcium and
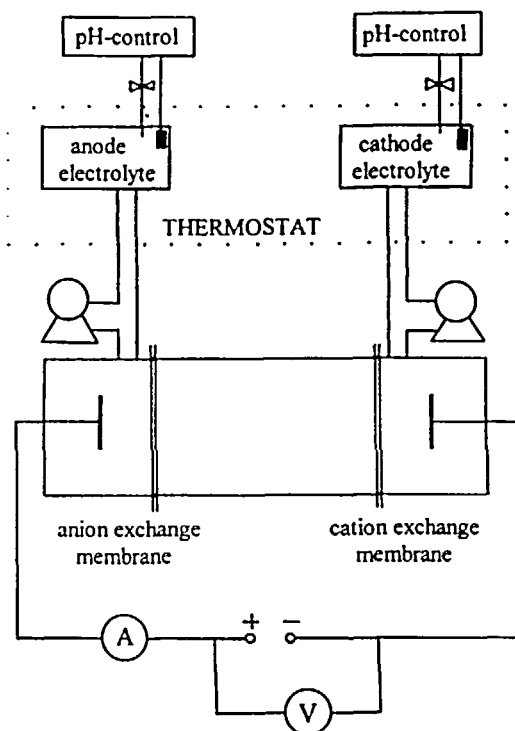
FIG. 2   Schematic representation of the laboratory electrodialysis apparatus.

TABLE 1
Basic Characteristics of the Ion-Exchange Membranes Used
(electrochemical properties measured in 0.1 M NaCl solution)[a]

	Cation-exchange membrane, RALEX C	Anion exchange membrane, RALEX A
Functional group	$-SO_3^-$	$-(CH_3)_3N^+$
Thickness of swollen membrane (mm)	0.4–0.6	0.5–0.8
Area specific resistance (ohm·cm²)	5–11	4–12
Specific resistance (ohm·cm)	100–180	80–200
Transport number of counterion	>0.97	>0.96
Capacity (mval/dry g)	2.2	1.8

[a] Membranes characteristics provided by the producing company.

only a negligible amount of cadmium were deposited at the cathode in the course of the experiments. Ten milliliters of the sample was pipetted from each electrode compartment periodically and analyzed using atomic absorption spectroscopy (detection limit 0.01 mg/L for both calcium and cadmium). As the relatively small volume of the middle compartment did not allow periodic sampling, the concentrations of calcium and cadmium in it were measured only after finishing each experiment. Each electrodialysis experiment was repeated four times, and the resulting data were treated by the linear regression method. All the chemical reagents used in this work were of analytical grade, and demineralized water was used for preparation of the solutions.

RESULTS AND DISCUSSION

To confirm the applicability of the theoretical equilibrium diagrams constructed for the Ca–Cd–EDTA system, a laboratory-scale batch electrodialysis apparatus was used to separate an equimolar mixture of calcium and cadmium both in the absence and in the presence of EDTA. As the pH value of the system was an important factor influencing the complex equilibria, the equimolar Ca–Cd solutions containing EDTA were treated by electrodialysis at the six different pH values: 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0. The results of the laboratory scale-electrodialytical processing of the equimolar mixture of calcium nitrate and cadmium nitrate at pH 2.0 without EDTA are shown in the Fig. 3, while the results of processing the same mixture in the presence of EDTA at the different pH values are summarized in Fig. 4(a–f).

FIG. 3   Time dependence of the transport degree $\Delta m/m$ for calcium and cadmium ions in the absence of EDTA [$Ca(NO_3)_2$ = 0.01 M, $Cd(NO_3)_2$ = 0.01 M, pH 2.0]. Calcium transport toward cathode (——); cadmium transport toward cathode (- - -).
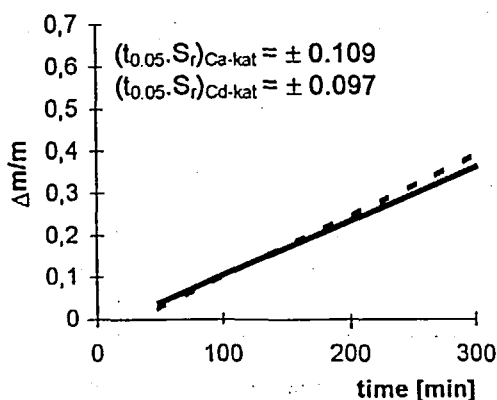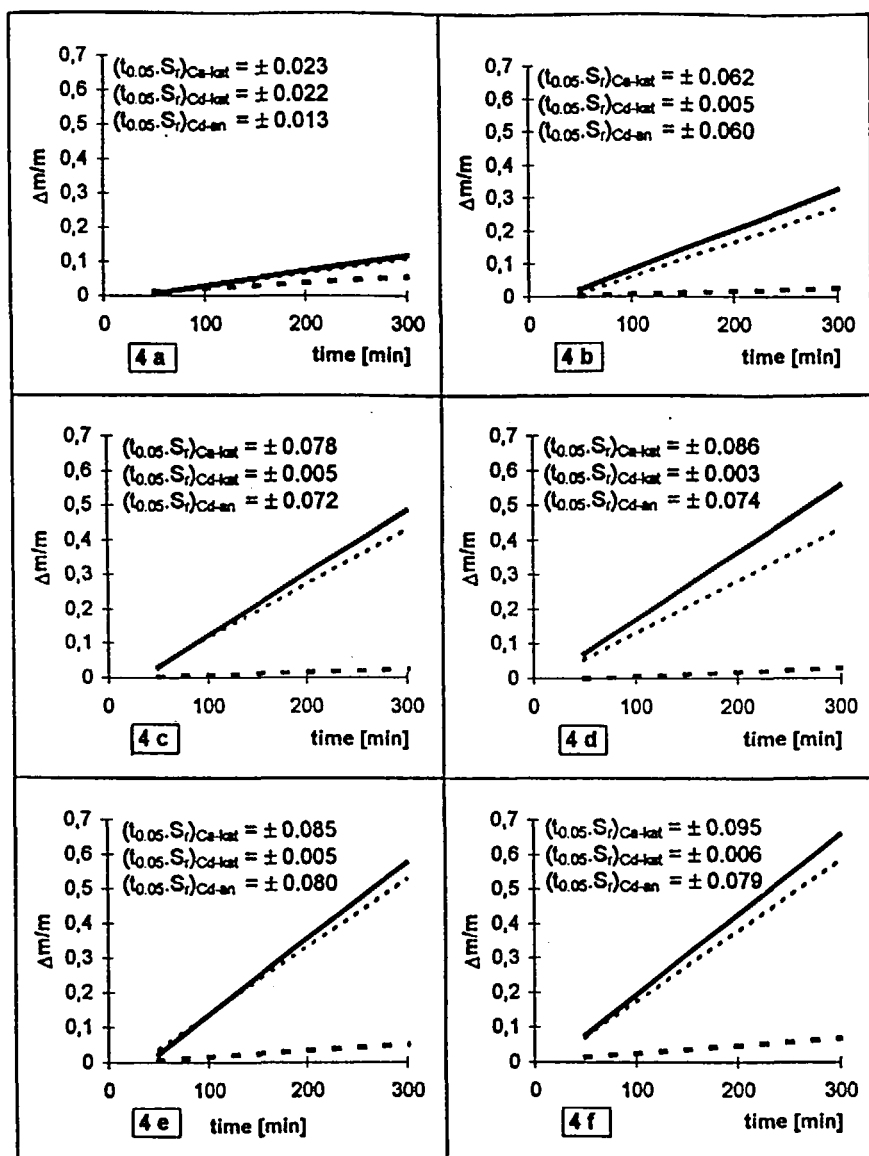
FIG. 4   Time dependence of the transport degree $\Delta m/m$ for calcium and cadmium ions in the presence of EDTA [$Ca(NO_3)_2 = 0.01$ M, $Cd(NO_3)_2 = 0.01$ M, $Na_2EDTA = 0.01$ M, a) pH 1.5, b) pH 2.0, c) pH 2.5, d) pH 3.0, e) pH 3.5, f) pH 4.0]. Calcium transport toward cathode (——) and anode (——); cadmium transport toward cathode (- - -) and anode (- - -).

TABLE 2

Current Efficiencies for Different Compositions in the Middle Compartment
of the Electrodialysis Apparatus

Middle compartment composition	Current efficiency (R_i)					
	Transport to the cathode			Transport to the anode		
	Ca^{2+}	Cd^{2+}	Na^+	Ca complex	Cd complex	NO_3^-
Without EDTA, pH 2.0	0.061	0.068	—	—	—	0.482
EDTA, pH 1.5	0.032	0.029	0.022	0.000	0.004	0.470
EDTA, pH 2.0	0.086	0.007	0.052	0.000	0.042	0.442
EDTA, pH 2.5	0.107	0.013	0.072	0.000	0.067	0.405
EDTA, pH 3.0	0.147	0.009	0.098	0.000	0.087	0.392
EDTA, pH 3.5	0.155	0.013	0.140	0.000	0.125	0.361
EDTA, pH 4.0	0.169	0.014	0.166	0.000	0.140	0.349

The straight-line time dependencies included in Figs. 3 and 4 are the results of linear regression of the experimental data based on the four repeated experiments at each pH value. The experimental data were treated by the least-squares method to provide the linear lines defined by

$$\Delta m/m = bt + a \pm (t_{0.05}^+ S_r)$$

where $\Delta m/m$ is the increment of the species in the electrode compartments relative to the original amount in the middle compartment, t represents time, a and b represent constants resulting from linear regression treatment, and the expression $(t_{0.05}^+ S_r)$ defines the confidence limits, in which $t_{0.05}^+$ is a constant that follows from the Student distribution and S_r is the estimated standard deviation.

Table 2 summarizes the values of current efficiencies R_i obtained by determining the charges transported by different ions relative to the total charge passed using the equation

$$R_i = Q_i/Q_t$$

where Q_t is the total charge passed through the cell in the course of the experiment and Q_i is defined by

$$Q_i = M_i nF$$

where M_i is the molar amount of a metal in the anode or cathode compartment at the end of the experiment resulting from linear regression treatment, n is the valency of the ion transferred, and F is the Faraday constant (96,500 C/mol).

When an equimolar solution of calcium and cadmium was treated by electrodialysis in the absence of EDTA, both metals were quantitatively transported to the cathode (Fig. 3). The transport rates of these two ions toward the cathode were very similar, which does not fully correspond to the values of their ionic mobilities in bulk solution which are slightly different [$\mu_{Ca} = 617 \times 10^{-6}$ cm^2/V·s, $\mu_{Cd} = 736 \times 10^{-6}$ cm^2/V·s for infinite dilution (15)]. The very similar transport rates observed in our experiments could result from the characteristics of the cation-exchange membrane used, which might have a preference for calcium transport. Unfortunately, no experimental data were found in the references dealing with the permselectivity of RALEX ion-exchange membranes for ion systems with a 2+ valency. It further follows from the numerical values of the confidence intervals included in Fig. 3 that the data from our repeated experiments were not fully consistent (new pieces of membrane were used for each experiment). For heterogeneous ion-exchange membranes, however, the lower reproductibility of the experimental results is expected when compared with homogeneous membranes.

Figure 4(a) shows the transport behavior in the system containing calcium and cadmium in the presence of EDTA at pH 1.5. At this pH value about 60% of the total cadmium content should theoretically be in complexed form (CdHY$^-$) and consequently be transported toward the anode according to the equilibrium diagram. In the experiments performed, only about 40% of the cadmium totally removed from the middle compartment was found in the anode section, which might correspond to the simplifications made during construction of the diagram. As emphasized above, the distribution lines in the real solution are shifted to a certain extent when compared with the theoretical diagram because concentrations were used instead of activities in the diagram's calculations. It follows from Fig. 4(a) and Table 2 that only a small part of the current which passed through the system was employed to transport the calcium and cadmium forms present, while most of the current transported the other ions present: H$^+$, Na$^+$, NO$_3^-$.

Figure 4(b) shows the results from experiments performed with the system containing calcium and cadmium in the presence of EDTA at pH 2.0. At this pH value approximately 90% of the total cadmium present may be expected to be complexed as the CdHY$^-$ form while the calcium is practically only in the form of the Ca^{2+} ion, according to the equilibrium diagram. In good agreement with the diagram, calcium was practically completely (no measurable calcium in the anode section) transported to the cathode in the form of positively charged ions while more than 90% of the cadmium totally removed from the middle compartment migrated toward the anode.

Figures 4(c–f) show the results of experiments carried out in systems containing calcium and cadmium in the presence of EDTA at the pH values of

2.5, 3.0, 3.5, and 4.0. It follows from the distribution diagram that only a very small part of cadmium is theoretically expected to be in the form of uncomplexed Cd^{2+} ion at pH 2.5, and practically no uncomplexed cadmium should exist at pH values higher than approximately 3.0. Theoretically, calcium is expected to be only in the form of the Ca^{2+} ion in the 2.5–4.0 pH range. The experimental results measured in the 2.5–4.0 pH range show a very similar transport behavior for both complexed and uncomplexed species. Although practically no uncomplexed Cd^{2+} ions are predicted by the equilibrium diagram for this pH range, small amounts of cadmium were found in the cathode section in all these experiments. As shown in Table 2, the amounts of cadmium transported toward the cathode ranged between about 5–10% of the cadmium totally removed from the middle compartment. This partial cadmium accumulation in the cathode compartment suggests that the real transport behavior in the Ca–Cd–EDTA system is not fully in agreement with predicitions based on the theoretical equilibrium diagram.

It further follows from Table 2 that the current efficiencies of uncomplexed calcium and complexed cadmium species increase with increasing pH values in the middle compartment, which can be explained by decreasing participation of hydrogen ions in the passing current.

The linear dependencies shown in Figs. 3 and 4(a–f) do not intersect the zero value on the x-axis, which means that calcium and cadmium species were initially detected in the anode and cathode sections after a definite time interval had passed. These time intervals ranged between about 25–40 minutes. As the membranes used in the experiments were in the Na^+ form (cation-exchange membrane) and the NO_3^- form (anion-exchange membrane), before being introduced into the experimental apparatus, the first step in time might be accounted for by the transport of the ions which originally saturate the membranes.

It follows from Fig. 4(a–f) that transport degrees of uncomplexed calcium and complexed cadmium ions were very similar in all the experiments which included EDTA. As the Ca^{2+} ion size is assumed to be much smaller than that of the complexed cadmium ion, quite different transport rates were expected. For example, it was shown by Cherif et al. (13), who studied electrodialytic separation in the system Ag–Zn–EDTA, that the transport rate of uncomplexed Ag^+ ions was about three times higher than that of complexed zinc ions. The very similar transport rates of uncomplexed calcium and complexed cadmium ions observed in the system Ca–Cd–EDTA suggests as a hypothesis the formation of some kind of associated product in the middle compartment which includes both calcium and cadmium, thus limiting the transport of Ca^{2+} ions into the cathode compartment.

CONCLUSIONS

·The electrodialysis of an equimolar mixture of calcium and cadmium in the presence of ethylenediaminetetraacetic acid (EDTA) was found to be an effective method to separate calcium and cadmium.

In a system containing 0.01 M $Ca(NO_3)_2$, 0.01 M $Cd(NO_3)_2$, and 0.01 M Na_2EDTA, calcium remained practically completely in the form of the Ca^{2+} ions in the whole pH range studied. Starting from pH 2.0, most of cadmium present in the solution was complexed in the form of negatively charged ions. When calcium was introduced into the middle compartment of the experimental electrodialyzer, it was exclusively transported toward the cathode within the 1.5–4.0 pH range. In the 2.0–4.0 pH range, about 90–95% of cadmium totally removed from the middle compartment was transported toward the anode. The remaining 5–10% of cadmium totally removed from the middle compartment was transported toward the cathode in this pH range.

REFERENCES

1. H. K. Lonsdale, *J. Membr. Sci.*, *10*, 81–181 (1981).
2. P. M. Bungay, H. K. Lonsdale, and M. N. de Pinho, *Synthetic Membranes: Science, Engineering and Application*, D. Riedel Publishing Co., Dordrecht, Holland, 1986.
3. A. Lounis and C. Gavach, *J. Membr. Sci.*, *52*, 332–348 (1990).
4. T. C. Huang and J. K. Wang, *Can. J. Chem. Eng.*, *67*, 385–391 (1988).
5. M. Boundet-Dumy, A. Lindheiner, and C. Gavach, *J. Membr., Sci.*, *57*, 57–68 (1991).
6. T. C. Huang and I. Y. Yu, *Ibid.*, *35*, 193–206 (1988).
7. A. T. Dibenedetto and E. N. Lightfoot, *AIChE J.*, *8*, 79–86 (1962).
8. A. T. Dibenedetto and E. N. Lightfoot, *Ind. Eng. Chem. Fundam.*, *50*, 691–696 (1958).
9. A. Kitamoto and Y. Takashima, *J. Chem. Eng. Jpn.*, *3*, 54–61 (1970).
10. W. G. B. Mandersloot, *Bull. Chem. Soc. Jpn.*, *37*, 1443–1449 (1964).
11. T. C. Huang and T. T. Wang, *Desalination, 21*, 327–340 (1977).
12. T. C. Huang and J. K. Wang, *Ibid.*, *86*, 257–271 (1992).
13. A. T. Cherif, A. Elmidaoui, and C. Gavach, *J. Membr. Sci.*, *76*, 39–49 (1993).
14. A. E. Martell, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, 1964.
15. Y. B. Acar and A. N. Alshawabkeh, *Environ. Sci. Technol.*, *27*, 2638–2647 (1993).