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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Recovery of Manganese(II) by Electrodialysis with Liquid Membranes Based on Di(2-ethylhexyl)phosphoric Acid

T. Zh. Sadyrbaeva

Institute of Inorganic Chemistry of Riga Technical University, Salaspils, Latvia

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Abstract—Electrodialysis membrane extraction of manganese(II) from sulfuric acid solutions with liquid membranes containing di(2-ethylhexyl)phosphoric acid and tri-*n*-octylamine in 1,2-dichloroethane was studied. The effect of the electrodialysis conditions and the composition of the organic phase and aqueous solutions on the transport rate of manganese(II) ions was examined. The conditions of quantitative recovery of the metal from a 0.01 M $MnSO_4$ solution were determined.

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Di(2-ethylhexyl)phosphoric acid (D2EHPA) effectively extracts metal cations from weakly acidic and neutral solutions and is widely used in hydrometallurgy [1]. The method of membrane extraction is promising for recovery, separation, and concentration of rare and toxic elements. Di(2-ethylhexyl)phosphoric acid has been used as a transport agent for recovery of manganese(II) with emulsion [2], bulk [3], and impregnated [4, 5] liquid membranes. Application of an external electric field intensifies the ion transport across liquid membranes and facilitates the re-extraction of metals [6]. There are no published data on the electrodialysis membrane extraction of manganese(II) with D2EHPA. The recovery of copper(II) from sulfate solutions with D2EHPA-containing liquid membranes under electrodialysis conditions was studied in [7–9].

It has been found previously [10, 11] that liquid membranes containing technical-grade D2EHPA and tri-*n*-octylamine (TOA) can effectively recover Cu^{2+} and Ag^{+} ions from weakly acidic solutions and separate copper cations from anionic chloro complexes of palladium(II) and platinum(IV) under galvanostatic electrodialysis conditions.

This communication reports on a study of the electrodialytic transport of manganese(II) from sulfuric acid solutions across bulk liquid membranes composed of solutions of D2EHPA with addition of TOA in 1,2-dichloroethane. TOA is used because the electrical conductivity of solutions of technical-grade D2EHPA containing a considerable amount of a strongly associated monoalkylphosphoric acid [1] is low.

EXPERIMENTAL

The recovery of manganese(II) ions was studied in a five-chamber fluoroplastic cell comprising two electrode chambers, chambers of the donating and receiving solutions, and a vertical liquid membrane confined between cellophane films:

(+) Pt, H_2SO_4	$MnSO_4$, H_2SO_4	D2EHPA TOA 1,2-dichloroethane	Receiving solution	H_2SO_4, Pt (–)

The diameter, average thickness, and volume of the liquid membrane were 3 cm, 0.28 cm, and 0.2 cm^3, respectively. A *dc* current was delivered to planar platinum electrodes and the process was performed in the galvanostatic mode. The current density was calculated on the basis of the liquid membrane area of 7.1 cm^2. The cellophane films confining the liquid membrane were preliminarily soaked in water. The electrode chambers (volume 17 cm^3) were separated from the chambers of the donating and receiving solutions (volume 13 cm^3) by MA-40 solid ion-

exchange membranes. As electrode solutions was used 0.15 M H_2SO_4.

As liquid membranes served solutions of technical-grade D2EHPA with addition of TOA (pure grade) in 1,2-dichloroethane. The content of the main substance in the technical-grade D2EHPA, $c \geq 63\%$; in addition, the extractive agent contained about 16% of mono(2-ethylhexyl)phosphoric acid, 6% of tri(2-ethylhexyl)-phosphate, and alcohols. As a rule, 20 vol % (0.36 M) solutions of D2EHPA with addition of 0.1 M of TOA were used as liquid membranes. The donating solution was prepared by dissolution of $MnSO_4$ in 0.01 M sulfuric acid. Anhydrous salt $MnSO_4$ was obtained by calcination of $MnSO_4 \cdot 5H_2O$ at 400°C. The initial manganese(II) concentration was commonly 0.01 M. As a rule, 0.1 or 0.25 M H_2SO_4 was used as a receiving solution. The content of manganese(II) ions in aqueous solutions was determined by the spectrophotometric method with formaldoxime [12]. The optical density of the solutions was measured with an SF-46 spectrophotometer.

The interaction of D2EHPA with TOA in organic solutions is accompanied by the proton transfer and formation of an ionic pair [13]:

$$R_3N + HA \rightleftarrows R_3NH^+A^-, \quad (1)$$

where R_3N is tri-*n*-octylamine, and HA stands for D2EHPA.

The recovery of manganese(II) cations into the organic phase occurs by the binary extraction mechanism:

$$Mn^{2+}_{aq} + SO^{2-}_{4aq} + 2R_3NHA_{org} \rightleftarrows MnA_{2\,org} + (R_3NH)_2SO_{4\,org}, \quad (2)$$

where "aq" and "org" denote the aqueous and organic phases.

The manganese(II) complex being extracted can dissociate in a polar organic solvent [14]:

$$MnA_{2\,org} \rightleftarrows Mn^{2+}_{org} + 2A^-_{org}. \quad (3)$$

Cations Mn^{2+} from the bulk of the donating solution are transferred to the phase boundary by diffusion and interact with the extractive agent. The resulting complex is transferred across the liquid membrane by means of electromigration. The reextraction of manganese(II) from the organic phase occurs by the reaction that is reverse with respect to (2), under the action of the electric field. It was found in preliminary experiments that, without an electric field, only 6.5% of manganese(II) is extracted into the liquid membrane in 1 h and manganese(II) almost does not pass into the 0.25 M H_2SO_4 receiving solution. Application of an electric field substantially intensifies the recovery of Mn^{2+} ions from the donating solution and the metal is transferred across the liquid membrane. The driving force of the membrane extraction in electrodialysis is the electric field gradient, whereas in dialysis for metal recovery with organic acids, this is the pH gradient between the donating and receiving solutions [15]. Under the conditions of electrodialysis, hydrogen cations are transported across liquid membranes in the same direction as metal cations, and, therefore, neither high acidity of the receiving solution, nor adjustment of the pH of the receiving solution are necessary, in contrast to the case of a zero electric field. Anions from the receiving solution interact with the extractive agent and are transferred in the opposite direction, into the donating solution:

$$2R_3NHA_{org} + SO^{2-}_{4aq} \rightleftarrows (R_3NH)_2SO_{4\,org} + 2A^-_{org}. \quad (4)$$

As the electrodialysis current density increases within the range 2.1–8.5 mA cm^{-2}, the rate of the transmembrane transport of Mn^{2+} ions grows (Table 1). A nearly complete recovery of manganese(II) from a starting solution containing 0.01 M of $MnSO_4$ is achieved at current densities $i \geq 2.8$ mA cm^{-2}, with an experiment duration of 30 to 140 min, depending on the electrodialysis conditions. At a higher current density (8.5 mA cm^{-2}), the rate of metal recovery into the liquid membrane is at a maximum, but the degree of re-extraction into the receiving solution is insufficiently high ($E < 40\%$). At a low current density (2.8 mA cm^{-2}), the transfer of manganese(II) into the receiving solution begins 30 min after the electrodialysis is commenced (Table 1) and about 88% of the metal passes across the liquid membrane in the course of a prolonged experiment. With 0.1 M H_2SO_4 used as the receiving solution, the electrodialysis duration is, as a rule, limited by a steep rise in the voltage in the system (Fig. 1). This is due to a fall of the electrical conductivity of the starting solution, which apparently occurs because of the desalting of the donating solution as a result of the transfer of Mn^{2+} and H^+ cations into the liquid membrane and transport of SO_4^{2-} anions across the solid anion-exchange membrane into the anode chamber. With a more concentrated sulfuric acid solution, there is no rise in voltage, but quantitative recovery of manganese(II) from the starting solution is not achieved.

It should be noted that the process kinetics is strongly affected by the state of the MA-40 solid

Table 1. Effect of the current density i and composition of the receiving solution on the degree of recovery of manganese(II) ions, R, and transfer rate J[a]; c_{D2EHPA} = 20 vol %, c_{TOA} = 0.1 M

i, mA cm^{-2}	τ, min	Receiving solution (0.1 M)	R_1, %	R_2, %	$J_1\times10^5$, mol m^{-2} s^{-1}	$J_2\times10^5$, mol m^{-2} s^{-1}
2.1	130	H_2SO_4	79.4	57.6	1.9	1.4
2.8	30	The same	18.1	1.8	1.9	0.2
2.8	60	″	56.3	25.2	2.9	1.3
2.8	90	″	66.0	47.4	2.3	1.6
2.8	137	″	99.9	87.9	2.2	2.0
4.2	58	″	98.2	56.3	5.2	3.0
4.2	48	HCl	98.9	46.3	6.3	3.0
4.2	60	HNO_3	97.0	52.9	5.0	2.7
4.2	60	$HClO_4$	63.8	33.2	3.3	1.7
4.2	38	H_2O	98.6	29.5	8.0	2.4
6.4	32	H_2SO_4	97.9	43.2	9.4	4.2
8.5	26.5	The same	98.0	38.0	11.5	4.4

[a] (1) Into the liquid membrane and (2) into the receiving solution.

membranes. It was found that repeated use of anion-exchange membranes in experiments leads to a decrease in the rate of manganese(II) recovery and to an increase in the electrodialysis duration.

The current efficiency with respect to Mn^{2+} cations in a system with 0.01 M of $MnSO_4$ is about 13% at current densities of 2.1–6.4 mA cm^{-2}. The charge transfer across the liquid membrane is mostly by hydrogen cations from the donating solution and SO_4^{2-} anions from the receiving solution.

According to the data in Table 1, the transfer of Mn^{2+} cations occurs with approximately the same efficiencies into dilute solutions of sulfuric, hydrochloric, and nitric acids. With perchloric acid, the recovery rate decreases and the voltage remains constant during 1 h of electrodialysis (Fig. 2b, curve *4*). With

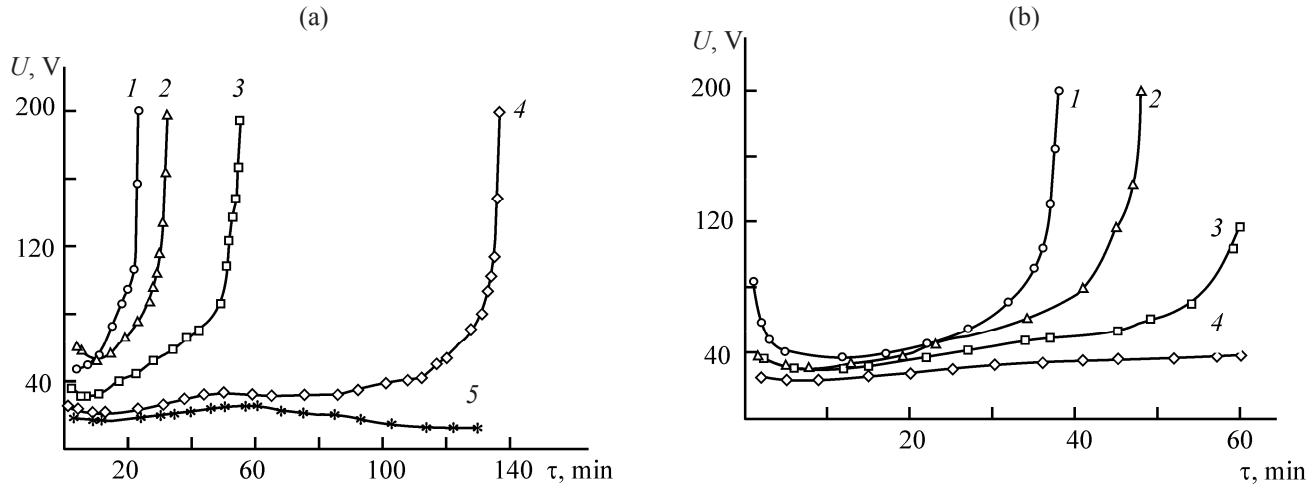

Fig. 1. Voltage U vs. the time τ at different (a) current densities and (b) compositions of the receiving solution. (a) Receiving solution 0.1 M H_2SO_4. i (mA cm^{-2}): (*1*) 8.5, (*2*) 6.4, (*3*) 4.2, (*4*) 2.8, and (*5*) 2.1. (b) i = 4.2 mA cm^{-2}, c_{D2EHPA} = 20 vol %, c_{TOA} = 0.1 M; the same for Fig. 3. Receiving solution (M): (*1*) H_2O, (*2*) 0.1 M HCl, (*3*) 0.1 M HNO_3, and (*4*) 0.1 M $HClO_4$.

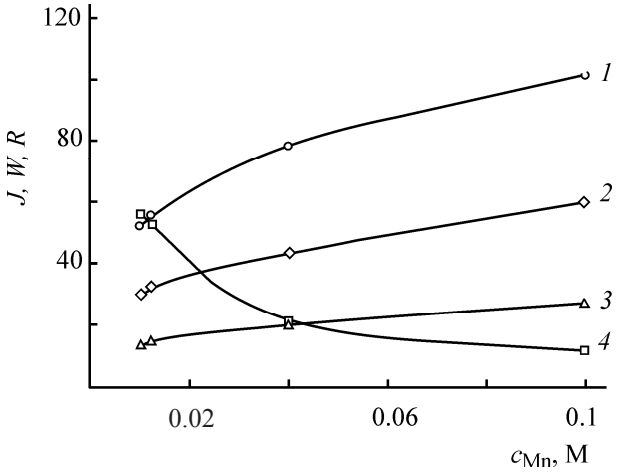

Fig. 2. Transfer rate J into (*1*) liquid membrane and (*2*) receiving solution, (*3*) current efficiency W, and (*4*) degree R of manganese(II) recovery vs. the manganese concentration cMn in the donating solution. i = 4.2 mA cm^{-2}, τ = 60 min, c_{D2EHPA} = 20 vol %, c_{TOA} = 0.1 M, receiving solution 0.1 M H_2SO_4.

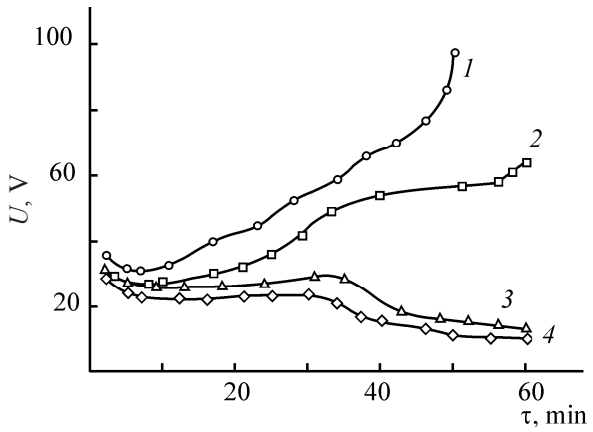

Fig. 3. Voltage U vs. the time τ at different manganese(II) concentrations in the donating solution. c_{Mn} (M): (*1*) 0.01, (*2*) 0.012, (*3*) 0.04, and (*4*) 0.1.

water used as a receiving solution, the rate of Mn^{2+} recovery into the liquid membrane is the highest, but, as a result, the voltage grows and the possible experiment duration decreases, with the degree of metal recovery into the receiving solution being lower than that in systems with acid solutions.

As the manganese(II) concentration in the sulfuric acid donating solution increases within the range 0.01–0.1 M, the rate of transfer of Mn^{2+} ions across the interfaces between the donating solution and the liquid membrane and between the liquid membrane and the receiving solution grows and the current efficiency becomes higher, but the degree of recovery decreases (Fig. 2). The voltage in systems with low manganese(II) concentration strongly increases already after several tens of minutes because of the complete recovery of the metal into the liquid membrane. At a high (≥0.04 M) concentration of Mn^{2+} ions, chronopotentiograms show a decrease in the voltage, which is probably due to accumulation of water in the liquid membrane (Fig. 3). Water is transferred into the liquid membrane in hydration-solvation shells of ions being extracted and via electroosmosis [16]. In the course of electrodialysis, through water channels can be formed in the organic phase, which leads to an electrical breakdown (an abrupt drop in voltage) and impairs the transport properties of the liquid membrane.

Raising the sulfuric acid concentration in the donating solution to above 0.01 M leads to a substantial decrease in the rate of manganese(II) recovery into the liquid membrane and the receiving solution (Fig. 2). This is due to a fall of the extracting capacity of D2EHPA upon an increase in the acidity of the aqueous phase. In the presence of an excess amount of the acid acting as a supporting electrolyte, charge is mostly transported across the membrane by hydrogen cations and the current efficiency by Mn^{2+} ions decreases.

Raising the content of the transport agent D2EHPA in the organic phase from 10 to 40 vol % at a constant concentration of the amine leads to a rise in the degree of manganese(II) recovery into the liquid membrane, but has nearly no effect on the transmembrane transport rate (Fig. 4a). Raising the TOA content of the liquid membrane at a constant transport agent concentration leads to a certain decrease in the recovery rate of

Table 2. Effect of the sulfuric acid concentration in the starting solution on the degree of recovery of manganese(II) ions, R, and transfer rate J. i = 6.4 mA cm^{-2}, τ = 60 min, receiving solution 0.25 M H_2SO_4

$c(H_2SO_4)$, M	R_1, %	R_2, %	$J_1\times10^5$, mol m^{-2} s^{-1}	$J_2\times10^5$, mol m^{-2} s^{-1}
10^{-4}	64	45	3.3	2.3
10^{-3}	83	54	4.2	0.9
10^{-2}	44	26	2.3	1.3
10^{-1}	10	4	0.5	0.2

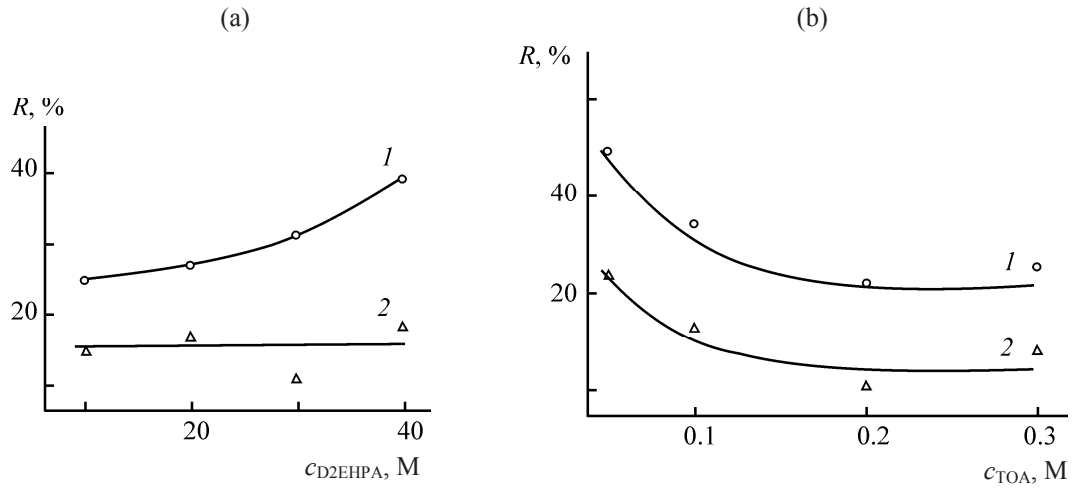

Fig. 4. Degree R of manganese(II) recovery into (*1*) liquid membrane and (*2*) receiving solution vs. the concentrations (a) c_{D2EHPA} of the transport agent and (b) c_{TOA} of the additive. i = 6.4 mA cm^{-2}, τ = 60 min, receiving solution 0.25 M H_2SO_4; (a) c_{TOA} = 0.1 M and (b) c_{D2EHPA} = 20 vol %.

Mn^{2+} ions into the organic phase and the receiving solution (Fig. 4b). An increase in the amine concentration may lead to a faster transport of SO_4^{2-} anions across the membrane from the receiving solution and to a decrease in the current efficiency by manganese(II).

The electrical conductivity of the membrane system is determined by the composition of the organic phase. Raising the TOA concentration in the liquid membrane leads to an increase in the conductivity and a decrease in the voltage, whereas raising the content of the transport agent D2EHPA has the opposite effect (Fig. 5). In the course of electrodialysis in systems with 0.25 M H_2SO_4 as the receiving solution, the voltage decreases and an electrical breakdown may occur. The decrease in the voltage is due to an increase in the total content of ions in the organic phase in extraction of manganese(II) and sulfuric acid and to accumulation of water in the liquid membrane.

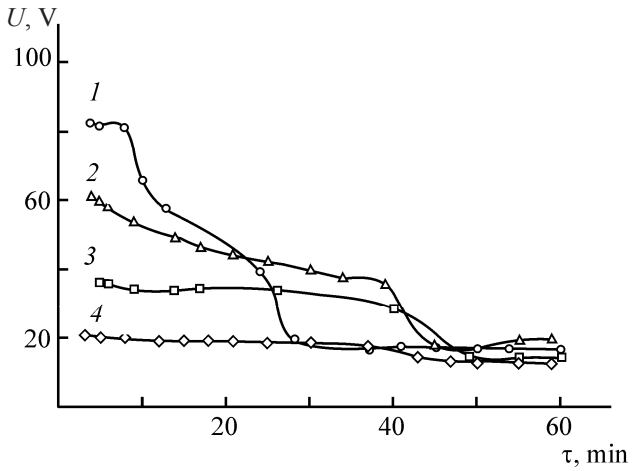

Fig. 5. U vs. the time τ at different concentrations of the transport agent D2EHPA and additive TOA. Receiving solution 0.25 M H_2SO_4. c_{TOA} (M): (*1*) 0.05, (*2, 3*) 0.1, and (*4*) 0.3. c_{D2EHPA} (vol %): (*1, 4*) 20, (*2*) 40, and (*3*) 10.

CONCLUSIONS

(1) Liquid membranes containing di(2-ethylhexyl)-phosphoric acid and tri-*n*-octylamine in 1,2-dichloro-ethane provide an efficient single-stage recovery of manganese(II) from sulfuric acid solutions of 0.01 M of $MnSO_4$ in galvanostatic electrodialysis.

(2) The rate of manganese(II) recovery depends on the current density and metal concentration in the starting solution and is weakly dependent on the concentration of di(2-ethylhexyl)phosphoric acid in the organic phase. Raising the concentration of sulfuric acid in the starting solution and that of tri-*n*-octylamine in the liquid membrane adversely affects the rate of the transmembrane transfer of Mn^{2+} ions. The optimal electrodialysis conditions in which 88% of the metal passes into the receiving solution are described.

(3) The membrane extraction of manganese(II) occurs at approximately equal rates into dilute solutions of sulfuric, hydrochloric, and nitric acids and is lower in the case of perchloric acid solutions and

water. The highest rate of recovery of Mn^{2+} ions into the liquid membrane is obtained in the case of transfer into water.

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