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Deep Eutectic Solvent (TOPO/D2EHPA/Menthol) for Extracting Metals from Synthetic Hydrochloric Acid Leachates of NMC-LTO Batteries

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Abstract: The recycling of lithium-ion batteries is increasingly important for both resource recovery and environmental protection. However, the complex composition of cathode and anode materials in these batteries makes the efficient separation of metal mixtures challenging. Hydrometallurgical methods, particularly liquid extraction, provide an effective means of separating metal ions, though they require periodic updates to their extraction systems. This study introduces a hydrophobic deep eutectic solvent composed of trioctylphosphine oxide, di(2-ethylhexyl)phosphoric acid, and menthol, which is effective for separating Ti(IV), Co(II), Mn(II), Ni(II), and Li^+ ions from hydrochloric acid leachates of NMC ($LiNi_xMn_yCo_{1-x-y}O_2$) batteries with LTO ($Li_4Ti_5O_{12}$) anodes. By optimising the molar composition of the trioctylphosphine oxide/di(2-ethylhexyl)phosphoric acid/menthol mixture to a 4:1:5 ratio, high extraction efficiency was achieved. The solvent demonstrated stability over 10 cycles, and conditions for its regeneration were successfully established. At room temperature, the DES exhibited a density of 0.89 g/mL and a viscosity of 56 mPa·s, which are suitable for laboratory-scale extraction processes. Experimental results from a laboratory setup with mixer-settlers confirmed the efficiency of separating Ti(IV) and Co(II) ions in the context of their extraction kinetics.

Keywords: liquid extraction; lithium-ion batteries; deep eutectic solvents; recycling; mixer-settler

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Citation: Kozhevnikova, A.V.; Milevskii, N.A.; Lobovich, D.V.; Zakhodyaeva, Y.A.; Voshkin, A.A. Deep Eutectic Solvent (TOPO/D2EHPA/Menthol) for Extracting Metals from Synthetic Hydrochloric Acid Leachates of NMC-LTO Batteries. *Metals* **2024**, *14*, 1441. https://doi.org/10.3390/met14121441

Academic Editor: Alexandre Chagnes

Received: 30 October 2024
Revised: 9 December 2024
Accepted: 12 December 2024
Published: 16 December 2024

1. Introduction

The growing demand for lithium-ion batteries, driven by their superior performance over nickel-metal hydride and nickel-cadmium alternatives, has led to a corresponding surge in the demand for lithium precursors such as lithium hydroxide and carbonate. This increase, coupled with the rising prices of raw materials, has prompted further advancements in battery technology. The early generations of lithium-ion batteries, particularly those with $LiCoO_2$ cathodes, were known for their fragility and safety concerns, spurring the search for safer and more cost-effective alternatives [1,2]. One promising approach involves replacing lithium ions with sodium [3], which significantly reduces production costs while enhancing operational safety. Conversely, the development of modern lithium-based cathode materials, such as NMC, has enabled a significant increase in both energy density and battery lifespan [4]. As the demand for lithium precursors has risen, the expansion of extraction and production enterprises has resulted in a continuous decline in lithium prices [5]. In addition, the lithium-titanate anode (LTO, $Li_4Ti_5O_{12}$) has gained widespread use, significantly enhancing the safety of lithium-ion batteries [6]. Thus, the production of lithium-ion batteries remains highly relevant. Consequently, there is an urgent need to recycle spent lithium-ion batteries, as this is both economically viable and can reduce environmental impacts [7].

To date, numerous studies have focused on the recycling of lithium-ion battery cathodes with various chemical compositions [8–13]. The most common method for processing lithium-ion batteries with an NMC-type cathode ($LiNi_xMn_yCo_{1-x-y}O_2$) is hydrometallurgy [14–17]. This approach involves leaching the active material with mineral acid, followed by the extraction and separation of the resulting mixture of elements [18,19]. Liquid extraction is a sustainable technique that does not require high temperatures or significant energy consumption, making it easily scalable and capable of yielding target substances with high purity. However, a notable drawback of this method is the reliance on large volumes of mineral acids and organic solvents. In developing hydrometallurgical approaches for both leaching and extraction, researchers have proposed various systems to enhance the efficiency and environmental sustainability of the process. Considerable attention has been given to ionic liquids, which are used effectively for the leaching and extraction of valuable metals [20–23]. Ionic liquids have not, however, been widely adopted due to their typically high viscosity [24], challenging synthesis, and potential toxicity [25]. A more promising class of systems that can replace both mineral acids for leaching and volatile organic solvents in the extraction process is that of deep eutectic solvents (DESs) [26]. Hydrophilic compositions based on organic acids can achieve high efficiency in metal leaching [27–30]. Hydrophilic DESs are also used to leach metal ions in combination with ultrasound, which accelerates the process of metal transfer into the DES phase [31]. At the same time, the direct extraction of valuable elements from leaching solutions using liquid extraction is feasible with the introduction of hydrophobic deep eutectic solvents (HDESs) [32]. A substantial number of studies have been published on the synthesis of HDESs using substances with known extraction capabilities for metal ions. Currently, the most popular classes of extractants used as components of hydrophobic deep eutectic solvents include organophosphoric acids [33–35], phosphine oxides [36–38], and salts of quaternary ammonium bases [39–41], among others. Typically, the second component in these systems serves as an inert solvent and is chosen based on considerations of environmental friendliness and availability. Recently, however, researchers have published numerous studies examining the influence of all components in the system on the extractability of metals, including those components that do not exhibit extractive properties [42]. Thus, in a study by Tereshatov et al. [43], kerosene and the eutectic solvent dodecanoic acid:menthol were compared as diluents for di(2-ethylhexyl)phosphoric acid (D2EHPA). In the case of In(III), a higher distribution coefficient was observed in kerosene, whereas the opposite was true for Tl(I) extraction.

Vargas et al. [37] demonstrated that trioctylphosphine oxide (TOPO) in hydrophobic deep eutectic solvents forms more hydrogen bonds with thymol than with dodecanoic acid, due to its tendency to dimerise. Consequently, the HDES thymol/TOPO exhibits a lower extraction capacity for Pd(II), resulting in an increased separation coefficient between Pd(II) and Pt(IV) ions.

One of the authors' previous works [44] found that the energy of the bound TOPO complex as an extractant, in conjunction with various hydrogen bond donors that lack extraction ability, correlated well with the degree of Sm extraction under the same conditions. Specifically, the degree of Sm extraction increased in the order of thymol/TOPO < para-tert-butylphenol/TOPO < phenol/TOPO, with an improvement of over 40%. In addition, there is considerable interest in studying the synergistic effects arising from the interactions of different components in HDESs, as these can significantly enhance extraction efficiency. In a study by Hanada et al. [38], several eutectic mixtures exhibiting high extraction capacity for lithium were proposed; this was attributed to the synergistic effect arising from the interaction between diketones and organophosphorus extractants. Hydrophobic deep eutectic solvents of similar composition were subsequently employed to regenerate lithium from Li_2CO_3 masterbatch solutions, demonstrating high efficiency [45,46]. In a study by Ni et al. [47], a triple deep eutectic solvent (DES) composed of 1-dodecanol, oleic acid, and bis(2-ethylhexyl)amine (in a ratio of 9:1:5) was successfully applied for the synergistic separation of yttrium from heavy rare earth elements. Hydrophobic deep eutectic solvent

(HDES) was easily regenerated through a two-step stripping process using water and a $Na_2C_2O_4$ solution. Other synergistic mixtures are known, such as D2EHPA/TOPO in an organic solvent, which exhibits high selectivity for transition metals [48], as well as uranium [49].

The authors have previously demonstrated the extraction ability of organophosphorus extractants based on HDESs with a number of metals. Thus, in [33], a D2EHPA and menthol-based HDES in a molar ratio of 1:1 was used for the extraction of Ni(II), Cu(II), and Al(III). It was shown that at a phase ratio of O/A = 1/5, the extraction degree of all metals increased with increasing pH from 0 to 5, with the maximum value of the Cu(II) and Ni(II) extraction degree reaching 57.9 and 24.6% at pH 4.9 and 3.1, respectively, while the extraction degree of Al is more than 99% at pH > 2. In [50], the previous extractant and HDES Aliquat 336/menthol were used to separate Ni(II), Co(II), Cu(II), Fe(III), Al(III), and Li from hydrochloric acid leaching solutions of lithium-ion batteries. Process schemes for metal separation from cathode leach solutions were proposed, where HDES Aliquat 336/menthol was used for selective Cu(II) and Co(II) extraction, while HDES D2EHPA/menthol was used to extract aluminium from the mixture in two steps of countercurrent extraction at pH 2.5, O/A = 1. Under these conditions, the Al extraction rate was more than 98%. In the following work [35], an HDES was used for the extraction of Mn and Co. It was shown that at O/A = 5/1, the extraction rate of Mn(II) and Co(II) increases with increasing pH value, and the maximum extraction rates of 59.5 and 29.3% are reached at pH 3.5. The obtained data show the possibility of both co-extraction and separation of metals.

The authors have previously demonstrated [51] that a mixture of D2EHPA and TOPO can be considered an HDES with extraction properties. This system generates significant interest for further detailed investigation, as it has the potential to exhibit synergism in metal extraction. A D2EHPA/TOPO HDES at a molar ratio of 8:2 was used to extract Co(II) and Al(III), which showed at pH 4 and O/A = 5/1 recovery efficiencies of 30 and 99%, respectively. To improve the physical properties of the system and reduce the concentration of D2EHPA and TOPO, and thus lower the cost of the HDES, the natural component menthol was employed as a “diluent”. The use of menthol eliminates the need for toxic and volatile organic solvents, making the system more environmentally friendly, safer, and more suitable for industrial applications. In the current work, the eutectic solvent TOPO/D2EHPA/menthol has been examined, along with the practical aspects of its application for processing lithium-ion batteries with an NMC cathode and LTO anode. Previously, the authors studied the leaching process of these batteries and identified optimal conditions [52]. The quantitative composition of the resulting hydrochloric acid leaching solution was 2.492 g/L Li, 9.724 g/L Co, 2.113 g/L Ni, 1.209 g/L Mn, and 0.048 g/L Ti, with a residual HCl concentration of 1 mol/L. The target metals in this study were Li, Ti, Co, Ni, and Mn.

The aim of this work was to study the extraction of a number of metals (Ti, Co, Mn, Ni, and Li), which are the components of NMC-LTO batteries, by a new three-component hydrophobic deep eutectic solvent, TOPO/D2EHPA/menthol, to select optimum conditions and parameters of the process of effective and selective extraction of metals from synthetic hydrochloric acid leachates of NMC-LTO batteries, and to implement these processes on a laboratory setup.

2. Materials and Methods

2.1. Reagents

The reagents used in this study, as listed in Table 1, were employed without additional purification.

Table 1. Reagents.

Reagent	Supplier	CAS	Purity, wt% *
TOPO	Macklin, Shanghai, China	78-50-2	98
D2EHPA	Macklin, Shanghai, China	298-07-7	98
L-Menthol	Acros, Geel, Belgium	2216-51-5	99.5
$MnCl_2 \cdot 4H_2O$	Acros, Geel, Belgium	13446-34-9	≥99
$CoCl_2 \cdot 6H_2O$	Acros, Geel, Belgium	7646-79-9	≥98
$NiCl_2 \cdot 4H_2O$	Acros, Geel, Belgium	7791-20-0	≥98
LiCl	Macklin, Shanghai, China	7447-41-8	≥98
$TiOSO_4$	Macklin, Shanghai, China	13825-74-6	≥95
H_3PO_4	Acros, Geel, Belgium	7664-38-2	≥85
H_2SO_4	Acros, Geel, Belgium	7664-93-9	96
H_2O_2	Merck, Darmstadt, Germany	7722-84-1	37
HCl	Aldosa, Moscow, Russia	7647-01-0	37
Solvent	Hydranal Honeywell, Seelze, Germany	-	-
Titrant 5	Hydranal Honeywell, Seelze, Germany	-	-
Coulomat A	Hydranal Honeywell, Seelze, Germany	-	-
Coulomat CG	Hydranal Honeywell, Seelze, Germany	-	-

* Declared by suppliers.

2.2. Preparation of HDESs

All HDESs were prepared by mixing the components and weighed on Explorer analytical scales (OHAUS, Nanikon, Switzerland) in a thermostatically controlled Enviro-Genie SI-1202 shaker (Scientific Industries, Inc., Bohemia, NY, USA) at 60 °C and with a rotation speed of 35 rpm for 30 min until a homogeneous mixture was formed. The resulting HDESs were colourless, transparent liquids at room temperature.

2.3. Characterisation of HDESs

The density of the HDESs was measured using an Anton Paar DMA 1001 device (Anton Paar, Graz, Austria) with an accuracy of ±0.00001 g/mL. The refractive index was determined using an Anton Paar Abbemat 3200 refractometer (Anton Paar, Graz, Austria) with an accuracy of ±0.0001. The viscosity of the HDESs was studied through rotational rheometry using a Physica MCR301 rheometer (Anton Paar, Graz, Austria) equipped with a cone-plane measuring unit (cone diameter 50 mm, cone angle 1°). The water content in the deep eutectic solvents was determined by the Karl Fischer titration method using the T-40VC automatic titrator (MT Measurement, Moscow, Russia). Titration of the HDES samples was performed by the coulometric method before contact with water and by the volumetric method subsequently.

2.4. Extraction and Stripping Processes

The initial metal salt solutions were prepared by dissolving their suspensions in distilled water acidified with hydrochloric acid. All experiments to establish the regularities of metal extraction in systems with an HDES were carried out from individual hydrochloric acid solutions with initial metal concentrations in solutions of 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti. Experiments on the laboratory setup were carried out on synthetic leaching solution, by qualitative and quantitative composition identical to the average composition of real leaching solution of NMC-LTO batteries: 9.724 g/L Co, 1.209 g/L Mn, 0.048 g/L Ti, 2.492 g/L: Li, and 2.113 g/L Ni in 1 mol/L HCl. With an increase in the concentration of HCl in the synthetic leaching solution, the concentrations of metals were 5.304 g/L Co, 0.659 g/L Mn, 1.359 g/L Li, and 1.152 g/L Ni in 6 mol/L HCl. To evaluate extraction isotherms, metal solutions with different initial concentrations were prepared: from 0.001 to 0.2 mol/l for Co(II) and Mn(II) ions and from 0.01 to 0.37 mol/l for Ti(IV) ions. All extraction experiments were conducted in 15 mL graduated tubes at room temperature and atmospheric pressure with a 1:1 volume ratio of aqueous to organic phases. The tubes were placed in an IKA Treyster shaker (IKA, Cologne, Germany) and mixed at a rotational speed of 45 rpm until thermodynamic equilibrium was reached. Following this, the tubes were centrifuged in a SIA ELMI CM-6MT centrifuge (SIA ELMI, Riga, Latvia) at 2500 rpm to achieve complete phase separation. The aqueous phase was then separated from the organic phase using a separating funnel.

The concentration of metals in the aqueous phase was measured using inductively coupled plasma optical emission spectrometry (ICP-OES) on a ICAP PRO XP device (Thermo Scientific, Waltham, MA, USA), while the concentration of metals in the organic phase was determined through material balance calculations.

The degree of extraction (E, %) was calculated using the following equation:

$$E(\%) = \frac{n_{in} - n_{\mathrm{aq}}}{n_{in}} \cdot 100\%, \tag{1}$$

where n_{in} and n_{aq} are the number of moles of metal in the initial solution before extraction and the number of moles of metal in the aqueous phase after extraction, respectively.

The degree of stripping (S, %) was calculated using the following equation:

$$S(\%) = \frac{n_{\mathrm{S}}}{n_{\mathrm{HDES}}} \cdot 100\%, \tag{2}$$

where n_{S} and n_{HDES} are the number of moles of metal in the aqueous phase after stripping and the number of moles of metal in the organic phase before stripping, respectively.

The experimental data presented are the result of a series of three experiments, which were processed using mathematical statistics.

2.5. Laboratory Extraction Plant

The suitability of the technology cannot be fully assessed using only data on the physicochemical properties of the system, its extraction capacity, or technological calculation. Therefore, one of the important steps in the study is the approbation of the method of extraction equipment. In this study, metal extraction experiments were conducted using a SOLVEX 8.04 mixer-settler extractor (Solvex, Moscow, Russia). The operational scheme of the apparatus is illustrated in Figure 1. This type of equipment represents a fundamental design in extraction systems, which offers simplicity and cost-efficiency in its construction while enabling effective simulation and optimisation of liquid extraction processes. It should be noted that the used unit is semi-industrial equipment, which allows for evaluating the technological suitability of new extraction systems in the closest way to real conditions. A comprehensive description of the technical specifications of the apparatus has been provided in a previous publication [53].

The initial model leach solution, identical to the real leach solution of NMC-LTO batteries, and the HDES phase were introduced into the device using a BT-100M (Shenzhen Pump Medical System Co., Ltd., Shenzhen, China) equipped with an AMC series working head, allowing for multi-channel connections. Silicone peristaltic tubes with an inner diameter of 3 mm and a wall thickness of 1 mm were used; these were capable of delivering volume flow rates ranging from 0.03 to 45.4 mL/min. The volumetric flow rate of the phases was maintained at a maximum of 1 L/h due to the operational constraints of the equipment. The residual concentration of metals in the raffinate after each experiment was analysed using the ICP-OES method, based on three 10 mL samples collected from the discharge of the heavy phase after a stable hydrodynamic regime had been established. A total of 10 mL of the raffinate phase was sampled to analyse the metal content of the solution. A stable hydrodynamic regime was deemed achievable after the passing of a volume of fluid through the apparatus that was equivalent to five times the apparatus's volume (250 mL). It should be noted that in this mode, the volume of phases in the chambers did not change during the whole operation time of the setup. During the operation, no stable emulsions were formed, and the heavy and light phases were discharged separately without contamination.

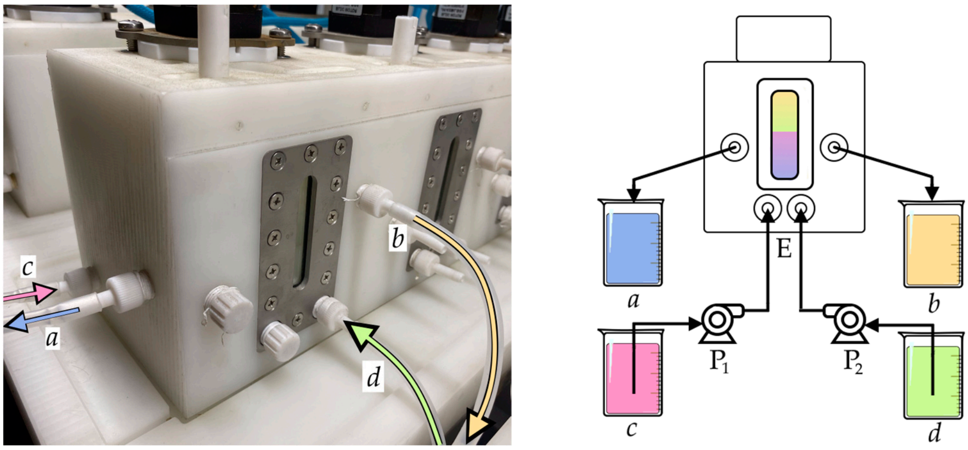

Figure 1. A photo and scheme of a laboratory installation in operation: *a*—raffinate solution, *b*—extract solution, *c*—initial solution with appropriate metal concentration and HCl, *d*—HDES, P—pump, E—extractor.

3. Results and Discussion

3.1. Physical Properties of HDES TOPO/D2EHPA/Menthol 4:1:5

The density and viscosity of the hydrophobic deep eutectic solvent (HDES) composed of TOPO/D2EHPA/menthol in a 4:1:5 molar ratio (Figure 2) were investigated. This composition exhibited significantly improved physical properties compared with the binary mixture of TOPO/D2EHPA [51]. At room temperature, the density of the HDES examined was measured at 0.89 g/mL, while the dynamic viscosity was found to be 56 mPa·s (Figure 2a,b). Most industrial extractors operate effectively with a density ratio of light to heavy phases of no more than 0.95; a lower density facilitates more efficient emulsion separation under the influence of centrifugal forces or gravity. The measured viscosity was satisfactory, as the most technologically suitable systems typically have viscosities of no more than 100 mPa·s.

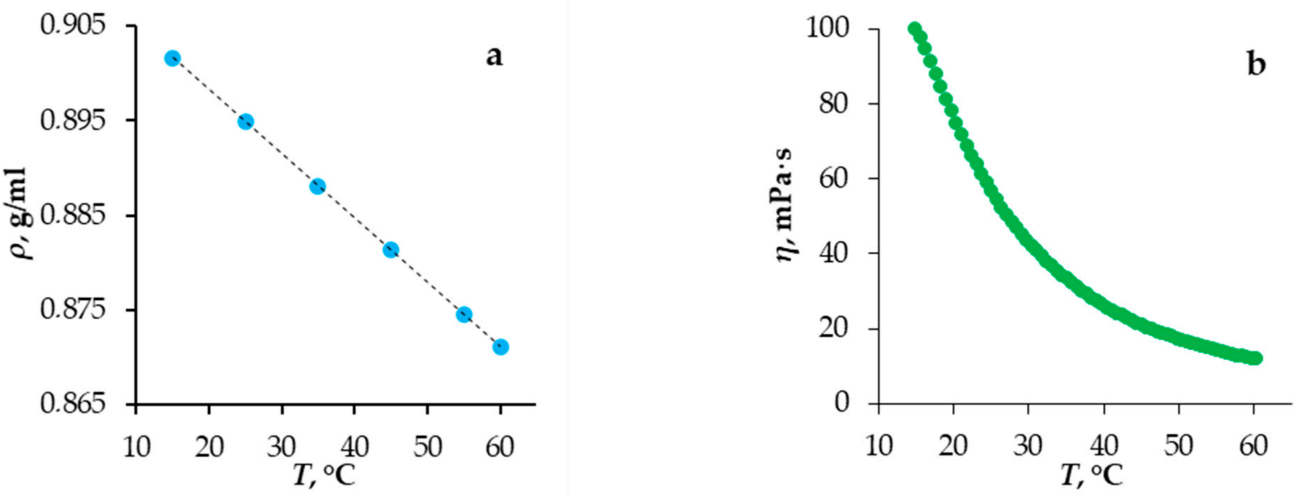

Figure 2. Dependence of density (**a**) and dynamic viscosity (**b**) of the HDES composed of TOPO/D2EHPA/menthol in a 4:1:5 ratio on temperature.

The concentration of components in the proposed HDES composed of TOPO/D2EHPA/menthol in a 4:1:5 ratio was calculated based on the density obtained, resulting in the following concentrations: [TOPO] = 1.35 mol/L, [D2EHPA] = 0.34 mol/L, and [menthol] = 1.69 mol/L. It is worth noting that TOPO at this concentration is insoluble in traditional solvents such as kerosene, making HDES the most suitable solvent for this extractant.

In addition, the water content in this HDES was assessed both before and after 24 h of contact with water. Initially, the water content was measured at 0.24 wt%, which increased to 2.45 wt% after the contact period.

3.2. Selection of HDES Composition and Investigation of Its Extraction Properties

3.2.1. The Effect of Menthol Content in the HDES

The dependence of the degree of metal ion extraction on the menthol content in the mixture was established, with the molar ratio of D2EHPA to TOPO maintained at 1:1 (Figure 3).

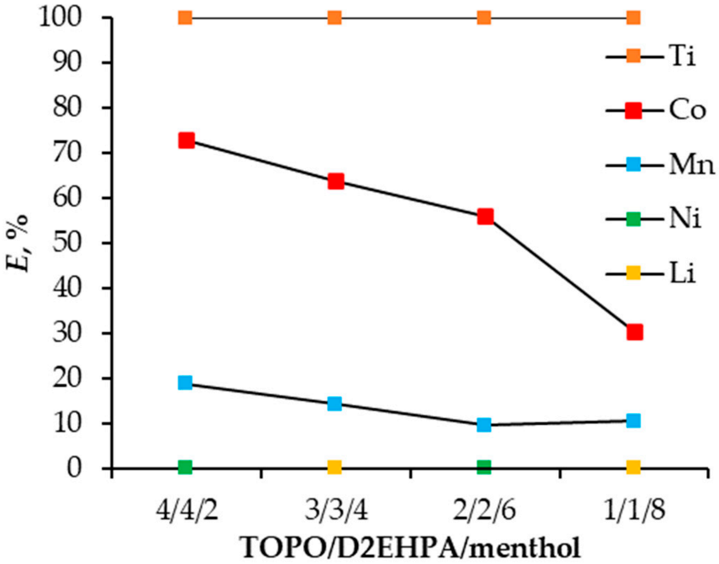

Figure 3. Dependence of the degree of extraction of metal ions on the menthol content in the HDES. HDES phase: $\chi_{TOPO}/\chi_{D2EHPA}$ = 1:1. Aqueous phase: [HCl] = 8 mol/L; V_{aq}/V_{HDES} = 1/1; mixing time was 30 min.

The data obtained indicate that as the amount of menthol in the mixture increased, the extraction efficiency for Ti(IV) ions remained constant, while the extraction of Mn(II) and Co(II) ions declined. Under these conditions, Ni(II) and Li^+ ions were not extracted. The reduction in extraction efficiency for Mn(II) and Co(II) ions was expected, as menthol lacks extraction capability for the metals studied. Since menthol has no extraction capacity, increasing its concentration leads to a decrease in the concentration of the extracting component, which reduces the extraction efficiency of Mn(II) and Co(II). In this case, the slope of the extraction curve for Mn(II) is less steep than that for Co(II), suggesting that the addition of menthol adversely affected cobalt extraction more than that of manganese. In addition, the separation coefficient of the challenging Mn/Co pair increased with a reduction in menthol concentration, further enhancing the separation of this metal pair. It is worth noting that the use of menthol as a component of the HDES is an ecological and safe alternative to the use of traditional organic solvents.

For the subsequent experiment, the mole fraction of menthol was maintained at a constant value of 4. This concentration was sufficient to reduce the concentrations of TOPO and D2EHPA in the mixture while minimising losses in extraction efficiency.

3.2.2. The Impact of TOPO Content in the HDES

The next step in selecting the most effective and selective composition of the HDES was to vary the ratio of the molar fractions of TOPO and D2EHPA, with their total value being 6 and menthol being 4. The results demonstrate that as the molar fraction of TOPO increased and the proportion of D2EHPA decreased, the extraction efficiency for Co(II) and Mn(II) ions improved, while Ti(IV) ions were quantitatively extracted across the entire range studied. Ni(II) and Li^+ ions remained unextracted (Figure 4).

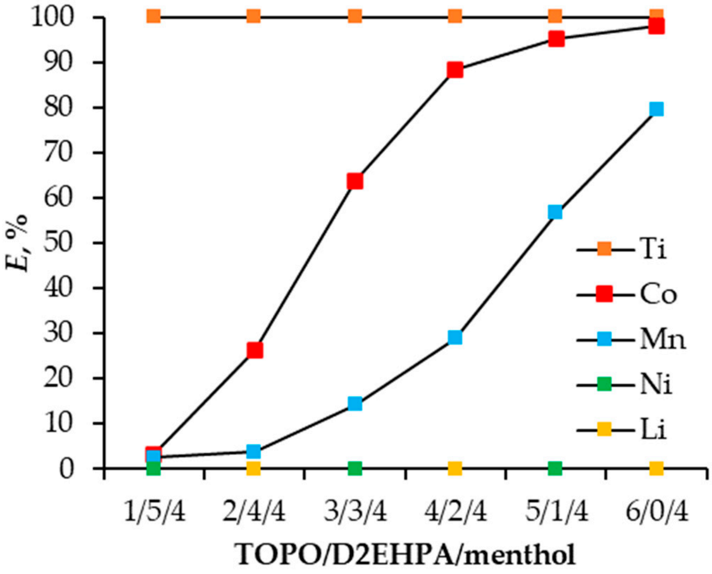

Figure 4. The dependence of the degree of extraction of metal ions on the content of TOPO and D2EHPA in the HDES. HDES phase: $\chi_{menthol} = 4$. Aqueous phase: [HCl] = 8 mol/L, 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti; $V_{aq}/V_{HDES} = 1/1$; mixing time was 30 min.

This trend suggests that TOPO is a more effective extractant for Mn(II) and Co(II) ions in a hydrochloric acid medium than D2EHPA. Furthermore, the resulting graph indicates that the optimal separation of the Mn/Co pair occurred at a TOPO molar fraction of 4. For subsequent experiments, the molar fraction of TOPO was maintained at 4.

3.2.3. The Effect of D2EHPA Content in the HDES

The next step involved investigating the effect of varying amounts of D2EHPA on the efficiency of metal ion extraction while keeping the TOPO content in the mixture constant ($\chi_{TOPO} = 4$) (Figure 5). The resulting graph illustrates that as the molar fraction of D2EHPA increased to 1, the extraction efficiency for Ti(IV) and Co(II) ions increased. However, beyond this point, the extraction of Ti(IV) remained constant, while the extraction efficiency for Co(II) began to decline. Ni(II) and Li^+ ions continued to show no extraction. In addition, the extraction efficiency for Mn(II) ions decreased throughout the entire studied range.

This behaviour of Ti(IV) and Co(II) ions can be attributed to the initial increase in D2EHPA, which enhances the total extractant concentration, thereby improving extraction efficiency. Conversely, further increases in extractant concentration may hinder extraction, probably due to the formation of strong hydrogen bonds between TOPO and D2EHPA that interfere with the extraction process.

Importantly, the increase in the molar fraction of D2EHPA to 1 also led to a decrease in the extraction efficiency of Mn(II) ions, as well as Co(II) ions, providing an additional advantage for the separation of this metal pair.

Thus, it was determined that the optimum TOPO/D2EHPA ratio is 4/1; to maintain this molar ratio, the mole fraction of menthol was increased to 5. Varying the ratio of the

HDES components and comparing the extraction efficiencies enabled the identification of the composition of the TOPO/D2EHPA/menthol mixture in a 4:1:5 ratio. This formulation demonstrated the highest selectivity and efficiency for the metal ions studied, facilitating the separation of the Co/Mn pair in particular.

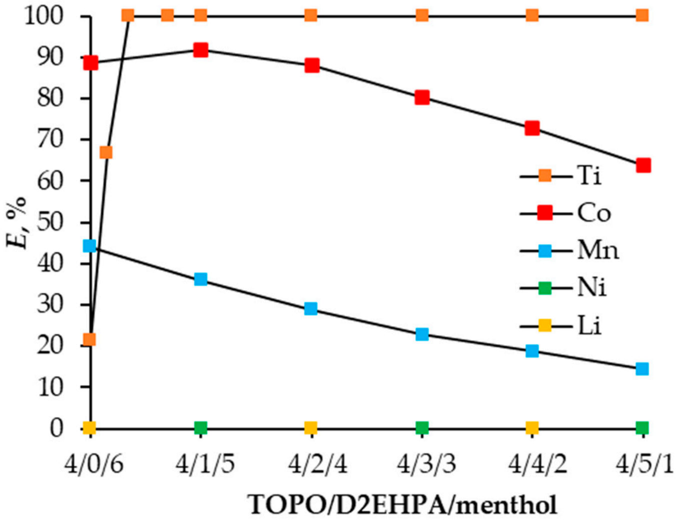

Figure 5. Dependence of the degree of metal ion extraction on the molar fraction of D2EHPA. Aqueous phase: [HCl] = 8 mol/L, 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti. HDES phase: χ_{TOPO} = 4; V_{aq}/V_{HDES} = 1/1; mixing time was 30 min.

3.2.4. Influence of Phase Contact Time

Kinetic dependences of the degree of extraction of metal ions from 6 mol/l HCl HDES TOPO/D2EHPA/menthol 4:1:5 solution were obtained in the range from 1 to 60 min (Figure 6). From the data obtained, it can be seen that thermodynamic equilibrium was achieved for Ti(IV) ions in 1 min, for Co(II) ions in 5 min, and for Mn(II) ions in 20 min; Ni(II) and Li^+ were not extracted. The relatively short time of the extraction process, especially in the case of titanium and cobalt, will allow this system to be used with industrial extraction equipment. Such a significant time difference between cobalt and manganese is an additional advantage for their kinetic separation.

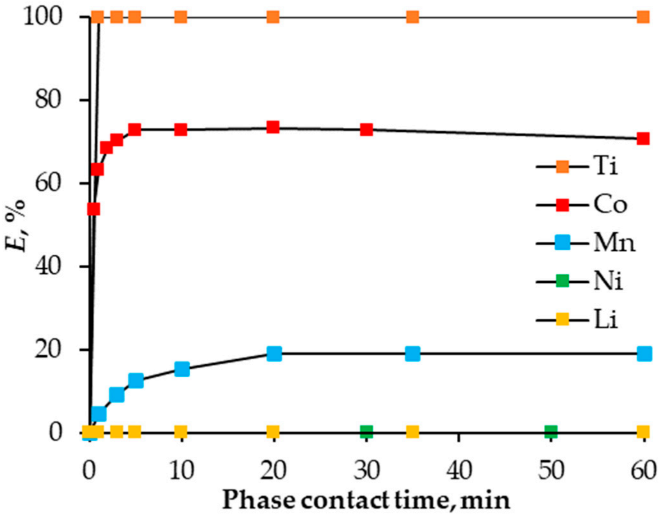

Figure 6. Dependence of the degree of extraction of metal ions on the phase contact time. HDES phase: TOPO/D2EHPA/menthol = 4:1:5. Aqueous phase: [HCl] = 6 mol/L, 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti; V_{aq}/V_{HDES} = 1/1.

For comparison, the extraction of Co(II), Ni(II), Mn(II), Ti(IV), and Li(I) with metal concentrations of 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti with 6 mol/L HCl with a solution of 1.35 mol/L TOPO in toluene was carried out. The experimental results are summarised in Table 2.

Table 2. Extraction degree of metals from solution [HCl] = 6 mol/L, 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti with 1.35 mol/L TOPO in toluene.

Metals	**Ti**	**Co**	**Mn**	**Ni**	**Li**
E, %	99.9	90.9	40.8	1.2	0

The results show that in the system with HDES TOPO/D2EHPA/menthol (4:1:5), the extraction of Co(II) and Mn(II) is slightly lower compared to 1.35 M TOPO in toluene, which is explained by the decrease in the extraction ability of TOPO in the HDES due to the formation of strong intermolecular hydrogen bonds.

3.2.5. The Effect of the Acidity of the Medium

The effect of medium acidity on the extractability of metal ions from the hydrophobic deep eutectic solvent (HDES) was investigated over a range of hydrochloric acid concentrations from 0.1 to 10 mol/L (Figure 7).

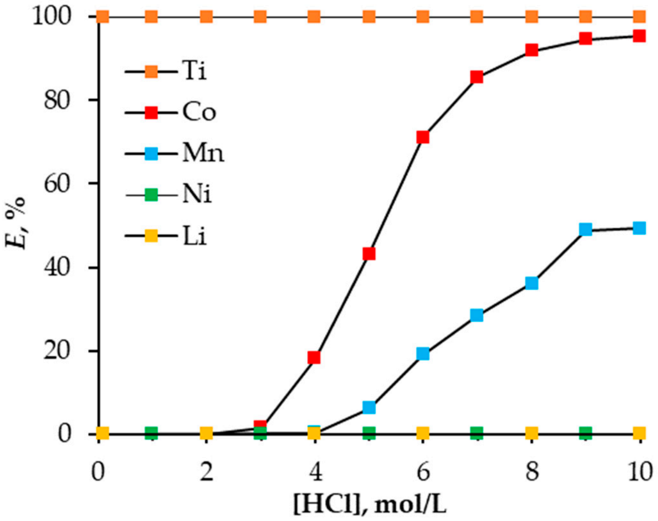

Figure 7. The dependence of the degree of extraction of metal ions on the concentration of HCl. HDES phase: TOPO/D2EHPA/menthol = 4:1:5. Aqueous phase: 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti; V_{aq}/V_{HDES} = 1/1; mixing time was 30 min.

The data obtained indicate that as the concentration of hydrochloric acid (HCl) increased, the degree of extraction of Co(II) and Mn(II) ions also increased. In contrast, Ni(II) and Li^+ ions were not extracted, even at 10 mol/L HCl, while Ti(IV) ions were quantitatively extracted into the HDES phase across the entire range of acid concentrations. In this HDES, two components exhibited extraction capabilities for metals: TOPO and D2EHPA. TOPO, a neutral extractant, demonstrated an increased extraction ability with increasing acidity in the medium. The extraction mechanism can generally be described as follows [54,55]:

$$nH^{+}{}_{aq} + MeCl_{m}^{n-}{}_{aq} + xTOPO_{org} \leftrightarrow H_nMeCl_m{\cdot}xTOPO_{org}, \quad (3)$$

where *Me* is a metal ion.

D2EHPA is a cation exchange extractant at low acid concentrations [33].

$$Me^{n+}{}_{aq} + nHA_{org} \rightleftharpoons MeA_{n\,org} + nH^{+}_{aq}, \quad (4)$$

where HA is D2EHPA.

However, with an increase in the acidity of the medium, its dissociation is suppressed, and the extraction mechanism is replaced by a neutral one [56].

$$nH^{+}{}_{aq} + MeCl_{m}^{n-}{}_{aq} + nHA_{org} \rightleftharpoons (H_{n}MeCl_{m})(nHA)_{org} \tag{5}$$

Thus, both TOPO and D2EHPA extract metal ions in the form of chloride-anionic complexes upon the addition of HCl. In addition, the graph indicates that by varying the amount of HCl, it is possible to selectively isolate Ti, followed by Co and then Mn. The effective extraction of Ti(IV) ions across the entire range of HCl concentrations can be attributed to the high level of efficiency of organophosphorus extractants, particularly TOPO, in extracting titanium [57]. The lack of extraction of Ni(II) and Li^{+} ions may be explained by the instability of their chloride-anionic complexes within this HCl concentration range.

Lithium can be selectively separated either at the final stage from the raffinate containing Li and Ni or at an earlier stage, after Ti extraction, from the raffinate containing Co, Mn, and Ni. Membrane methods can be used for this purpose [58].

3.2.6. The Effect of the Volumetric Phase Ratio

An important parameter in all extraction processes is the volume phase ratio. The effect of the aqueous to organic phase ratio on the efficiency of metal ion extraction was studied in the range from 0.5 to 5 (Figure 8). The results indicate that as the volume of the organic phase decreased, the degree of metal ion extraction also decreased. This decrease can be attributed to the reduced excess of the extractant relative to the metal ions. In this case, the most suitable ratio of the aqueous to organic phases was 1, as a ratio of 0.5 resulted in the excessively high consumption of the extractant.

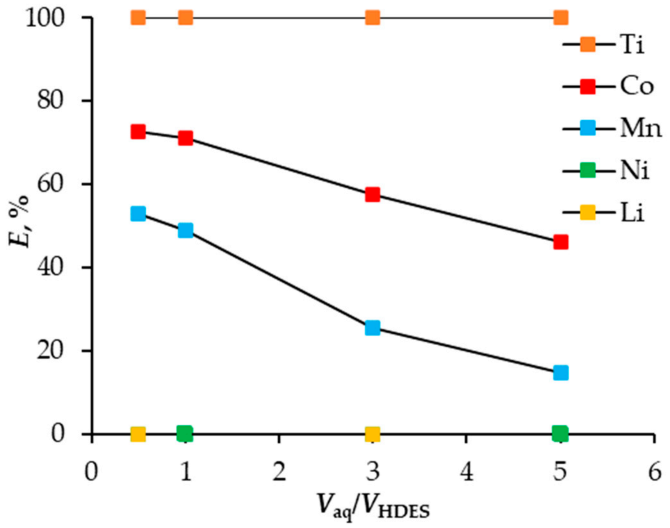

Figure 8. Dependence of the degree of extraction of metal ions on the volume ratio of the aqueous and organic phases. HDES phase: TOPO/D2EHPA/menthol = 4:1:5. Aqueous phase: 0.069 g/L Li, 0.589 g/L Co, 0.587 g/L Ni, 0.549 g/L Mn, and 0.479 g/L Ti; mixing time was 30 min.

3.2.7. The Influence of the Initial Concentration of Metal Ions

Since the concentration of metal ions in real leaching solutions can vary significantly, this factor must be considered. Figure 9 presents the extraction isotherms for a series of metals in the TOPO/D2EHPA/menthol system. The isotherms for Co(II) and Mn(II) display linear relationships, indicating a constant distribution coefficient throughout the concentration range investigated. This, in turn, greatly simplifies the modelling of multi-stage continuous extraction processes and ensures consistent results when using feed materials with varying concentrations of target metal ions. The extraction behaviour of Ti(IV) differed from that of Co(II) and Mn(II), as it was extracted significantly more efficiently, although its linearity was maintained in the initial portion of the isotherm. It is notable that saturation of the extractant during the extraction of Co(II) and Mn(II) did not occur, even at an initial metal concentration of 11.787 g/L and 10.988 g/L, respectively. In contrast, saturation did occur during the extraction of titanium when its concentration in the organic phase reached 14.389 g/L.

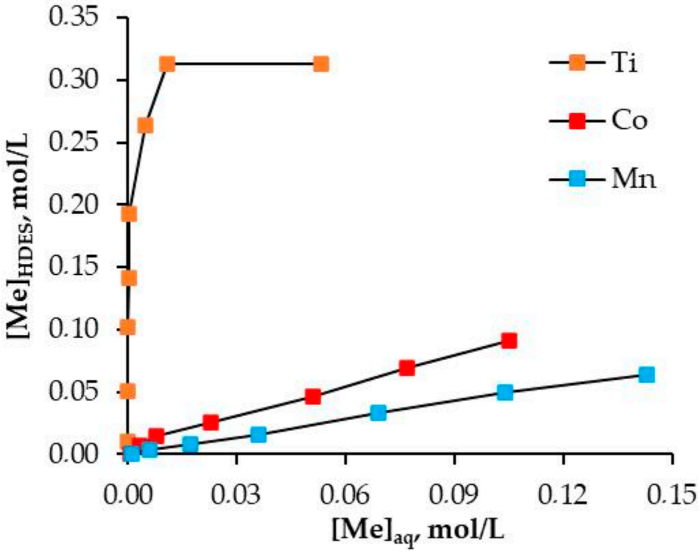

Figure 9. Isotherms of the Me extraction with TOPO/D2EHPA/menthol = 4:1:5. Aqueous phase: [HCl] = 1, 6, 9 mol/L for Ti(IV), Co(II), and Mn(II) ions, respectively; V_{aq}/V_{HDES} = 1/1; mixing time was 30 min.

3.2.8. Study of Metal Stripping from the HDES Phase

Titanium ions exhibit slow stripping kinetics from acidic organophosphorus extractants, making stripping on laboratory extraction equipment challenging, especially since the selected HDES includes D2EHPA. Solutions of mineral acids and their sodium salts are commonly used as re-extractants for Ti(IV) ions [59–61]. However, the interaction of sodium salts with D2EHPA may lead to the precipitation of sodium D2EHPA salt, which is why the present study considered mineral acid solutions as stripping solutions.

For the stripping of Co(II) and Mn(II) ions from the HDES phase, a 1 mol/L HCl solution was used, with a volume ratio of the HDES phase to the re-extractant phase set at 1:1. The stripping efficiency exceeded 99% for both Co(II) and Mn(II) ions within a 10 min processing time.

Given that Ti(IV) ions are quantitatively extracted into the organic phase across the entire range of HCl concentrations, an HCl solution would be ineffective for stripping. However, it is known that titanium ions exhibit a strong affinity for sulphate ions. Furthermore, the presence of H_2O_2 promotes the formation of stable complexes such as $TiO(H_2O_2)SO_4$. Experiments were conducted on the stripping of Ti(IV) from the organic phase using 1M H_2SO_4 solutions supplemented with 2 vol.% H_2O_2 at a 1:1 phase volume ratio over 2 h. The stripping efficiency was recorded at 14.2%. Increasing the H_2O_2 concentration to 10 vol.% enhanced the stripping efficiency to 19.6%.

Subsequently, a 1 mol/L phosphoric acid solution was used, with 3 vol.% H_2O_2, as the re-extractant for the metal ions. The volume ratio was maintained at 1:1, with a mixing time of 60 min. The stripping efficiency for titanium ions reached 88.3%. When the phosphoric acid concentration was raised to 3 mol/L, the stripping efficiency increased to 99.9% within 60 min.

Kinetic dependencies for the stripping of Ti(IV) ions from the organic phase using a 3 mol/L H_3PO_4 solution with 3 vol.% H_2O_2, along with Co(II) and Mn(II) ions using a 1 mol/L HCl solution, were established (Figure 10).

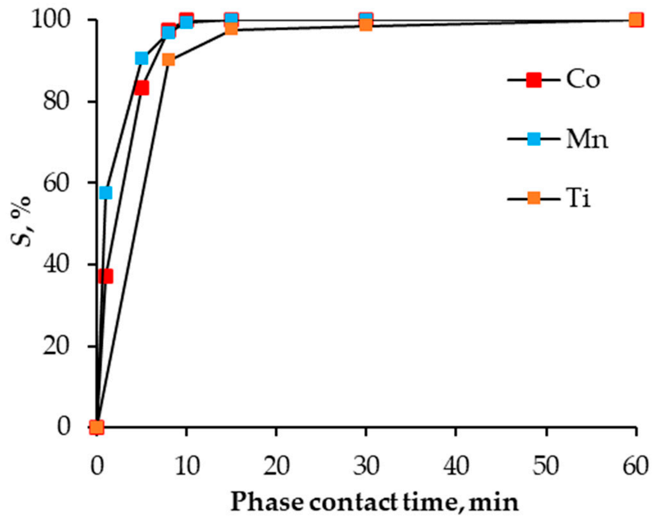

Figure 10. Dependence of the degree of stripping of Ti(IV), Co(II), and Mn(II) ions on the phase contact time. Extraction conditions for Ti(IV), Co(II), and Mn(II): [HCl] = 1, 6, and 9 mol/L, respectively. Stripping conditions for Ti(IV): [H_3PO_4] = 3 mol/L, 3 vol.% H_2O_2; for Co(II) and Mn(II): [HCl] = 1 mol/L.

It is evident from the obtained graph that thermodynamic equilibrium is reached in 15 min. Thus, the following conditions were chosen to perform the stripping of Ti(IV) ions from the HDES phase: 3M H_3PO_4 + 3 vol.% H_2O_2, O/A = 1/1, mixing time was 15 min.

3.2.9. Stability Assessment of the HDES

An important characteristic of the extractant is its stability; this relates to the preservation of its extraction properties throughout many extraction/stripping cycles. The loss of extractant extraction properties negatively affects the efficiency and long-term operation of the extraction process. Also, the low stability of the extractant or its solubility in water might lead to a quantitative loss of the extractant and wastewater pollution, which has a negative impact on the environment. Thus, the possibility of reuse of the extractant without the loss of extraction efficiency is an important property for industrial applications. A study of this characteristic of the HDES TOPO/D2EHPA/menthol 4:1:5 was carried out using 10 extraction/stripping cycles. The results obtained for the extraction of Ti(IV), Co(II), and Mn(II) HDES ions are shown in Figure 11, while the stripping was always 100%.

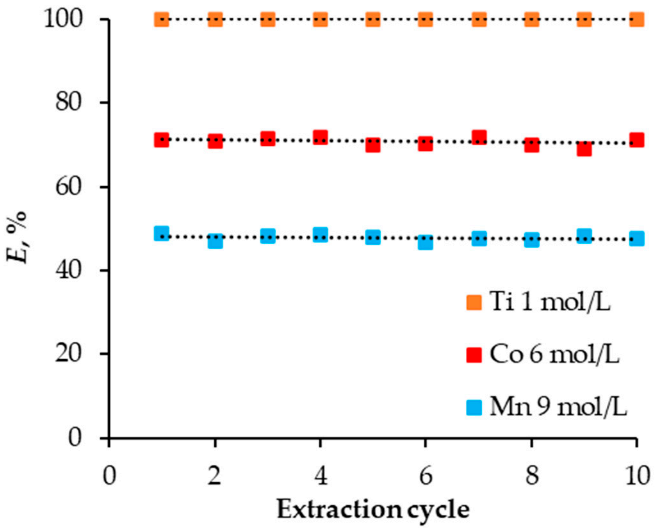

Figure 11. The possibility of the reuse of TOPO/D2EHPA/menthol 4:1:5. Conditions for the stripping of Ti(IV): [H_3PO_4] = 3 mol/L, 3 vol.% H_2O_2; Co(II) and Mn(II) ions: [HCl] = 1 mol/L.

Based on the obtained data, it can be said that the proposed extractant perfectly retains its extraction capacity without reducing the extraction efficiency. This indicates that TOPO/D2EHPA/menthol = 4:1:5 is technologically suitable in terms of stability and has the possibility of use in closed-loop technologies.

3.3. Investigation of Continuous Metal Extraction

An analysis of the results presented in Figure 7 indicates that a gradual increase in the acidity of the medium is essential for the sequential extraction of metal ions from their mixture using the TOPO/D2EHPA/menthol system in a 4:1:5 ratio. To evaluate the behaviour of the proposed hydrophobic deep eutectic solvent using actual extraction equipment, experiments involving the continuous extraction of Ti(IV), Mn(II), Co(II), Ni(II), and Li(I) ions from hydrochloric acid solutions were performed. These experiments were conducted on a laboratory installation comprising settling-mixers, under both milder conditions ([HCl] = 1 mol/L) and harsher conditions ([HCl] = 6 mol/L). The metal concentrations used were consistent with those in the leaching solution of NMC-LTO batteries: 9.724 g/L Co, 2.113 g/L Ni, 1.209 g/L Mn, 0.048 g/L Ti, and 2.492 g/L Li.

This study clearly shows the need for research into the behaviour of new systems on equipment. The results from the study of the extraction process for Ti(IV), Co(II), Ni(II), Mn(II), and Li(I) from their hydrochloric acid solutions, at various volume flow rates of the phases using the HDES TOPO/D2EHPA/menthol in a 4:1:5 ratio, are illustrated in Figure 12. It was observed that with an increase in volume flow, the degree of extraction linearly decreased for all components extracted. Increasing the volume flow rate resulted in the liquid phases being in the mixing chamber for a shorter period of time. In turn, this resulted in a decrease in the time it took for the substance to cross the surface unit. Consequently, thermodynamic equilibrium was not achieved, resulting in a reduced degree of extraction. This phenomenon could be corrected by increasing the stirrer speed, leading to a decrease in emulsion droplets by more rapid dispersion, increasing the contact area between the phases, and increasing the rate of substance transfer from one phase to another, but increasing the stirrer speed led to a departure from the stable hydrodynamic regime due to the formation of phase turbidity.

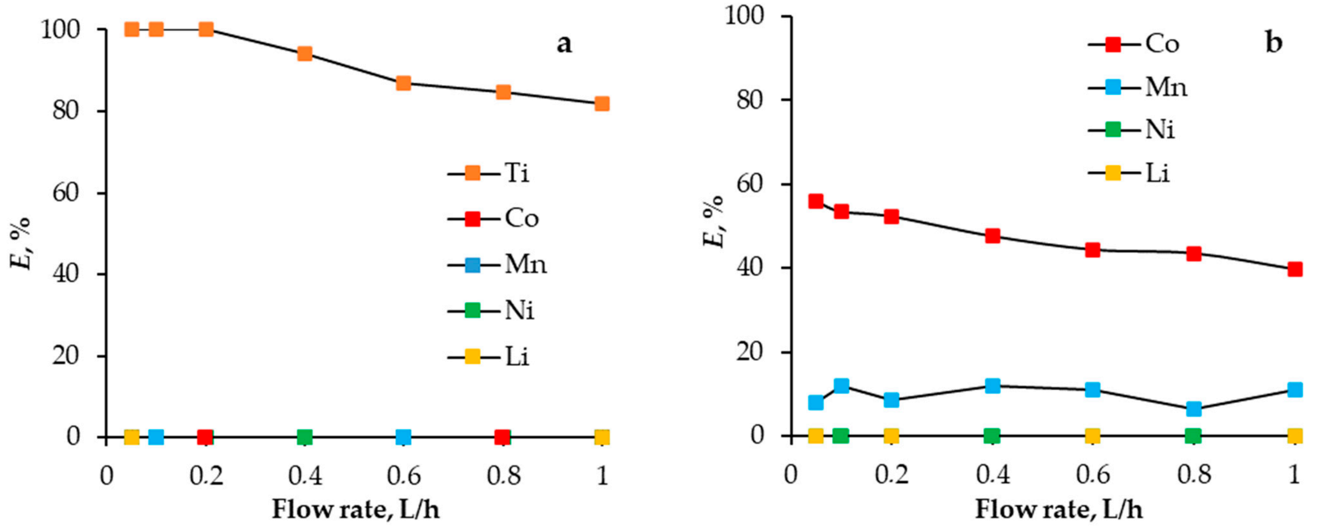

Figure 12. Dependence of the degree of extraction of metals from HCl 1 mol/L solution (**a**) and Co(II) and Mn(II) from HCl 6 mol/L solution (**b**) on the volume flow rate of the phases.

At a hydrochloric acid concentration of 1 mol/L, the HDES demonstrated extraction ability exclusively for Ti(IV) without extracting Co(II), Ni(II), Mn(II), and Li(I). This specificity allows for the extraction of titanium at any volume flow rate of the phases without introducing impurities. The highest level of extraction performance without loss of efficiency occurred at a flow rate of 0.2 L/h, which enabled the complete extraction of Ti(IV) in a single step. From Figure 12b, it is evident that the proposed extraction system successfully extracted the studied metal ions, yielding the expected results. Values for the degree of extraction achieved during continuous experiments with a phase flow rate of up to 0.2 L/h align with equilibrium data. When the phase flow rate increased beyond this point, however, the extraction values declined linearly. This decrease can be attributed to the reduced contact time of the phases in the mixing chamber of the apparatus, resulting in the failure to achieve thermodynamic equilibrium.

Thus, the results of the study of the physical properties of the HDES have shown its technological suitability for extraction processes. The determination of the dependence of the extraction capacity in relation to the metals included in the leaching solutions of LTO batteries allowed for determining the optimal conditions for the separation of elements and the effective composition of the HDES. Finally, the process was implemented on a laboratory unit, including a mixer-settler extractor operating in a stable hydrodynamic regime.

4. Conclusions

The present work demonstrates that, despite the relatively low technological readiness of extraction processes using deep eutectic solvents, exploring various combinations of HDES components can identify promising and technologically suitable systems. This study proposes a deep eutectic solvent composed of TOPO/D2EHPA/menthol, with menthol serving as a modifier of physical properties and a "diluent" to reduce the concentrations of TOPO and D2EHPA. By varying the composition of the HDES, the molar ratio of 4:1:5 for TOPO/D2EHPA/menthol was identified as being optimal in terms of efficiency and selectivity for metal ion extraction. The extraction patterns of a number of Ti(IV), Co(II), Ni(II), Mn(II), and Li(I) ions from their individual hydrochloric acid solutions in the system with HDES TOPO/D2EHPA/menthol (4:1:5) have been established. This composition not only exhibits excellent extraction capabilities for metals present in the leaching solution of LTO-NMC-type lithium-ion batteries but also possesses suitable physical properties for technological applications. Consequently, a series of continuous experiments were conducted using mixer-sump-type extractors. The results indicate the high compatibility of the proposed system with laboratory equipment, achieving a stable hydrodynamic regime without traces of emulsion in the raffinate and extract phases. Therefore, the experimental data obtained in this study highlight the increasing potential for using HDES in complex continuous hydrometallurgical processes.

Author Contributions: A.V.K.: Conceptualization, Methodology, Writing—original draft; N.A.M.: Conceptualization, Formal analysis, Writing—original draft; D.V.L.: Data curation, Investigation, Validation; Y.A.Z.: Supervision, Writing—review and editing; A.A.V.: Project administration, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Russian Science Foundation (grant no. 20-13-00387, https://rscf.ru/en/project/20-13-00387/ (accessed on 14 December 2024)).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: This research was performed using the equipment of the JRC PMR IGIC RAS.

Conflicts of Interest: The authors declare no conflicts of interest.

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