Separation of Cobalt and Nickel by Solvent Extraction with Two Mutually Immiscible Ionic liquids

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The proof-of-principle for the separation of metals by solvent extraction using two mutually immiscible ionic liquids is given. Cobalt was extracted from the ionic liquid 1-ethyl-3-methylimidazolium chloride to the ionic liquid trihexyl(tetradecyl)phosphonium bis-(2,4,4-trimethylpentyl)phosphinate. A distribution ratio of 44 was obtained. Cobalt could be selectively separated from nickel, with a separation factor of 205. The extraction mechanism was elucidated using UV-VIS absorption measurements. The mutual solubility between the two ionic liquids was determined by ¹H NMR. Processing steps such as washing, stripping and regeneration of the ionic liquid phases are discussed.

Introduction

Solvent extraction (SX) is one of the most important hydrometallurgical processes in the refining of metals, especially of precious metals, rare earths and cobalt-nickel, by separation and purification.¹ Solvent extraction is based on the preferential distribution of the dissolved metal ions between two mutually immiscible phases, in general an aqueous phase and an organic phase. Transfer of the metal ion from one phase to the other is enabled by an extracting agent (extractant). During the last decade, considerable research efforts have been devoted to the replacement of the organic phase in solvent extraction systems by an ionic liquid.^{2–9} Ionic liquids are solvents entirely consisting of ions.^{10–12} They have a negligible vapour pressure, so that they are non-volatile and have a very high flash point. Substitution of the volatile hydrocarbon-based organics by ionic liquids could lead to inherently safer and environmentally friendlier extraction processes. So far, most studies on the application of ionic liquids in solvent extraction processes have made use of ionic liquids with fluorinated anions, e.g. hexafluorophosphate or bis(trifluoromethylsulfonyl)imide anions, because these ionic liquids are highly hydrophobic and hence immiscible with water. Unfortunately, fluorine-containing ionic liquids are expensive and there are issues with their stability (e.g. hydrolysis of hexafluorophosphate ions) and persistency in nature. There are few examples of solvent extraction studies with non-fluorinated ionic liquids, most of them make use of an organic solvent as diluent.^{13–16} Recently, we developed a very efficient solvent extraction process for the separation of cobalt and nickel from chloride solutions based on the undiluted ionic liquid trihexyl(tetradecyl)phosphonium chloride as organic phase.¹⁷

In this paper, we give the proof-of-principle for the separation of metal ions by distribution between two mutually immiscible ionic liquids. The example of separation of cobalt and nickel is

discussed. Substitution of the aqueous phase by an ionic liquid phase in a solvent extraction process has several advantages. First of all, the extraction mechanism can be different, offering the possibility to change the distribution ratios and to improve the separation factors. Secondly, the more polar ionic liquid can be used as a leaching solution to dissolve metal oxides and metal salts.^{18,19} This allows leaching at elevated temperatures, without the need of using autoclaves. More selective leaching is possible as well.^{20,21} Mutually immiscible ionic liquids have been reported,^{22–24} but their use in separation processes has been restricted to the extraction of organic compounds.²⁶ There exist some examples of extraction systems containing an inorganic molten salt and an organic phase,^{26–28} but none for the metal distribution between two mutually immiscible ionic liquids.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate) (Cyphos[®] IL 104, > 97%) and 1-ethyl-3-methylimidazolium chloride (>98%) were purchased from Iolitec (Heilbronn, Germany). CoCl₂ (>97 %), NiCl₂ (>98%), sulfuric acid (95–97 %) were purchased from Sigma Aldrich. Dioxane (stabilized, 99.5 %) was purchased from Acros Organics (Geel). Ammonia (Analar Normapur, min. 25 w.%) was purchased from VWR. All chemicals were used as received, without further purification.

Instrumentation and analysis methods

A Mettler Toledo DL 39 Karl Fischer Coulometer was used for determination of the water content in ionic liquids. To quantify the metal content, a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker) was used. For quantification of the metal in [P₆₆₆₁₄][R₂POO] and [C₂mim]Cl,

about 0.2 g of the ionic liquid solution was diluted in dioxane and water (20 mL) respectively. Then a gallium solution (in HNO₃) was added as an internal standard to the solution. An aliquot of 10 µL of solution was put on a quartz glass carrier, dried in a hot-air-oven at 60 °C, then measured with a measurement time of 400 s. A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of the samples after extraction. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer, operating at 300 MHz for ¹H. The samples were dissolved in deuterated chloroform and the chemical shifts are given in ppm relative to tetramethylsilane (TMS). ³¹P NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 161.98 MHz for ³¹P. The samples were dissolved in methanol-d₆. A delay time (*dI*) of 60 s was applied in the NMR pulse sequence, to avoid saturation effects in the ³¹P NMR spectra, so that quantitative interpretation of the NMR spectra was possible. UV-VIS absorption spectra were recorded with a Varian Cary 5000 spectrophotometer, with a cuvette holder, which was heated to 80 °C by a circulating water bath. Quartz cuvettes with an optical path length of 0.1 mm were used to record the spectra of the highly absorbing solutions.

Extraction experiments

Cobalt extraction between two mutually immiscible ionic liquids: Cobalt(II)chloride (5 g/L Co) was dissolved in 1-ethyl-3-methylimidazolium chloride, [C₂mim]Cl, (5.55 g, 5 mL) at 95 °C and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate ([P₆₆₆₁₄][R₂POO] with R = 2,4,4-tri(methylpentyl) (5 mL) was used as extraction phase. The mixture of the two ionic liquids was stirred for 10 minutes at 95 °C and the metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Extraction between two mutually immiscible ionic liquids from solution containing both cobalt and nickel:

CoCl₂ and NiCl₂ (both with a metal concentration of 5 g L⁻¹) were dissolved in [C₂mim]Cl (5.55 g, 5 mL) at 95 °C. and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate, [P₆₆₆₁₄][R₂POO] (5 mL) was used as extraction phase. The extraction was stirred for 10 minutes at 95 °C and the metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Washing of the extraction phase:

the cobalt-loaded extraction phase (5mL) was washed with water (5mL) and stirred at 50 °C for 10 minutes. After washing, the phases were centrifuged (3000 rpm, 10 min.) and the water phase was analyzed for its metal content.

Stripping of cobalt from the extraction phase: After extraction, cobalt was stripped from the [P₆₆₆₁₄][R₂POO] phase with a 2M aqueous sulfuric acid solution. A volume ratio of 1:1 was used and the phases were stirred for 5 minutes at 50 °C. The metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Recovery of the extraction phase: The extraction phase [P₆₆₆₁₄][R₂POO] was regenerated after stripping by washing with an ammonia solution (2 M). A volume ratio of 1:1 was used and the phases were stirred for 5 minutes at 50 °C. The metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Distribution coefficients and separation factor

The distribution ratios for cobalt, D_{Co}, were calculated for all experiments, as follows:

$$D_{\text{Co}} = \frac{[\text{Co}]_{\text{phos}}}{[\text{Co}]_{\text{im}}} = \frac{[\text{Co}]_0 - [\text{Co}]_{\text{im}}}{[\text{Co}]_{\text{im}}} \quad (1)$$

where [Co]₀ is the initial cobalt concentration in the [C₂mim]Cl phase before extraction, [Co]_{im} is the cobalt concentration in the [C₂mim]Cl phase after the extraction, and [Co]_{phos} is the cobalt concentration in [P₆₆₆₁₄][R₂POO] after extraction. Distribution ratios for nickel, D_{Ni}, were calculated using the following equation:

$$D_{\text{Ni}} = \frac{[\text{Ni}]_{\text{phos}}}{[\text{Ni}]_{\text{im}}} = \frac{[\text{Ni}]_{\text{phos}}}{[\text{Ni}]_0 - [\text{Ni}]_{\text{phos}}} \quad (2)$$

where [Ni]₀ is the initial cobalt concentration in the [C₂mim]Cl phase before extraction, [Ni]_{phos} is the nickel concentration in the [P₆₆₆₁₄][R₂POO] ionic liquid after extraction, and [Ni]_{im} is the nickel concentration in [C₂mim]Cl after extraction. The efficiency of separation of cobalt from nickel is described by the separation factor:

$$\alpha_{\text{Ni}}^{\text{Co}} = \frac{D_{\text{Co}}}{D_{\text{Ni}}} \quad (3)$$

Results and Discussion

Selection of a suitable pair of ionic liquids

Earlier work has shown that mixtures of some hydrophilic and some specific hydrophobic ionic liquids gave rise to two phases, in particular when there are large structure differences in either the cation or the anion.²² Mutual immiscibility of the two ionic liquids is a necessary, but not sufficient condition. The hydrophilic ionic liquid, replacing the aqueous phase, needs to be an ionic liquid with coordination anions to enable the dissolution of inorganic metal salts. The hydrophobic ionic liquid, acting as the organic phase, has to be able to dissolve the extracted metal complex. In principle, an ionic liquid with a dissolved extractant could be used, but we preferred to look for a non-fluorinated ionic liquid with coordinating anions. Moreover, although the expression “mutually immiscible ionic liquids” is used, it must be realized that there is always a partial miscibility between any pair of ionic liquids. After screening of several ionic liquid combinations, the most promising system proved to be the one consisting of 1-ethyl-3-methylimidazolium chloride ([C₂mim]Cl) and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)-phosphinate, [P₆₆₆₁₄][R₂POO] or Cyphos[®] IL 104 (Figure 1). [P₆₆₆₁₄][R₂POO] has been explored by other authors as extractant for metals.³⁰⁻³² Because the melting point of the ionic liquid [C₂mim]Cl is 77–79 °C, the extraction studies needed to be performed at elevated temperatures.

Figure 1: Chemical structures of (a) 1-ethyl-3-methylimidazolium chloride, [C₂mim]Cl, and (b) trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, [P₆₆₆₁₄][R₂POO].

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Metal extraction

The results for the extraction experiments are shown in Table 1. To be sure that the equilibrium condition was reached, the distribution ratio of an extraction with a stirring time of 10 minutes was compared with the distribution ratio of an extraction with a stirring time of 2 hours. For both stirring times, the distribution ratios for cobalt were identical, meaning that the extraction equilibrium was reached within 10 minutes. Therefore, a stirring time of 10 minutes was used for all further extraction experiments. A distribution ratio of 44.0 (±0.4) was found for the distribution of cobalt between the two mutually immiscible ionic liquids, for a solution with only CoCl₂ present. Under the same condition, nickel is hardly extracted to the [P₆₆₆₁₄][R₂POO] phase (D_{Ni} = 0.06 (±0.008)). The extraction experiments showed a selectivity of cobalt. A separation factor between cobalt and nickel of 200 was obtained. In Figure 2, the layering of the two mutually immiscible ionic liquids [C₂mim]Cl and [P₆₆₆₁₄][R₂POO] on top of each other and the distribution of CoCl₂ and NiCl₂ between them, is shown.

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Figure 2: Sample showing the ionic liquid [P₆₆₆₁₄][R₂POO] layered on top of the ionic liquid [C₂mim]Cl, before (left) and after (right) cobalt(II) extraction.

Table 1: Summary of the analysis results for the distribution of cobalt and nickel between the ionic liquids [C₂mim]Cl and [P₆₆₆₁₄][R₂POO] at 95 °C, calculated for cobalt and nickel present in two different solutions (column A), and for cobalt and nickel present in the same solution (column B).

Extraction parameters ^a	A	B
[Co] _{im} (ppm)	110 (± 1)	318 (± 14)
[Ni] _{phos} (ppm)	283 (± 35)	332 (± 4)
D _{Co}	44.0 (± 0.4)	14.7 (± 0.7)
D _{Ni}	0.060 (± 0.008)	0.071 (± 0.001)
SF _{Co-Ni}	733 (± 104)	207 (± 12)

^a [Co]_{im}: cobalt concentration in [C₂mim]Cl after extraction, [Ni]_{phos}: nickel concentration in [P₆₆₆₁₄][R₂POO] after extraction; D_{Co}: distribution ratio for cobalt; D_{Ni}: distribution ratio for nickel; SF_{Co-Ni}: separation factor for the cobalt-nickel separation.

Comparing the separation factors calculated for the extraction experiment in which cobalt and nickel are present in two different solutions with the one in which both cobalt and nickel are present in the same solution (Table 1) shows that the separation factor is about 3.5 times lower in the latter case. This decrease in separation factor is ascribed to the decrease in cobalt extraction, caused by a competition effect between cobalt and nickel to bind to the phosphinate ligands (*vide infra*).

To elucidate the extraction mechanism, the absorption spectra of cobalt(II) chloride dissolved in the [C₂mim]Cl ionic phase were compared with that of the extracted cobalt(II) complex in the ionic liquid [P₆₆₆₁₄][R₂POO] (Figure 3). The absorption spectrum of CoCl₂ in [C₂mim]Cl shows the typical spectrum of the tetrachlorocobaltate(II) complex, [CoCl₄]²⁻.^{32,33} The absorption spectrum of cobalt in [P₆₆₆₁₄][R₂POO] is totally different, which excludes the extraction of cobalt(II) as an anionic tetra(chloro)cobaltate species. The absorption spectrum is similar to those reported in the literature for Co(R₂POO)₂,^{31,34} indicating that cobalt(II) is present in [P₆₆₆₁₄][R₂POO] as the tetrahedral Co(R₂POO)₂ complex. The following extraction mechanism is proposed:

In [C₂mim]Cl, cobalt(II) is present as the [CoCl₄]²⁻ species. Upon mixing with [P₆₆₆₁₄][R₂POO], chloride ligands are replaced by phosphinate ligands, which have a high affinity for cobalt(II), and the [Co(R₂POO)₂] species is formed. Due to the large structural similarity of this complex with the hydrophobic ionic liquid [P₆₆₆₁₄][R₂POO] it will prefer this phase, resulting in an extraction of cobalt from the [C₂mim]Cl phase to the [P₆₆₆₁₄][R₂POO] phase. The absorption spectrum of NiCl₂ dissolved in [C₂mim]Cl indicates that the [NiCl₄]²⁻ species is present (Figure 3).^{32,33} After mixing of the nickel-containing [C₂mim]Cl with [P₆₆₆₁₄][R₂POO], the color of the [C₂mim]Cl phase switched from blue to pale yellow. The corresponding absorption spectrum with an absorption maximum at 381 nm is typical one that is expected for an octahedral nickel complex. It is assumed that a mixed chloro-phosphinate nickel(II) complexes octahedral species of the type [NiCl_x(R₂POO)_{6-x}]^(2-x-y) are formed, which cannot be extracted due to their polar character. The formation of the mixed complexes implicates the loss of phosphinate ligands to the [C₂mim]Cl phase.

Figure 3: Absorption spectrum of CoCl_2 and NiCl_2 dissolved in the ionic liquid $[\text{C}_2\text{mim}]\text{Cl}$ at 80°C (optical path length of 0.1 mm), showing the presence of the $[\text{CoCl}_4]^{2-}$ and the $[\text{NiCl}_4]^{2-}$ anions and further of the octahedral nickel species $[\text{NiCl}_x\text{R}_2\text{POO}_y]^{2-x-y}$ after extraction. With spectrum 1 corresponding to CoCl_2 in $[\text{C}_2\text{mim}]\text{Cl}$ before extraction; 2 to CoCl_2 and NiCl_2 in $[\text{C}_2\text{mim}]\text{Cl}$ before extraction; 3 to NiCl_2 in $[\text{C}_2\text{mim}]\text{Cl}$ before extraction; 4 to cobalt in $[\text{C}_2\text{mim}]\text{Cl}$ after extraction; 5 to cobalt and nickel in $[\text{C}_2\text{mim}]\text{Cl}$ after extraction; and 6 to nickel in $[\text{C}_2\text{mim}]\text{Cl}$ after extraction.

Influence of temperature on distribution coefficient

When the distribution ratio of cobalt was determined as a function of temperature between 95 and 140°C , a linear decrease of the distribution ratio with temperatures was observed (Figure 4).

Fig 4: Distribution ratio for cobalt(II) as a function of temperature.

This behaviour can be explained by an increased solubility of both the phosphinate anion and the cobalt(II) phosphinate complex in the ionic liquid $[\text{C}_2\text{mim}]\text{Cl}$ with temperature. The solubility of $[\text{R}_2\text{POO}]^-$ in $[\text{C}_2\text{mim}]\text{Cl}$ was quantified at 140°C , by ^1H NMR measurement after bringing the two ionic liquids in contact by stirring their mixture for 10 minutes (see supporting information). An increase in the phosphinate concentration of about $2000(\pm 120)\text{ ppm}$ was observed, compared to the solubility at 95°C , which was about 1000 ppm . Because both the

phosphinate and cobalt concentration are increasing with temperature in the $[\text{C}_2\text{mim}]\text{Cl}$ phase after extraction, there will certainly be a correlation between these observation. To verify the influence of phosphinate ligand on the cobalt extraction, absorption spectra were measured of the $[\text{C}_2\text{mim}]\text{Cl}$ phase after extraction, both at 95°C and 140°C (Figure 5). A weak broad absorption band, with absorption maxima at 667 and 640 nm is observed. This band is laying in between the absorption bands of $[\text{CoCl}_4]^{2-}$ ($697, 670, 633\text{ nm}$) and $\text{Co}(\text{R}_2\text{POO})_2$ at ($640, 590$ and 563 nm) (see supporting information), suggesting that both species are present in solution at certain ratio. The increase of light absorption at 140°C compared to the spectra measured at 95°C , also suggests the concentration increase of the phosphinate anion directly bonded to cobalt in the $[\text{C}_2\text{mim}]\text{Cl}$ phase and is a direct evidence that the phosphinate concentration present in $[\text{C}_2\text{mim}]\text{Cl}$ influences the cobalt extraction behavior. Upon extraction, the cobalt(II) phosphinate species are distributed over the two phases and this ratio is temperature dependent. This provides a logical explanation for the differences in distribution ratios at different temperatures.

Figure 5 Absorption spectra of the $[\text{C}_2\text{mim}]\text{Cl}$ phase after extraction at 95 and 140°C .

Quantification of the mutual solubility

To quantify the solubility of $[\text{C}_2\text{mim}]\text{Cl}$ in $[\text{P}_{66614}][\text{R}_2\text{POO}]$, a ^1H NMR spectrum was recorded after bringing the two ionic liquids in contact by stirring their mixture for 10 minutes at 95°C . These conditions resemble those of the solvent extraction experiments (*vide supra*). The presence of $[\text{C}_2\text{mim}]\text{Cl}$ in the $[\text{P}_{66614}][\text{R}_2\text{POO}]$ phase was quantified by integrating characteristic resonances in the NMR spectrum, corresponding to one of the two ionic liquid molecules (see supporting information). The peak at $\delta = 11.7\text{ ppm}$, originating from the hydrogen atom at C2 position of the imidazolium ring, was integrated and related to the integration of the peak at $\delta = 2.5\text{ ppm}$, originating from the eight hydrogen atoms at C1 position of the phosphonium cation. A solubility of $9.2\text{ wt. \%}$ (or $31\text{ mol. \%}$) of $[\text{C}_2\text{mim}]\text{Cl}$ in $[\text{P}_{66614}][\text{R}_2\text{POO}]$ was determined from the ratio of the integrated peaks. The same procedure was applied to measure the solubility of the $[\text{P}_{66614}]^+$ cation in $[\text{C}_2\text{mim}]\text{Cl}$. The signals were too weak for a reliable integration. Although an accurate determination of the solubility

of the phosphonium cation $[P_{66614}]^+$ in $[C_2mim]Cl$ was not possible, it can be concluded that the solubility is very low. However, only measuring the solubility of the cation is not sufficient, since anions can exchange as well (phosphinate anions then replace chlorides). The solubility of the phosphinate anions can be measured by integration of the resonances in the 1H NMR spectrum at $\delta = 0.89$. A solubility of about 1000 ppm was found. Since the process is used for the extraction of cobalt, which has a high affinity for phosphinate ligands, the phosphinate concentration in $[C_2mim]Cl$ is expected to be even lower, after mixing the phases.

Further processing steps

Because the solubility of $[C_2mim]Cl$ in $[P_{66614}][R_2POO]$ is about 9 wt.% (*vide supra*), $[C_2mim]Cl$ needs to be recovered from the extraction phase to avoid unacceptable losses of ionic liquid. $[C_2mim]Cl$ dissolved in $[P_{66614}][R_2POO]$ could be selectively removed from the cobalt-loaded $[P_{66614}][R_2POO]$ phase by washing with a neutral water solution, because $[C_2mim]Cl$ is water soluble and the other components, including the cobalt(II) phosphinate complex, are not, since this ionic liquid is immiscible with water. The $[C_2mim]Cl$ content in the $[P_{66614}][R_2POO]$ phase after the washing step, was only 0.12 wt.% (verified by 1H NMR, see supporting information). Only 7 ppm of cobalt was detected in the aqueous washing solution. $[C_2mim]Cl$ could be recycled from the washing solution by evaporation of water. Cobalt was stripped from the $[P_{66614}][R_2POO]$ ionic liquid phase by an aqueous 2M sulfuric acid solution, by which the bonded cobalt ions will be exchanged by protons. In one single stripping step, the cobalt content in the

$[P_{66614}][R_2POO]$ extraction phase was reduced to 127 ppm, showing that virtually all of the extracted cobalt could be recovered by stripping to the aqueous phase. Because phosphinic acid is formed during the stripping step (5), a deprotonation step is necessary to regenerate the phosphonium phosphinate ionic liquid (6):

This was achieved by washing the extraction phase which is immiscible with water, after stripping with a 2 M aqueous ammonia solution. After recovery, $[P_{66614}][R_2POO]$ contained 14.3 wt.% of water, which had to be removed by evaporation before reuse of the ionic liquid in a next extraction experiment with two immiscible ionic liquids. To prove that a 1:1 phosphonium-to-phosphinate ratio was retained in the ionic liquid $[P_{66614}][R_2POO]$, the extraction, stripping and regeneration procedure was repeated in the absence of cobalt (to avoid paramagnetic impurities), and ^{31}P NMR spectra were recorded (see supporting information). A 1:1 ratio was found for the integrations of the peaks at $\delta = 38.11$ and $\delta = 43.63$, corresponding to the trihexyltetradecyl-phosphonium cation and bis(2,4,4-trimethylpentyl)phosphinate anion, respectively. It can be concluded that no components of the ionic liquid $[P_{66614}][R_2POO]$ are lost during the processing procedure. All processing steps used for the cobalt-nickel separation are summarized in the flow chart shown in Figure 6.

Figure 6: Flow chart for cobalt-nickel separation using mutually immiscible ionic liquids.

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Conclusion

For the first time the separation of metals by solvent extraction using two mutually immiscible ionic liquids has been shown. Cobalt was extracted from the ionic liquid 1-ethyl-3-methylimidazolium chloride to the ionic liquid trihexyl(tetradecyl)phosphonium bis-(2,4,4-trimethylpentyl)-phosphinate. A distribution ratio of 44 was obtained. Cobalt could be selectively separated from nickel, with a separation factor of 205. Stripping of cobalt from the hydrophobic phosphonium ionic liquid phase, followed by regeneration of the ionic liquid, was demonstrated, showing the potential of the method for use in a continuous extraction process. By replacement of the aqueous phase in solvent extraction by an ionic liquid phase, one can no longer speak about a hydrometallurgical process. The term to use is “ionometallurgy”³⁶ or “solvometallurgy”, rather than hydrometallurgy.

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Notes and references

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