Extraction of Nickel by Liquid Membranes in an Electric Field

V. E. Serga[a]; L. D. Kulikova[a]; B. A. Purin[a]

[a] INSTITUTE OF INORGANIC CHEMISTRY, SALASPILS, LATVIA

PLEASE SCROLL DOWN FOR ARTICLE

Extraction of Nickel by Liquid Membranes in an Electric Field

V. E. SERGA,* L. D. KULIKOVA, and B. A. PURIN

INSTITUTE OF INORGANIC CHEMISTRY

34 MIERA STR., SALASPILS, LV-2169, LATVIA

ABSTRACT

The known liquid membranes (impregnated and emulsion) based on di-2-ethyl-hexylphosphoric acid (D2EHPA) extract nickel only out of weakly acid and neutral solutions. We have found out that direct current applied to an extraction system contributes to the complete extraction of nickel cations (0.003–0.009 M NiSO$_4$) out of more acidic solutions ($C_{H_2SO_4} \leq 0.05$ M) as well. The organic membrane phase is a D2EHPA solution (20 vol%) in 1,2-dichloroethane with 5–20 vol% of tributyl phosphate (I) or 1–2 vol% n-trioctylamine (II) added. These additions increase the electrical conductivity of the system 10–20 times. This allows for the extraction of nickel cations at optimal values of current density (for I: $i \leq 2.1$ mA/cm^2; for II: $i \geq 4.9$ mA/cm^2). It is shown that the flow of nickel cations through the feed solution/organic phase interface increases with a certain increase of current density, metal content in the aqueous phase, and amount of addition of I or II in the studied concentration range. Chronopotentiograms can be used to estimate the efficiency of nickel extraction. If an electric field is applied, the transfer of nickel cations is codirected with that of hydrogen ions through the interface. Kinetic measurements of nickel cation as well as of hydrogen ion transport numbers revealed that the nickel cation extraction process was preceded by the transport of hydrogen ions through the feed solution/organic phase interface.
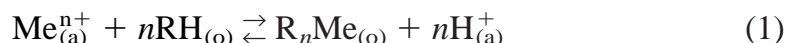
INTRODUCTION

Di-2-ethylhexylphosphoric acid (D2EPHA) is widely used in the nickel solvent extraction processes as well as for the separation of nickel and cobalt (1–3). The extraction of these metals in dependent on the pH value of the

* To whom correspondence should be addressed.

299

aqueous phase, the solution temperature, the nature of a diluent (4–6), as well as on the presence of condensed interfacial films affecting the kinetics of interfacial transfer (7–9). In practice, D2EPHA is often used in mixture with other substances (modifiers); for example, tributyl phosphate (TBP) (10–12), SME 418 (13), amines or quaternary ammonium salts (14). The effective solvent extraction of nickel is possible from weakly acid and neutral media (pH ≥ 4).

Different methods of membrane extraction (15–25), mostly with impregnated liquid membranes (16–18) and membrane extraction in a multiple emulsion (17–19, 26), are suggested for the extraction of nickel and the separation of nickel and cobalt. Membrane extraction is a promising technological method (27–29). It provides a higher degree of substance extraction out of highly diluted solutions and a much more effective separation of components that have similar properties at a smaller consumption of organic reagents when compared with the solvent extraction method. A cation-exchange extractant—D2EPHA (RH) in different diluents—is often used as a liquid membrane. In this case the reaction for the formation of a transported compound (R_nMe) can generally presented as

$$Me_{(a)}^{n+} + nRH_{(o)} \rightleftarrows R_nMe_{(o)} + nH_{(a)}^{+} \tag{1}$$

where nRH is the number of molecules $(C_8H_{17}O)_2(OH)PO$ involved in the reaction; R_n is the number of anions $(C_8H_{17}O)_2PO_2^{-}$ entering into the composition of a compound being formed, and (o) and (a) are the organic and aqueous phases, respectively.

The entire process, in general, is the counterdirected active transport of metal cations and hydrogen ions. That is why the pH value of a feed solution is reduced and mass transfer stops. It is shown in Ref. 17 that the membrane extraction of cobalt and nickel D2EPHA in CCl_4 in a multiple emulsion provides a deep (more than 95%) one-step extraction of these elements from aqueous solutions. To prevent the stoppage of mass transfer due to a displacement of hydrogen ions, the pH value in the feed solution should be kept constant (5.0). Lower pH values (2.25 and 3.1) make the nickel and cobalt extraction process into an emulsion ineffective (19). In a diffusive cell with an impregnated membrane (i.e., a nucleus filter impregnated with a D2EPHA solution in CCl_4), active transport of cobalt and nickel is abnormally slow (17) due to the formation of condensed interfacial films at an unrenewed phase interface (7).

In some cases an external electric field applied to the extraction process considerably strengthens the interfacial transfer phenomena (30, 31). For certain processes the application of an external electric field is a necessary condition (32).

The current paper investigates the influence of direct current on the extraction of nickel cations from acidic solutions by voluminous liquid membranes

enclosed between two semipenetrable films that are a mixture of extractants in a polar diluent.

EXPERIMENTAL

The experiments were carried out in a five-chambered Teflon dialyzer with two platinum electrodes and rigid anion-exchange membranes (MA-40) that separate the near-electrode chambers (a, f) from the feed (b) and strip (d) chambers:

a	b	c	d	f
$+$Pt,H_2SO_4	$NiSO_4$ H_2SO_4	liquid membrane	HCl	H_2SO_4,Pt$-$

MA-40	1	2	MA-40

where 1 is the feed solution/liquid membrane interface and 2 is the liquid membrane/strip solution interface.

The interface of such pattern is positioned vertically, and the electric field is distributed uniformly over the interface surface and the membrane volume. The liquid membrane is a D2EPHA solution with added TBP or n-triocty-lamine (Oct$_3$N). It is placed between two hydrocellulose films preliminary steeped in distilled water. The contact square (an observed surface of cellulose) is 7.1 cm^2. The thickness of the liquid membrane is $l_m = 0.2$ cm. The ratio of aqueous and organic phases B:O = 2.5:1. The extraction is carried out under a galvanostatic regime; variations in the system voltage are registered during extraction.

The Oct$_3$N content was 95%: $n_D^{20} = 1.449$, $d_4^{20} = 0.811$. D2EPHA was purified by the method in Ref. 33. A basic substance content was not less than 95% after purification. 1,2-Dichloroethane was purified by the method in Ref. 34 using a fraction with $t_{boil} = 83.4$–$83.5°C$.

Nickel solutions were prepared by using a previously weighted sample of nickel sulfate in a H_2SO_4 solution. The metal content in an aqueous solution was defined spectrophotometrically by using dimethylglyoxime (35); the content of chlorions was defined by using mercuric thiocyanate (36).

RESULTS AND DISCUSSION

D2EPHA was selected as the basic component of a liquid membrane used to extract nickel since this cation-exchanger satisfies the most requirements of extractants used in the extraction processes when an electric field is applied (37). However, solutions of this acid, even in such polar diluents as 1,2-

dichloroethane, have a low electric conductivity (see Table 1). The current density achieved does not permit complete extraction of nickel out of the aqueous phase. It is known (38) that a highly effective extraction is achievable if the electrodialysis process is conducted at nearly ultimate diffusion current densities for the ion under extraction. The current density in our system can be decreased either by reducing the thickness of a liquid membrane or by selecting the components of a liquid membrane that have a higher electric conductivity. It has been shown experimentally that if one uses a liquid membrane with a thickness $l_m < 0.2$ cm, this destabilizes the system and causes an electric breakdown (39).

Since D2EPHA solutions (10–30 vol%) with a low electric conductivity are likely to form stable dimers independent of the nature of the diluent (40, 41), in some cases a modifier, e.g., TBP, should be used because these inhibit the intermolecular extractant association (42).

An addition of 5–20 vol% TBP to a D2EPHA solution (20 vol%) increases its electric conductivity 2–4 times (see Table 1) which allows nickel to be extracted at higher current densities. Moreover, the flow of nickel cations through both interfaces increases (see Table 2) as well as does the degree of nickel extraction. An increase of TBP (to 20 vol%) in a membrane containing 20 vol% D2EPHA results in a significant increase in the flow of nickel

TABLE 1
Electrical Conductivity of a Liquid Membrane

Membrane composition	Vol%	$\chi \times 10^5 \; \Omega^{-1}\cdot\mathrm{cm}^{-1}$
D2EPHA	10	0.11
D2EPHA	20	0.16
D2EPHA	30	0.19
D2EPHA TBP	20 5	0.35
D2EPHA TBP	20 20	0.58
D2EPHA TBP	50 10	0.29
D2EPHA Oct_3N	20 1	1.56
D2EPHA Oct_3N	20 1.5	1.95
Oct_3N	1.5	0.33

TABLE 2
Dependence of the Flow of Nickel Cations through the Interfaces on the Experimental Conditions

Membrane composition	Vol%	i (mA/cm^2)	j(mol/m^2·s)	
			$j_1 \times 10^5$	$j_2 \times 10^5$
D2EPHA	20	—	0.2	0
		0.7	0.5	0.3
D2EPHA	30	1.1	0.7	0.4
D2EPHA	20	0.7	0.4	0.3
TBP	5	1.4	1.2	0.5
		2.1	1.4	0.9
D2EPHA	20	2.1	2.5	0.9
TBP	20			
D2EPHA	50	2.1	0.9	0.3
TBP	10			
D2EPHA	15	4.9	3.2	1.0
Oct$_3$N	1.5			
D2EPHA	20	4.9	2.6	1.0
Oct$_3$N	1			
D2EPHA	20	4.9	3.7	1.5
Oct$_3$N	1.5			

cations, j_1 (ion flow through the feed solution/liquid membrane interface), and an increase in their degree of extraction to 99.6% ($i = 2.1$ mA/cm^2), but j_2 (ion flow through the liquid membrane/strip solution interface) is not changed (see Table 2).

A content of 20 vol% D2EPHA and 5–20 vol% TBP obviously seems to be optimal for the electrodialysis extraction of nickel cations. An increase of D2EPHA to 50 vol% decreases the electric conductivity of a liquid membrane if it is compared to the optimal content (see Table 1) and the flow of nickel cations through both interfaces (see Table 2). Because of comparatively low densities of current flow through liquid membranes containing D2EPHA and TBP, electrodialysis transport processes of nickel cations take much time: the time for the quantitative extraction of nickel cations from a feed solution with a 0.003 M nickel sulfate concentration is 3000 seconds at $I = 2.1$ mA/cm^2. If the conditions of an experiment change (i.e., the concentration of nickel salt in the feed solution increases, liquid membranes with $l_m > 0.2$ cm are used, the volumes of the feed and strip solutions increase, etc.), the time for an experiment greatly increases, too. In this case, water was often found to accu-

mulate in the liquid membrane volume. The water accumulation is brought about by electroosmosis, by a tendency of TBP to form associates of the $(TBP \cdot nH_2O)$ type (43), and also by water transfer in the composition of the nickel cation hydration sheath. A direct dependence of the amount of water in a membrane on the salt concentration in a feed solution has been found. In the course of an experiment an forms emulsion in the membrane, and water drops containing nickel cations can form conducting channels in the emulsion. This results in an electrical breakdown (39); in this case the membrane becomes nonselective (44). Although an increase of current density through a system accelerates water accumulation in the liquid membrane, the time of an experiment decreases significantly at the same time. This fact permits determination of the conditions under which a liquid membrane can function without electrical breakdown.

The addition of small amounts of Oct_3N (1–1.5 vol%) results in a 20-fold increase of the electrical conductivity of liquid membranes (20 vol% D2EPHA solution) (see Table 1). It has been found out experimentally that the type of addition is not of principal importance [either an amine or its preliminary prepared salts Oct_3NHCl and $(Oct_3NH)_2SO_4$]. As a strong nucleophilic agent, Oct_3N can add the molecules of an acid to form salts (45). The electric conductivity of n-trioctylamine salt solutions in 1,2-dichloroethane is highly dependent on the nature of the anions. Solutions with more lypophilic anion salts $[ClO_4^-, Au(CN)_2^-]$ show a 4 to 8 times higher conductivity compared to, e.g., chloride ions (46). We presume that such a large increase in the electric conductivity of a solution containing 20 vol% D2EPHA and 1–1.5 vol% Oct_3N is related to the formation of Oct_3NHR salt in the membrane phase either due to the neutralization reaction (when the membrane has Oct_3N added) or due to anion exchange [when the membrane has Oct_3NHCl and $(Oct_3NH)_2SO_4$ added]. An increase of Oct_3N from 1 to 1.5 vol% at 20 vol% D2EPHA in the liquid membrane results in an increase of nickel cation flow through both interfaces. If the Oct_3N content remains constant (1.5 vol%), a decrease of D2EPHA to 15 vol% in the liquid membrane reduces these flows (see Table 2).

The investigations carried out lead us to propose that with such a liquid membrane content (20 vol% D2EHPA and 1.5 vol% Oct_3N), the nickel cations are effectively extracted directly from acidic solutions as well as from weakly acid and neutral ones without the pH value of the feed solution being corrected.

The dependence of the degree of extraction (E) and the nickel cation flow through both interfaces on the concentration of metal (Fig. 1) and the current density (Fig. 2) shows that at $i = 5.6$ mA/cm^2 and at a $NiSO_4$ concentration of 0.003 M, it is possible to extract nickel completely from the feed solution. However, while 60% of the nickel transfers into the strip solution (2 M HCl),
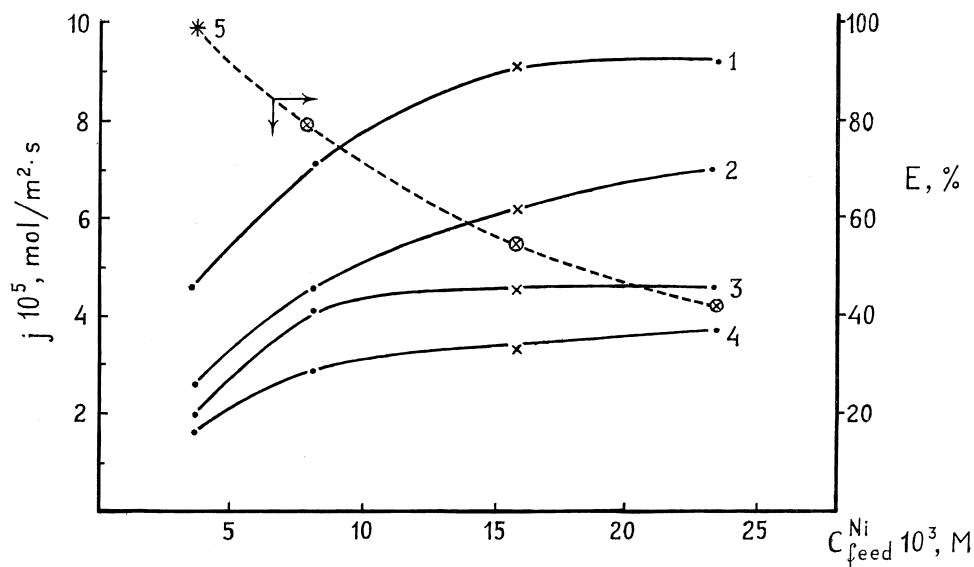
FIG. 1 Nickel flow (1–4) and degree of nickel extraction (5) versus the concentration of feed solution $NiSO_4$ in 0.005 M H_2SO_4; $C_{strip}^{HCl} = 2$ M; $t_{ex} = 900$ seconds ($*t_{ex} = 315$ seconds): (1, 2) the feed solution/liquid membrane interface; (3, 4) the liquid membrane/strip solution interface; (1, 3) $i = 7.0$ mA/cm²: (2, 4, 5) $i = 5.6$ mA/cm².

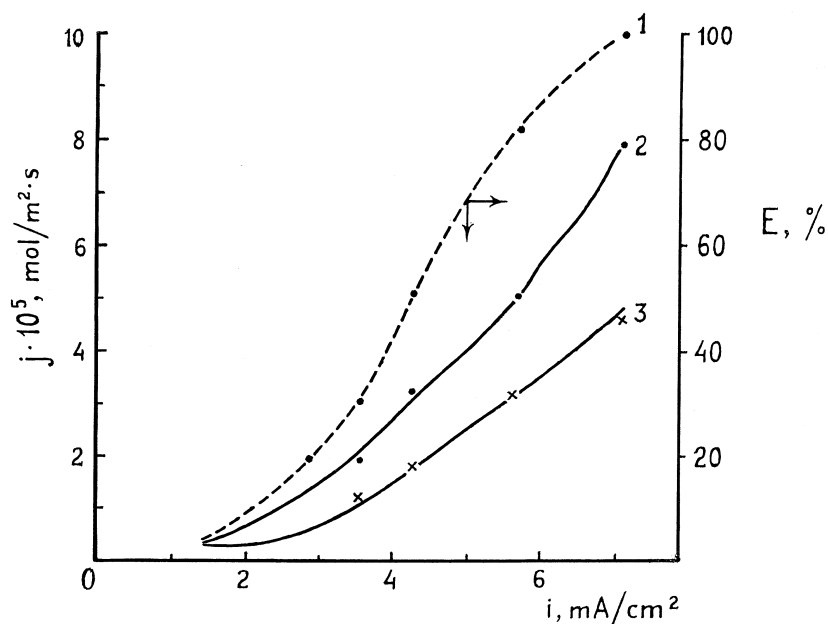**FIG. 2** Degree of nickel extraction (1) and flow (2, 3) versus the current density. $C_{feed}^{NiSO_4} = 0.008$ M in 0.005 M H_2SO_4. $C_{strip}^{HCl} = 2$ M; $t_{ex} = 900$ seconds. 2—the feed solution/liquid membrane interface; 3—the liquid membrane/strip solution interface.

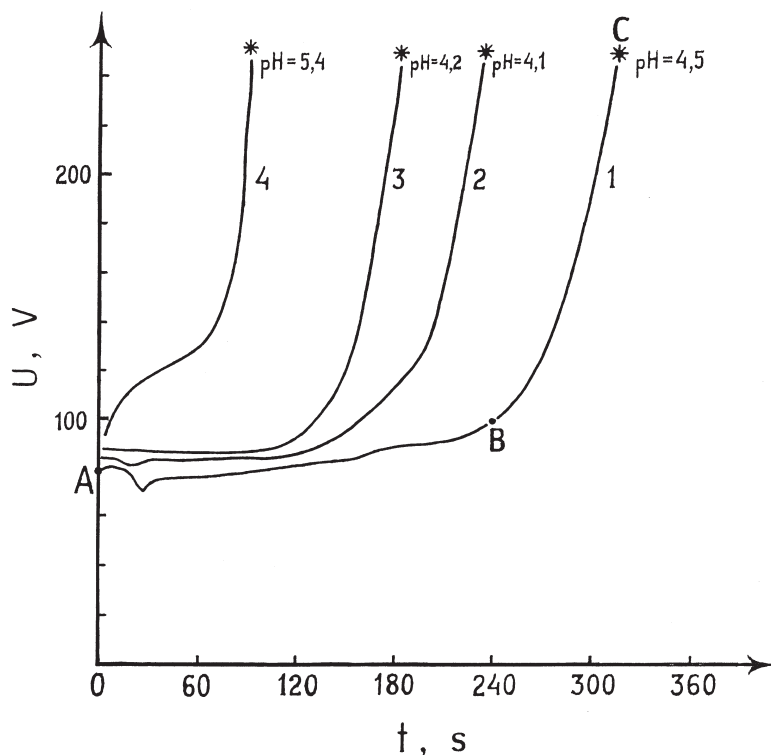**FIG. 3**   Voltage versus the time of experiment. $i = 5.6$ mA/cm^2; $C_{strip}^{HCl} = 0.1$ M. The feed solution contents: (1) 0.003 M NiSO$_4$ in 0.005 M H$_2$SO$_4$; (2) 0.003 M NiSO$_4$ in 5×10^{-4} H$_2$SO$_4$; (3) 0.005 M H$_2$SO$_4$; (4) 5×10^{-4} H$_2$SO$_4$. *Final pH values of the feed solutions.

40% stays in the liquid membrane. The increasing current density intensifies the nickel cation flow through both interfaces (Fig. 2), and the higher the content of nickel salt in the feed solution, the higher the current density that is needed for complete extraction of the metal.

The chronopotentiograms registered in the course of electrodialysis in the investigated systems have a specific shape (Figs. 3 and 4) and consist of two different parts (Fig. 3, Run 1). Part AB shows some gain in the electric conductivity of the system, the Part BC shows a sharp decrease in electric conductivity accompanied by a voltage jump. A major change of the pH value of the feed solution from 2.2 (Point A) to 3.8 (Point B) was registered in Part AB. In this region the current through Interface I is transported by cations of the feed solution ($t_H^+ \cong 0.3$ and $t_{Ni}^+ \cong 0.2$) and chlorions of the strip solution. Hence, if an electric field is applied to the investigated system with the liquid membrane, the extraction of nickel from acidic solutions goes codirectionally with the transfer of hydrogen ions. In Part AB (Fig. 3, Run 1) the electric conductivity of the system is mostly determined by the ohmic resistance of the membrane. Some increase of electric conductivity in the course of the process
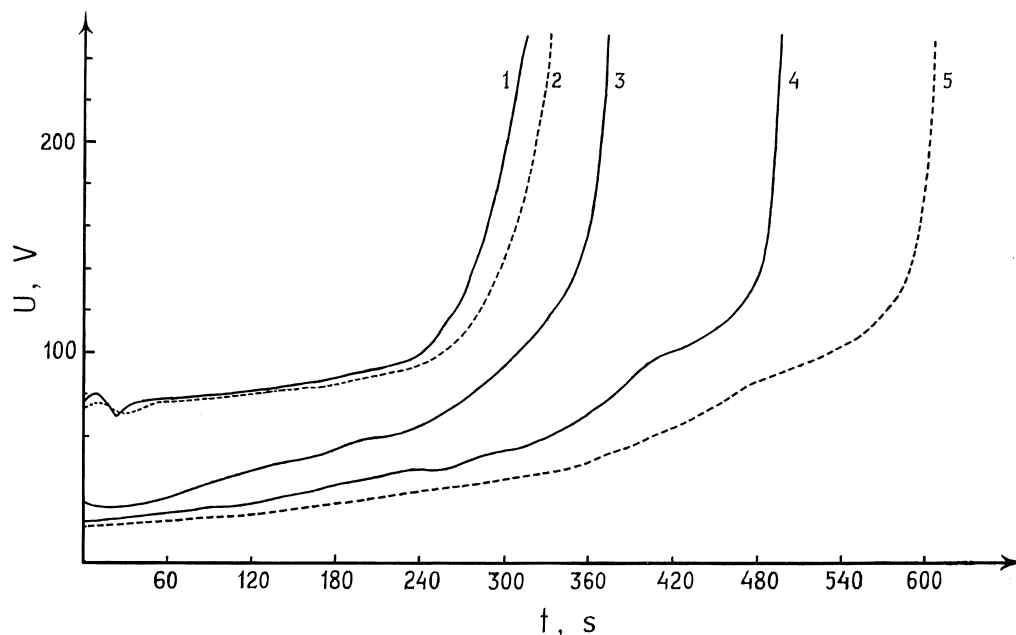
FIG. 4   Voltage versus the time of experiment. $i = 5.6$ mA/cm^2; $C_{\text{feed}}^{\text{NiSO}_4} = 0.003$ M in 0.005 M H$_2$SO$_4$; $C_{\text{strip}}^{\text{HCl}} = 0.1$ M. For the explanations of Runs 1–5, see in text.

is likely to be related to the formation of an emulsion in the liquid membrane volume when an external electric field is applied. Considering the high mobility and lower hydration energy of hydrogen ions as well as the above-mentioned transport numbers, one can say that hydrogen ion transport is mainly responsible for the increase, not of nickel cations, at least at the beginning of the process. The increase of the pH value to 3.8 (Point B) registered in Part AB of the feed solution makes it possible to extract D2EPHA nickel cations due to Eq. (1).

Part BC (Fig. 3, Run 1) differs greatly from Part AB. It is characterized by a sharp decrease of the system's electric conductivity due to some growth of the pH value of the feed solution from 3.8 (Point B) to 4.5 (Point C) and by an almost complete absence of nickel cations in the feed solution at the completion of the experiment (Point C). D2EPHA nickel cation extraction in this region is accompanied by the formation of NiR$_2$·H$_2$O compound which tends to aggregate in the organic phase (47). At that time the total electric current from the feed solution to the membrane is transported by nickel cations ($t_{\text{H}}^{+} \cong 0$ and $t_{\text{Ni}}^{+} \cong 0.6$). The current transported by chlorions of the strip solution through Interface 1 is $t_{\text{Cl}}^{-} \cong 0.4$. When the quantity of cations in the feed solution is insufficient, the resistance of Interface 1 in Part BC considerably exceeds the ohmic resistance of the membrane. As a result, the system conductivity drops.
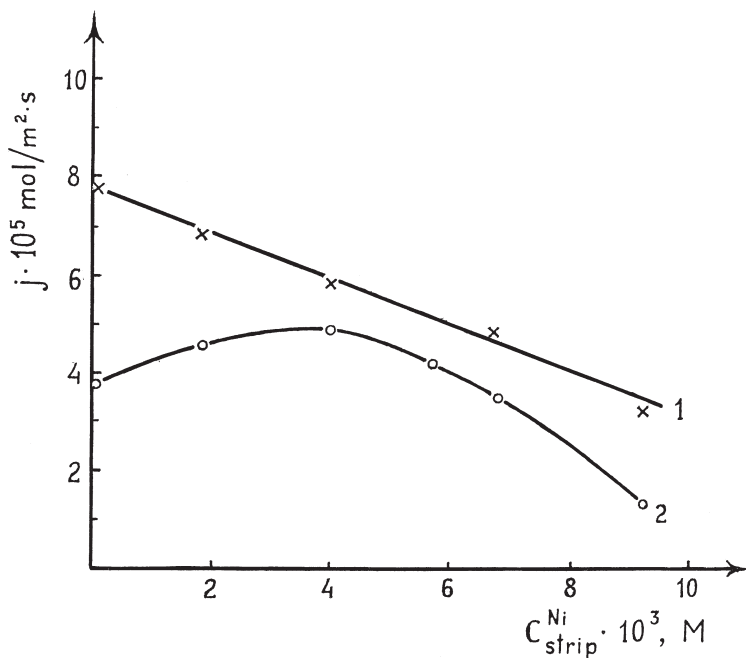
FIG. 5   Nickel cation flow through the interfaces versus the metal content in the strip solution. $C_{\text{feed}}^{\text{NiSO}_4} = 0.003$ M in 0.005 M H_2SO_4; $C_{\text{strip}}^{\text{HCl}} = 0.1$ M; $i = 5.6$ mA/cm^2: (1) the feed solution/ liquid membrane interface; (2) the liquid membrane/strip solution interface.

If after a complete extraction of metal we exchange the used nickel salt feed solution (chamber **b**) for a new one with the same initial nickel concentration (0.003 M in 0.005 M H_2SO_4), then for a multiple use of the membrane solution the volume of liquid membrane greatly increases as does the initial electric conductivity of the system (approximately 4 times after the liquid membrane is used twice) (Fig. 4, Runs 3, 4, and 5). This phenomenon occurs in the presence of a water/oil microemulsion (48). Still, the trend of the curves does not change. After the voltage jump occurred in all experiments of this series, there were almost no nickel cations in the feed solution. Hence, the chronopotentiograms can be used to estimate the efficiency of nickel extraction.

If one exchanges the solutions in feed chamber **b** and in chamber **c** of the liquid membrane by new ones following every experiment, then for five stages of the process the strip solution reaches a nickel concentration 3 times larger the initial one. j_1 increases until the metal concentration in the strip solution reaches that of the initial solution; j_2 is constantly tends to decrease as the metal concentration in the strip solution increases (Fig. 5).

The hydrogen ion concentration decreases by an order of magnitude when the nickel concentration is kept constant ($C_{\text{feed}}^{\text{NiSO}_4} = 0.003$ M), which considerably reduces the time needed for complete extraction of nickel from the ini-
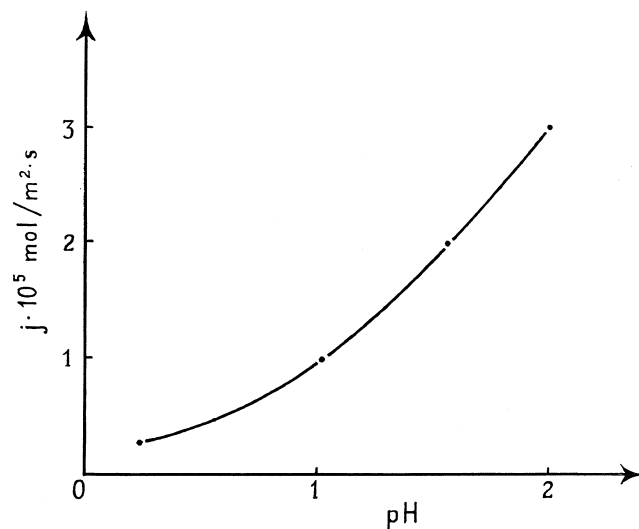
FIG. 6   Nickel cation flow through the feed solution/liquid membrane interface versus the pH value of the feed solution. $C_{feed}^{NiSO_4} = 0.003$ M; $C_{strip}^{HCl} = 0.1$ M; $i = 5.6$ mA/cm^2.

tial solution (Fig. 3, Run 2). The trend of the curve is the same, but the initial part is determined, as stated above, by emulsion formation due to the transport of hydrated nickel cations, and the transport of hydrogen ions into the organic phase is significantly reduced. Increasing the concentration of hydrogen ions in the feed solution sixfold increases the time of the experiment. If the feed solution has one type of cation—hydrogen ions (Fig. 3, Runs 3 and 4)—there is a reduction in the dependence of the initial part on Run 3 on $U = f(t)$ and a change of its shape on Curve 4. Without regard to the composition and acidity of the feed solution, the pH value registered at the completion of the process exceeds the initial one (Fig. 3).

The run in Fig. 6 validates the data because it shows an increase of cation flow through the feed solution/liquid membrane interface when the acidity of the aqueous phase decreases.

Figure 7 is a schematic presentation of the transfer of ions through the liquid membrane in the course of electrodialysis.

In case of liquid extraction, a complete transfer of nickel from the organic phase into the strip solution is achieved by acidic reextraction (3). Referring to the investigated system, an increase of HCl concentration from 0.001 M to 0.1 M in the strip solution does not change the j_2 value. A further increase of acid concentration to 2 M results in an approximately 2 fold decrease of j_2. These experimental data agree with the proposed model of ion transfer during electrodialysis. When an external electric field is applied under the effective conditions of nickel extraction (pH $\geq$ 3.8) and its accumulation in the organic phase, the

I + b Membrane d

Ni^{2+} H$^+$ $\dfrac{\text{Oct}_3\text{N} \quad \text{HR}}{\text{Oct}_3\text{NH}^+ * \text{R}^-}$ Cl$^-$

H$^+ \longrightarrow$ R$^-$ Oct$_3$NH$^+ \longleftarrow$ Cl$^-$

HR $\rightleftarrows$ (HR)$_2$

II H$^+ \longrightarrow$ R$^-$ Oct$_3$NH$^+ \longleftarrow$ Cl$^-$

R$^-$ H$^+ \longrightarrow$ Cl$^-$

Ni^{2+} Ni^{2+}

R$^-$ H$^+ \longrightarrow$

Ni^{2+}

H$^+$ H$^+ \longrightarrow$ R$^-$ Cl$^-$

H$^+ \longrightarrow$ R$^-$ Ni$^{2+} \longrightarrow$

HR $\rightleftarrows$ (HR)$_2$

III R$^-$ Oct$_3$NH$^+ \longleftarrow$ Cl$^-$

Ni^{2+}

R$^-$ Oct$_3$NH$^+ \longleftarrow$ Cl$^-$ Ni^{2+}

R$^-$ H$^+ \longrightarrow$

Ni^{2+}

R$^-$ H$^+ \longrightarrow$ Cl$^-$

H$^+ \longrightarrow$ R$^-$ Cl$^-$ Ni^{2+}

Cl$^-$ H$^+ \longrightarrow$ R$^-$ Ni$^{2+} \longrightarrow$

HR
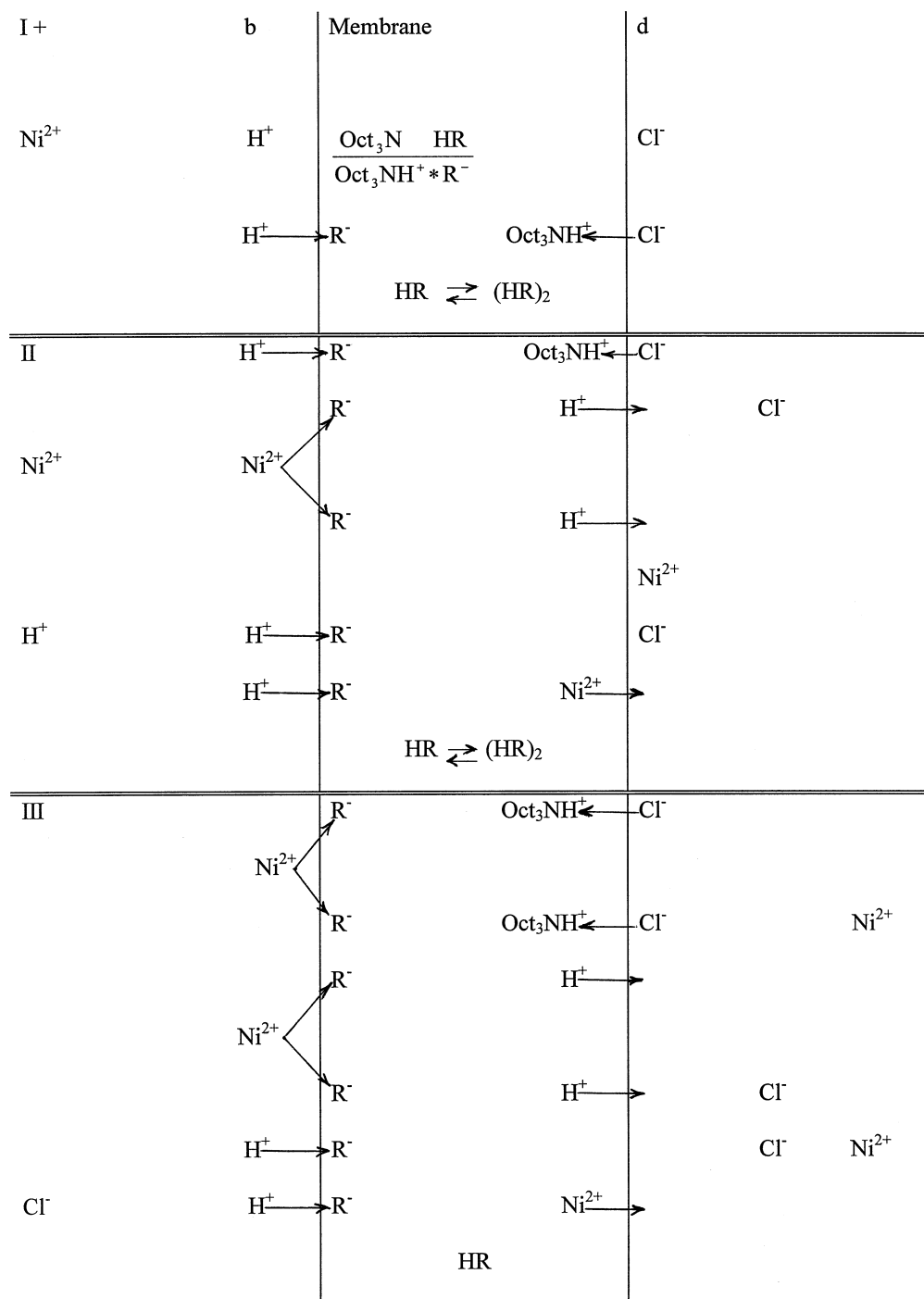
FIG. 7 Schematic of ion electrodialysis through the liquid membrane. Initial stage conditions: (I) $C_H^+ \cong C_{Ni}^{2+}$; (II) $C_H^+ < C_{Ni}^{2+}$; (III) $C_H^+ \ll C_{Ni}^{2+}$.

amount of protons in the initial solution is actually insufficient to implement a complete reextraction of nickel (Fig. 7, Stage III). It is impossible to accomplish qualitative extraction and reextraction of nickel simultaneously using the above method. The complete transport of nickel from the organic phase into the strip solution can be achieved by introducing the a second process stage, particularly by exchanging the solution in feed chamber **b** by a solution of acid after the metal is transported into the organic phase. The time of nickel extraction into the strip solution is determined by the concentration of acid in chamber **b**.

CONCLUSION

Our experimental results show that at the beginning of the extraction process the electrical current from the feed solution into the liquid membrane is transported mainly by hydrogen ions and partially by hydrated nickel cations, i.e., an electrodialysis transport of metal ions is accompanied by the formation of an emulsion in the organic phase. When the aqueous phase adjacent to the interface layer loses hydrogen ions, the nickel transport numbers increase. Due to the considerable decrease in hydrogen ion concentration, the pH value of the initial solution makes the extraction of D2EPHA nickel cations possible. At this stage the electric current from the feed solution to the liquid membrane is transported mainly by nickel cations.

NOTATION

D2EPHA (HR)	di-2-ethylhexylphosphoric acid
E	degree of extraction (%)
I	current density (mA/cm^2)
j_1	ion flow through the feed solution/liquid membrane interface (mol/m$^2\cdot$s)
j_2	ion flow through the liquid membrane/strip solution interface (mol/m$^2\cdot$s)
l_m	membrane thickness (cm)
M	concentration (mol/L)
Oct$_3$N	n-trioctylamine
TBP	tributyl phosphate
χ	electric conductivity of a liquid membrane ($\Omega^{-1}\cdot$cm^{-1})

REFERENCES

1. G. M. Ritcey and A. W. Ashbrook, "Cobalt and Nickel Separation," US Patent 3,339,055 (1968).
2. P. Mihalop, C. J. Barton, D. H. Logsdail, H. A. C. McKay, and D. Scargill, in *Proceedings of an International Conference on Solvent Extraction*, *Vol. 2*, Society of Chemical Industry, London, 1974, p. 1263.

3. A. A. Pushkov, V. P. Lanin, and V. F. Travkin, *Chem. Technol. Rare Earth*, *MHTI*, *143*, 33 (1986) (in Russian).

4. V. P. Lanin, I. V. Baronin, A. A. Pushkov, and V. F. Travkin, *Non-ferrous Met. 11*, 21 (1985) (in Russian).

5. A. S. Skripchenko and V. S. Soldatov, *Vesti Akad. Nauk B. SSR*, *6*, 14 (1986) (In Russian).

6. A. Rajab, D. Pareau, J. Moulin, and A. Chesne, *Bull. Soc. Chem. Fr.*, *1*, 29 (1987).

7. V. V. Tarasov, G. A. Yagodin, and A. A. Pichugin, "Kinetics of Extraction of Inorganic Substances," *VINITI*, *11* (1984) (in Russian).

8. M. A. Hughes, *Hydrometallurgy*, *3*(1), 85 (1978).

9. N. Ph. Kizim, Yu. P. Davydov, and A. P. Larkov, *Int. Solv. Ext. Conf.*, *Moscow*, *2*, 47 (1988).

10. G. M. Ritcey and A. W. Ashbrook, *Extraction. Principles and Application in Metallurgy*, Moscow, 1983 (in Russian), p. 407.

11. J. S. Preston and C. A. Fleming, in *3rd Int. Symp. Hydromet.*, *AIME Meet.*, *Atlanta* GA, 1985, p. 475.

12. A. M. Shatokhin, A. V. Mironov, G. V. Heustroyeva, S. A. Zoryukov, and A. I. Shilin, in *IX All-Union Conference on Extraction*, *Moscow*, 1991, p. 439, (in Russian).

13. D. S. Flett, J. Melling, and E. Itin, in *Int. Solv. Extr. Conf. Denver*, *CO*, 1983, p. 232.

14. I. L. Dukov, *Anal. Hab.*, *5*(4), 219 (1996).

15. W. Walkowiak and J. Gega, in *Chemical Separation with Liquid membranes* (ACS Symp. Ser. 642), 1996, p. 181.

16. D. J. Feike and H. C. Visser, *Compr. Supramol. Chem.*, *10*, 13 (1996).

17. V. B. Lisovsky, A. F. Gubin, and E. M. Volkhovskaya, *Physical and Chemical Problems of Chemical Industry*, MHTI, 1990, p. 64 (in Russian).

18. S. Yu. Ivachno and E. V. Yurtov, "Membrane Extraction," *VINITI*, *18* (1990) (in Russian).

19. I. Strzelticki and W. Charewicz, *Hydrometallurgy*, *5*(2/3), 234 (1980).

20. M. Nakano, K. Takahashi, and H. Takenchi, *J. Chem. Eng. Jpn.*, *20*(3), 326 (1987).

21. M. Teramoto, H. Matsujama, and H. Takaja, in *Int. Solv. Extr. Conf. Moscow*, *3*, 1988, p. 110.

22. A. Matsujama, Y. Katajama, and M. Kojima, *J. Chem. Eng. Jpn.*, *20*(3), 213 (1987).

23. T. Huang and T.-H. Tsai, in *Int. Solv. Extr. Conf. Kyoto*, 1990, p. 272.

24. L. D. Nichols, A. S. Obermayer, and M. B. Allen, *US Gov. Res. Rep.*, *20*, PB 82-218652, 4034 (1982).

25. T. Kataoka and T. Hucuru, *Chem Eng.*, *31*(12), 933 (1986).

26. R. Kuemmel, M. Schroeder, E. Uhlemann, and W. Micklor, *Chem. Tech. (Leipzig)*, *48*(4), 197 (1996).

27. M. Burgard and M. Deluzarche, *Bull. Union Physiciens*, *91*(793), 719 (1997).

28. R. Bartsch and J. D. Way, in *Chemical Separation with Liquid Membranes* (*ACS Symp. Ser.*, *642*), 1996, p. 1.

29. L. Chrisstoffels, A. J. de Jong, R. Feike, and N. David, *Ibid.*, p. 18.

30. B. A. Purin, *Izv. Akad. Nauk LatvSSR*, *5*, 31(1971) (in Russian).

31. E. V. Pronin and N. F. Kizim, in *IX All-Union Conf. on Extraction*, *Mosow*, 1991, p. 98 (in Russian).

32. B. A. Purin, V. P. Chibizov, and L. D. Kulikova, in *Int. Solv. Extr. Conf. Moscow*, *3*, 13, (1988).

33. J. A. Patrige and R. S. Jenser, *J. Inorg. Nucl. Chem.*, *31*(8), 2587 (1969).

34. A. Weissberger, E. Proskauer, J. Riddick and E. Toops, *Organic Diluents*, Moscow, 1958, p. 520 (in Russian).

35. G. Sharlo, *Methods Analytical Chemistry*. *Quantitative Analysis of Inorganic Compounds*, *Chemistry*, *Part II*, Moscow, 1969, p. 677 (in Russian).

36. N. S. Frumina, N. F. Lysenko, and M. A. Chernova, *Analytical Chemistry of Elements*, *Chlorine*, Nauka, Moscow, 1983, p. 54 (in Russian).

37. L. D. Kulikova, O. I. Petrichenko, T. Z. Sadyrbayeva, V. E. Serga, and A. K. Jansone, in *VI All-Union Conf. on Organic Reagents in Analytical Chemistry*, *Saratov*, *Part II*, 1989, p. 210 (in Russian).

38. A. N. Popov, S. K. Timofeyeva, and V. E. Serga, *Akad. Nauk LatvSSR. Ser. Chim.*, *6*, 675(199) (in Russian).

39. V. N. Golubev, A. N. Popov, and B. A. Purin, *Sov. Electrochem.*, *12*, 1478 (1976).

40. I. R. Ferraro, Y. W. Mason, and D. F. Peppard, *J. Inorg. Nucl. Chem.*, *22*, 285 (1961).

41. V. S. Ulyanova and P. A. Sviridova, *Radiochemistry*, *12*, 47 (1970) (in Russian).

42. S. Yu. Ivachno, A. V. Aphanasiev, and G. A. Yagodin, "Membrane Extraction of Inorganic Substances," *VINITI*, *13* (1985) (in Russian).

43. E. S. Stoyanov, in *X Conf. on Extraction*, *Moscow*, 1994, p. 126 (in Russian).

44. V. N. Golubev and A. S. Kontush, *Sov. Electrochem. 25*, 105 (1987).

45. V. S. Schmidt, *Extraction by Amines*, Atomizdat, Moscow, 1980, p. 2620 (in Russian).

46. A. N. Popov and S. K. Timofeyeva, *Izv. Akad. Nauk LatvSSR*, *Ser. Chim.*, *6*, 707 (1990) (in Russian).

47. A. Jada, I. Lang, and R. Zana, *J. Phys. Chem.*, *93*, 10 (1989).

48. R. D. Neuman, N.-F. Zhou, J. Wu, M. A. Jones, A. G. Gainkar, S. J. Park, and M. L. Agrawal, *Sep. Sci. Technol*, *25*(13–15), 1965 (1990).

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100100158