**Separation of Multicomponent Systems in Anionites by Ionite-Extraction Method**

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**Аbstract.** CuCl2 and NiCl2 were completely separated from multicomponent mixtures using a reagent-free ionite-extraction method with the strongly basic anionite ARA-4P. Separations were performed under both acidic and alkaline conditions, demonstrating that the process is independent of pH. Experimental results show that separation efficiency depends primarily on column geometry (diameter and height), solution flow rate, feed concentration, and resin properties.Also, using the heterophase model of the ionite structure, nitric acid was separated from strong electrolyte mixtures by the ionite-extraction method using the anionite ARA-4P. The distribution of the separated electrolytes in the ionite and electrolyte solution phases, the composition of the electrolyte solution in the ionite phase, the distribution constants of water and electrolytes, their activities, and the amount of sorbed water and electrolyte are calculated using an algorithm. The advantages of the ionite-extraction method and the conditions for carrying out the process are shown. In addition, it is shown that the sorption and hydration energies of water from different ion forms of ionites can be determined using experimental results, which makes it possible to separate components from the composition of various mixtures. It is noted that the greater the concentration of the solution at equilibrium, the higher the efficiency of the separation process**.**

**Keywords:** anion exchange; reagent-free separation; ion-exchange column; multicomponent mixtures; acidic-alkaline media.

**INTRODUCTION**

Ion‐exchange resins are indispensable in hydrometallurgical and analytical processes but generate large volumes of acidic or alkaline effluents during regeneration. Traditional regeneration with strong reagents (HCl, NaOH) consumes considerable water, reduces resin capacity through granule compression in concentrated electrolytes, and produces wastewater rich in metal salts that require costly treatment. Developing low reagent or reagent-free separation methods is thus critical for sustainable metal recovery and environmental protection.

The “acid retardation” method, first reported by Hatch and Dillon, exploits the unexpected physical sorption of strong monovalent acids (HCl, H2SO4, H3PO4) into nanopores of a Dowex 1 anion exchanger, such that acids elute after their salts when the column is flushed with water [1]. This finding overturned then accepted “ion exclusion” paradigm and demonstrated that nonionized acid molecules can be selectively retained and recovered from acid–salt mixtures, including FeCl2/HCl, NaCl/HCl, and HClO4/NaClO4.

Building on this foundation, Sidelnikov et al. developed a mathematical model describing dielectric constant and concentration gradients within sorbent pores to simulate nitric acid versus metal-nitrate breakthrough curves, accurately capturing the acid retardation effect in multicomponent feeds [2]. Glotova and co-workers extended these simulations by proposing methods to calculate local dielectric permittivity and ion/molecule distributions in the inner sorbent layer, matching modeled elution profiles to experimental data on nitric acid–nitrate separations [3].

Khamizov et al. introduced two major advances: (a) an “acid retardation” configuration wherein the anion-exchanger bed is pre-impregnated with an immiscible organic phase, enhancing acid–salt separation in concentrated streams and reducing post-digestion acidity for elemental analysis [4]; and (b) a dynamic three-layer model linking molecular retention forces to experimentally observed phosphoric acid purification curves, enabling extraction of key sorption parameters from breakthrough data [5].

Theoretical studies of ion-exchange thermodynamics and polymer swelling have further illuminated the physical basis of acid retardation. Dolgonosov’s heterophase model quantified electrostatic interactions and local permittivity effects in cross-linked polyelectrolyte beads, while Tokmachev et al. demonstrated that resin swelling—and thus available pore volume—is governed primarily by crosslink density and sorbed water activity, independent of external solution composition [6, 7]. Saidov and colleagues applied a heterogeneous-ionite model to compute equilibrium-constant and Gibbs energy variations in NaCl–HCl and MgCl2–HCl systems, validating reagent-free separation thermodynamics in binary electrolyte mixtures [8].

Ion hydration energetics critically influence acid-retardation selectivity: empirical models by Marcus relate hydration-shell width and number of immobilized water molecules to ionic charge/radius ratios, explaining preferential pore uptake of less-hydrated species (e.g., HCl) over highly hydrated metal ions [9]. Molecular dynamics studies by Chen & Ruckenstein and Liu et al. quantified hydration-shell structures and dynamics for alkali, alkaline-earth, and halide ions, linking coordination numbers and water-ion radial distribution functions to effective ionic diameters in sorption processes [10, 11].

Despite these advances, most reports focus on either acidic feeds or binary acid–salt systems; alkaline performance and true multicomponent separations under a single, reagent-free cycle remain underexplored. In this work, we apply the strong-base anion exchanger ARA-4P in a reagent-free ionite-extraction mode to achieve baseline separation (α₍Cu/Ni₎ ≥ 5) of Cu2+ and Ni2+ under both acidic and alkaline conditions, and extend the approach to six-component nitrate mixtures (Fe3+, Al3+, Sr2+, Cs+, Na+, HNO3). This study applies the ionite-extraction method with anion exchanger ARA-4P to separate Cu2+, Ni2+, Fe3+, Al3+, Sr2+, Cs+, and Na+ from multicomponent systems without added reagents.

Key parameters influencing separation efficiency in the ionite-extraction method include the ionite type and quantity, column dimensions, distribution constants of water and electrolytes, and mixture composition. In a typical frontal separation, a mixture of AX and AY passes through an ionite pre-equilibrated with water (acidic or alkaline) at flow rate W. Water (or acid) elutes first, followed by AY at concentration S'AY. Once the ionite’s exchange capacity is exhausted, the feed concentration emerges and the system reaches equilibrium. During the subsequent elution stage, water flushes the retained components, which are collected and analyzed.

Separation efficiency (E) and related parameters are calculated as follows:

(1)

(2)

(3)

(4)

(5)

(6)

where *M* is the ionite mass, *Ecat* is the catalog-specified exchange capacity, *nAX* is the amount of electrolyte AX sorbed, , – the amount of components in the ionite phase, qAX is the sorbed quantity, – the molal concentration of the electrolyte solution in the binary solution.

**EXPERIMENTAL PART**

The experiments used ARA‑4P strongly basic anionite (gel beads, 0.45–1.05 mm). The structure of anionite is shown in Figure 1.

 n  m p

**FIGURE 1.** Structure of the strongly basic anionite ARA-4P.

Analytical reagents included CuCl2 (xr grade), NiCl2, NaOH, HCl standards, NH₃ solution, EDTA, eriochrome black T, murexide, and phenolphthalein. Hydroxyl and hydrogen ions were determined titrimetrically; divalent cations by EDTA complexometry; and NH4⁺ by the formaldehyde method. A 75 ml suspension of ARA‑4P (exchange capacity 67 mg‑eq) was packed in the column.

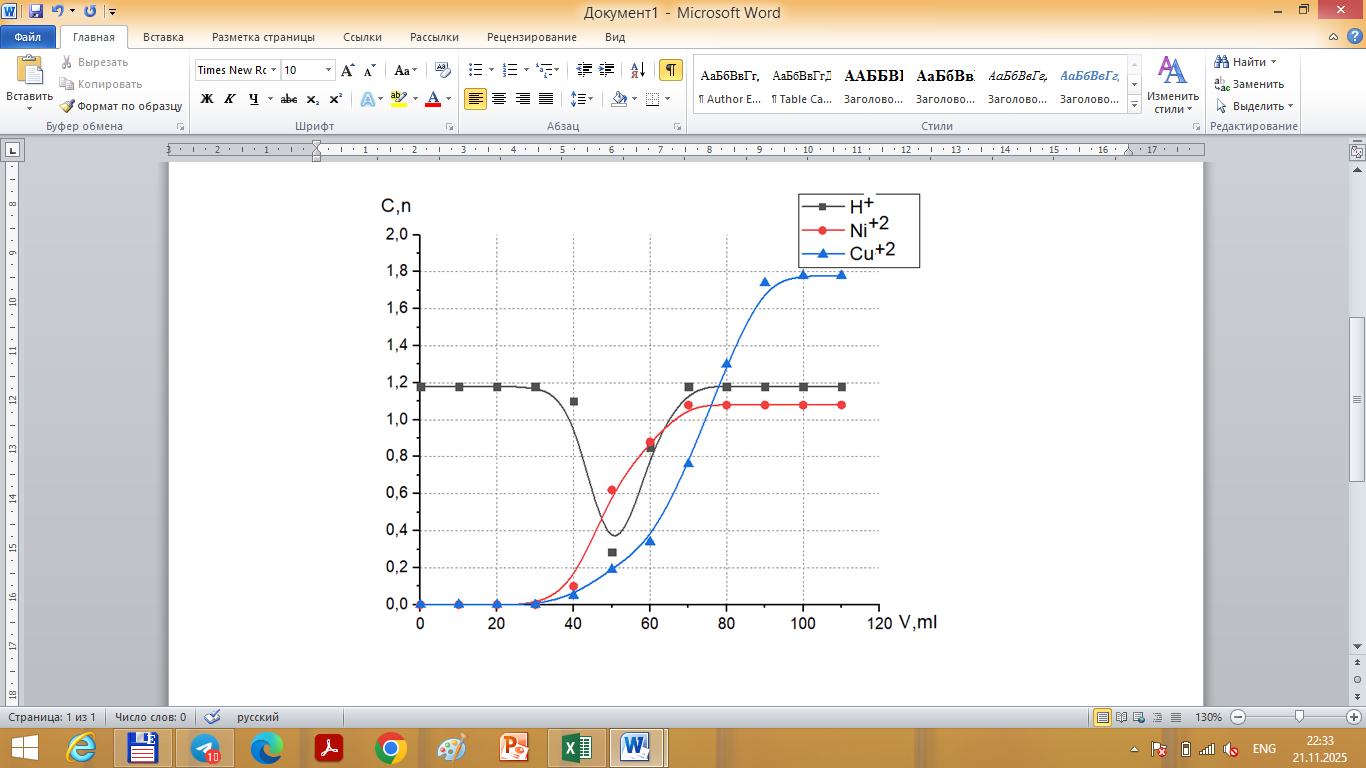
Frontal separations were performed in acidic medium (1.18 N HCl) or alkaline medium (1 M NH4OH) at 1 ml·min⁻1 upward flow; effluent was collected in 10 ml fractions up to 110 ml for ion analysis. Compression (elution) used 1 M HCl at 2 ml·min⁻1 downward. For multicomponent tests, a nitrate mixture (HNO3 plus Fe3⁺, Al3⁺, Sr2⁺, Cs⁺, Na⁺) was treated at 2 ml·min⁻1 upward.

**RESULTS AND DISCUSSION**

A feed containing 1.78 N CuCl2 and 1.08 N NiCl2 in 1.18 N HCl was passed upward at 1 ml·min-1. Ni2+ breakthrough occurred at ~30 ml and reached feed concentration by 100 ml, while Cu2+ eluted around 90 ml (see Figure 2; Table 1), demonstrating clear temporal separation based on differential resin affinity. This baseline resolution (α\_Cu/Ni ≥ 5) surpasses that seen with conventional sulfonated PS–DVB cation resins, which often require elution gradients to achieve even partial separation [12].

**TABLE 1.** ARA-4P – HCl - NiCl2 – CuCl2 system

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **V, ml** | **20** | **30** | **40** | **50** | **60** | **70** | **80** | **90** | **100** | **110** |
| **CH+, n** | 1,18 | 1,18 | 1,10 | 0,08 | 0,85 | 1,18 | 1,18 | 1,18 | 1,18 | 1,18 |
| **CNi+2, n** | 0 | 0 | 0,10 | 0,62 | 0,88 | 1,08 | 1,08 | 1,08 | 1,08 | 1,08 |
| **CCu+2, n** | 0 | 0 | 0,05 | 0,19 | 0,34 | 0,76 | 1,30 | 1,74 | 1,78 | 1,78 |

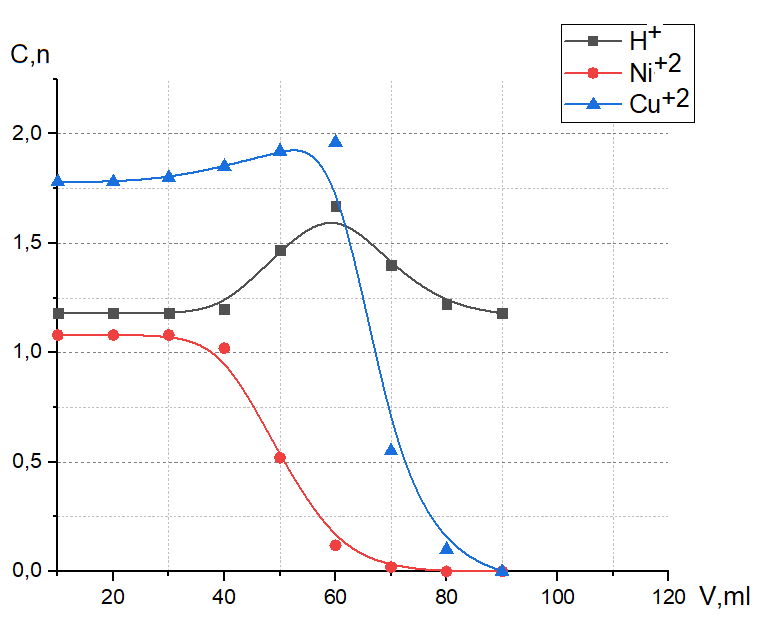


**FIGURE 2.** Frontal separation of CuCl2-NiCl2 mixture in acidic medium.

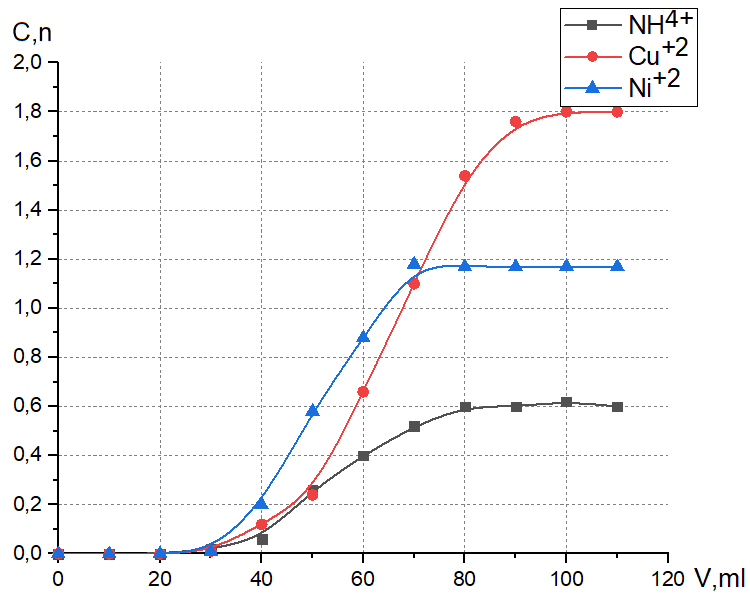
Elution with 1 M HCl at 2 ml·min-1 yielded NiCl2 by ~80 ml and CuCl2 by ~90 ml (Figure 3; Table 2). The sharp, nonoverlapping peaks and consistent elution volumes (< 3% variation) confirm effective desorption and resin stability. Unlike chelating resins such as Dowex D850—which, despite high selectivity, demand strong acid regeneration (≥1 M HCl) and pH-step protocols to strip Cu2+ [13]—ARA‑4P delivers full separation in a single reagent-free cycle [14]. Elution with 1 M HCl at 2 ml·min-1 yielded NiCl2 by ~80 ml and CuCl2 by ~90 ml (see Figure 3; Table 2). The sharp, nonoverlapping peaks and consistent elution volumes confirm effective desorption and resin stability.

**TABLE 2.** ARA-4P – HCl - NiCl2 – CuCl2 system

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **V, ml** | **20** | **30** | **40** | **50** | **60** | **70** | **80** | **90** | **100** | **110** |
| **CH+, n** | 1,18 | 1,18 | 1,20 | 1,47 | 1,67 | 1,40 | 1,22 | 1,18 | 1,18 | 1,18 |
| **CNi+2, n** | 1,08 | 1,08 | 1,02 | 0,52 | 0,12 | 0,02 | 0 | 0 | 0 | 0 |
| **CCu+2, n** | 1,78 | 1,80 | 1,85 | 1,92 | 1,96 | 0,55 | 0,10 | 0 | 0 | 0 |



**FIGURE 3.** Separation of CuCl2-NiCl2 mixture in acidic medium by compression method.

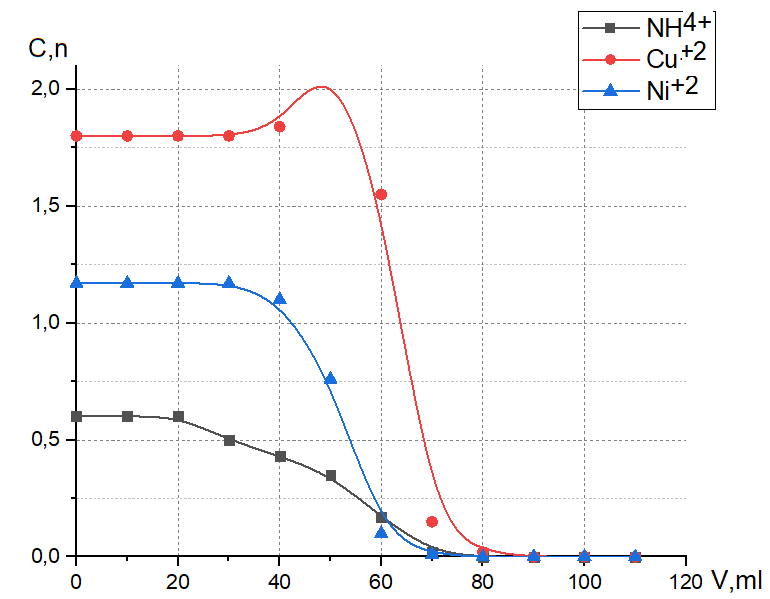


**FIGURE 4.** Frontal separation of CuCl2-NiCl2 mixture in basic medium.

**TABLE 3.** Separation of CuCl2-NiCl2 mixture in alkaline medium by substitution method.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **V, ml** | **20** | **30** | **40** | **50** | **60** | **70** | **80** | **90** | **100** | **110** |
| **CNH4+, n** | 0 | 0,02 | 0,06 | 0,26 | 0,40 | 0,52 | 0,60 | 0,60 | 0,62 | 0,60 |
| **CCu+2, n** | 0 | 0,01 | 0,12 | 0,24 | 0,66 | 1,10 | 1,54 | 1,76 | 1,80 | 1,80 |
| **CNi+2, n** | 0 | 0,01 | 0,20 | 0,58 | 0,88 | 1,18 | 1,17 | 1,17 | 1,17 | 1,17 |

Under 1 M NH4OH (1 ml·min-1), NH4+ eluted at ~20 ml, Ni2+ at ~60 ml, and Cu2+ at ~100 ml (Figure 4; Table 3). Subsequent downward elution produced the same sequence (see Figure 5; Table 4), indicating that pH does not compromise selectivity. Most published methods focus on acidic feeds and do not report alkaline performance aking these results a unique demonstration of ARA‑4P’s broad operational window.



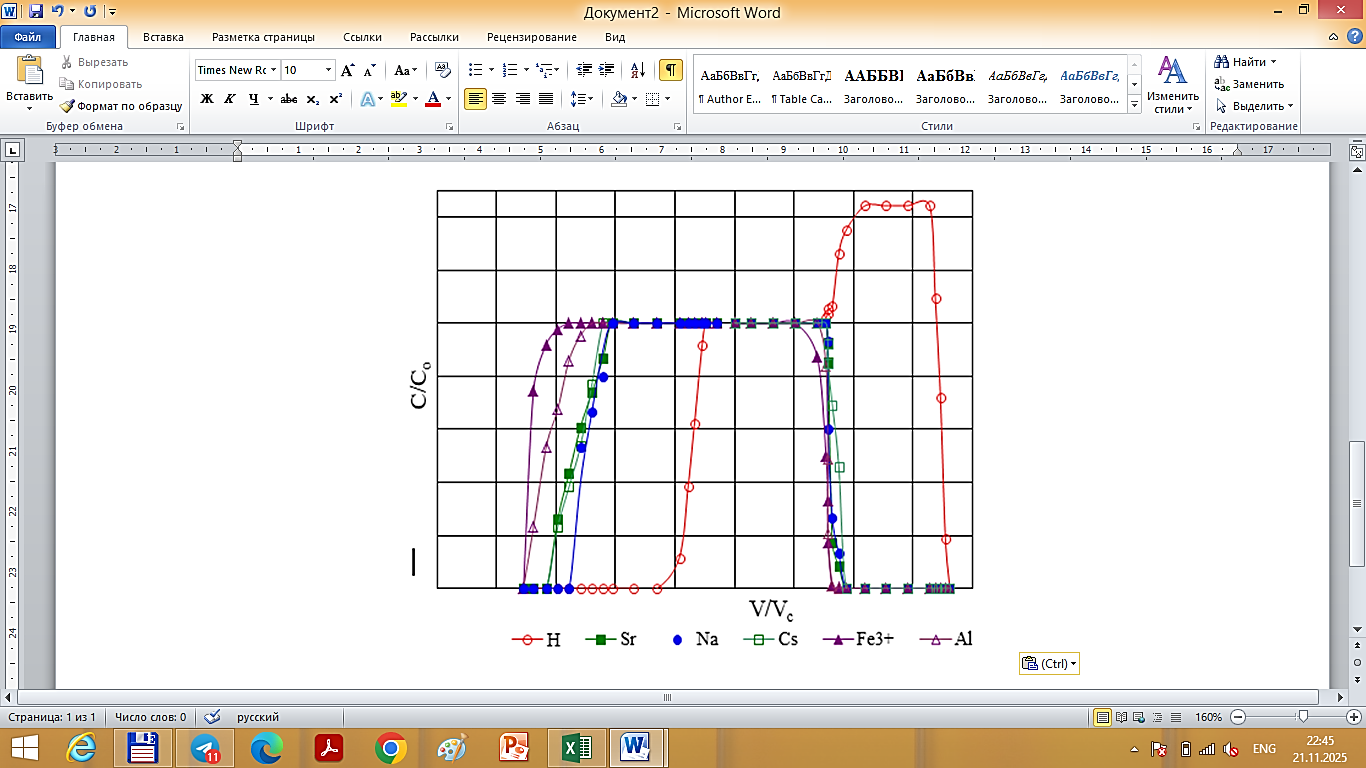
**FIGURE 5.** Separation of CuCl2-NiCl2 mixture in alkaline medium by substitution method.

**TABLE 4.** ARA-4P – NH4OH - NiCl2 – CuCl2 system

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **V, ml** | **20** | **30** | **40** | **50** | **60** | **70** | **80** | **90** | **100** | **110** |
| **CNH4+, n** | 0.60 | 0.50 | 0.43 | 0.35 | 0.17 | 0.02 | 0 | 0 | 0 | 0 |
| **CNi+2, n** | 1.17 | 1.17 | 1.10 | 0.76 | 0.10 | 0.01 | 0 | 0 | 0 | 0 |
| **CCu+2, n** | 1.80 | 1.80 | 1.84 | 2.15 | 1.55 | 0.15 | 0.02 | 0 | 0 | 0 |

A nitrate mixture containing HNO3 and nitrates of Fe3+, Al3+, Sr2+, Cs+, and Na+ was separated into six distinct elution zones between 20 ml and 110 ml (see Figure 6), highlighting applicability to complex multicomponent systems. Such broad multicomponent resolution is rarely reported; most prior studies address only binary separations, requiring multiple columns or stepwise elution.

Collectively, the data demonstrate that ARA‑4P provides efficient, reproducible, and reagent‑free separation of both binary and complex ion mixtures under mild conditions.



**FIGURE 6.** Reagent-free separation of a nitrate mixture (HNO3 va Fe3+, Al3+, Sr2+, Cs+, and Na+ using ARA-4P anionite.

**CONCLUSION**

Separation of multicomponent systems using the ionite‑extraction method is carried out in ion exchange columns with a height of 1.0–1.5 m and a diameter of 2–10 sm. The flow rate of the mixture or eluent through the column ranges from 2 to 10 ml·min-1. The separation efficiency was found to be high, with the sorption front position depending on the flow rate. It was demonstrated that Cu2+ and Ni2+ species can be effectively separated under both acidic and alkaline conditions, and that the solution environment does not significantly affect the process.

In the process of separating a strongly adsorbed electrolyte solution from a mixture of electrolytes using the ion-extraction method, only a certain amount of water is needed. It was found that in order to calculate the efficiency of the separation process, it is necessary to know the nature of the ion (its physicochemical properties), its amount, the distribution constant of water and low-molecular electrolyte, the dimensions of the separation column, and the composition of the mixture being separated.

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