# Extraction of Cobalt(II) with Mixtures of 4-Acyl-pyrazol-5-ols and Aliquat 336 in Toluene: Effect of the Pyrazolol Substituents

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Summary. The extractions of cobalt(II) from $1\,M$ (Na, H)ClO_4 medium with mixtures of 4-acyl-pyrazol-5-ols (HL) (17 species) and aliquat 336 in its perchlorate form (B^+, ClO_4^-) in toluene, at 25°C, have been studied. They are described by the equilibrium:

$$Co^{2+} + 3\,\overline{HL} + \overline{(B^+, ClO_4^-)} \rightleftarrows \overline{(B^+, CoL_3^-)} + 3\,H^+ + ClO_4^-.$$
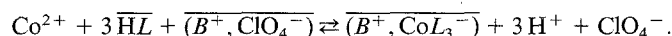
Its constant is partly determined by the anionic exchange equilibrium between $\overline{(B^+, ClO_4^-)}$ and $\overline{HL}$, which is favoured when HL substitutents are electron-attractive. Lipophilic substituents on HL favour the cobalt extraction, but conflicting effects can occur owing, for example, to steric hindrance.

Keywords. Aliquat 336; Methyl-tri-*n*-octyl-ammonium chloride; 4-Acyl-pyrazol-5-ol; Cobalt; Solvent extraction; Synergistic effect.

Extraktion von Kobalt(II) mit Mischungen von 4-Acyl-pyrazol-5-olen und Aliquat 336 in Toluol: Der Effekt des Pyrazolol-Substituenten

Zusammenfassung. Es wurde die Extraktion von Kobalt(II) aus $1\,M$ (Na, H)ClO_4-Medium mit Mischungen von 4-Acyl-pyrazol-5-olen (HL, 17 verschiedene Verbindungen) und Aliquat 336 in seiner Perchlorat-Form (B^+, ClO_4^-) bei 25 °C in Toluol untersucht. Es gilt folgendes Gleichgewicht:

$$Co^{2+} + 3\,\overline{HL} + \overline{(B^+, ClO_4^-)} \rightleftarrows \overline{(B^+, CoL_3^-)} + 3\,H^+ + ClO_4^-.$$
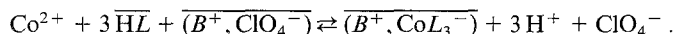
Die Gleichgewichtskonstante ist teilweise vom anionischen Austauschgleichgewicht zwischen $\overline{(B^+,}$ $\overline{ClO_4^-)}$ und $\overline{HL}$ bestimmt, das bevorzugt wird, wenn die Substituenten an HL elektronenanziehend sind. Lipophile Substituenten an HL sind für die Extraktion von Kobalt vorteilhaft, es können jedoch dabei auch gegenläufige sterische Hinderungseffekte auftreten.

Introduction

In previous papers [1–10], it has been shown that metal cations M^{m+}, with a usual coordination number $N_c > 2m + 2$ (lanthanides, actinides, Ni, Co, Zn, Cd, Mg, Li, ...) can be synergistically extracted by mixtures of an acidic chelating extractant (HL) and a lipophilic ammonium salt $\overline{(B^+, X^-)}$. The synergistic effect results from the substitution of water molecules, coordinated on the neutral metal complex

ML_m, by the chelating anion L^-, leading to the extracted species (B^+, ML_{m+1}^-). The synergistic equilibrium is:

$$\overline{ML_m} + \overline{(B^+, L^-)} \rightleftarrows \overline{(B^+, ML_{m+1}^-)}.$$
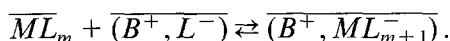
Of course, interactions occur between the acidic chelating extractant, $\overline{HL}$, and the anionic exchanger $\overline{(B^+, X^-)}$ according to

$$\overline{(B^+, X^-)} + \overline{HL} \rightleftarrows \overline{(B^+, L^-)} + H^+ + X^-$$
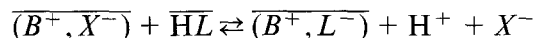
of constant K_{X-L}. This equilibrium determines the $\overline{(B^+, L^-)}$ activity, and consequently the magnitude of the synergy observed. It is obvious that the nature of X^- in the extraction system is quite important: the more is the hydration of X^-, the easier is the formation of $\overline{(B^+, L^-)}$ which follows the order $ClO_4^- < NO_3^- < Cl^- < SO_4^{2-}$. For example, $\log K_{X-L} = -7.0$, -4.2 and -2.7 for $X^- = ClO_4^-, NO_3^-$ and Cl^- respectively, HL = 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-ol, B^+ = ammonium cation of aliquat 336, diluent = toluene and ionic strength 1 M [8]. Under these experimental conditions, it follows that $\overline{(B^+, ClO_4^-)}$ prevails in perchlorate medium whereas $\overline{(B^+, L^-)}$ prevails in sulphate medium favouring the synergistic effect.

The present paper deals with the synergistic extraction of cobalt from 1 M perchlorate aqueous medium with mixtures of the perchlorate salt of aliquat 336 and various (17) 4-acyl-pyrazolol-5-ols (HL) in toluene: the effect of the substituents of HL both on the synergistic extraction and on the $\overline{HL}/\overline{(B^+, X^-)}$ anionic exchange has been studied. The perchlorate medium has been chosen to make certain that $\overline{(B^+, ClO_4^-)}$ remains the predominating ammonium species in the extraction system, whatever HL is.

The extractions of Co with HL alone are not given herein because, in many cases, the formation of a third phase prevents the determination of accurate extraction constants. Aggregation of the organic species are neglected, and all the constants given are conditional. Overlined symbols refer to the organic phase.

Materials and Methods
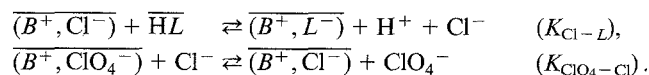
Reagents and Solutions

Most of the 4-acyl-pyrazol-5-ols (and some pyrazolones and acid chlorides) have been obtained from the "Société Nationale des Poudres et Explosifs" Vert-le-Petit, France, and prepared by J. C. Gautier and Coll., using Jensen's method [11]. Aliquat 336 (mostly methyl-tri-n-octyl ammonium chloride) was a Fluka chemical: the Cl^-/ClO_4^- anionic exchange was achieved by washing several times toluene solutions of aliquat 336 with (Na,H)ClO_4 1 M solutions. The concentration ranges of aliquat 336 and HL were $0.0-0.1$ M and $0.0-0.04$ M, respectively. The initial aqueous cobalt concentrations were $1.7 \cdot 10^{-3}$ $M \cdot pH$ was adjusted with 0.1 M NaOH or $HClO_4$ solutions of suitable compositions to keep the aqueous ionic strength 1 M. (The reversibility of the cobalt extraction was systematically controlled).

Anionic Exchange Between HL and $\overline{(B^+, ClO_4^-)}$

The anionic exchange between $\overline{HL}$ and $\overline{(B^+, ClO_4^-)}$ is described by the equilibrium

$$\overline{(B^+, ClO_4^-)} + \overline{HL} \rightleftarrows \overline{(B^+, L^-)} + H^+ + ClO_4^- \qquad (K_{ClO_4-L}).$$
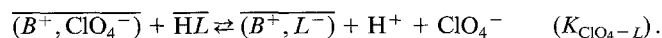
It can be considered as the summation of the two following equilibria

$$\overline{(B^+, Cl^-)} + \overline{HL} \quad \rightleftarrows \overline{(B^+, L^-)} + H^+ + Cl^- \qquad (K_{Cl-L}),$$
$$\overline{(B^+, ClO_4{}^-)} + Cl^- \rightleftarrows \overline{(B^+, Cl^-)} + ClO_4{}^- \qquad (K_{ClO_4-Cl}).$$

Arbitrarily neglecting any aggregation phenomenon under the experimental conditions herein, and taking $\log K_{ClO_4-Cl} = -4.3$ [8], it follows that $\log K_{ClO_4-L} = \log K_{Cl-L} - 4.3$.

K_{Cl-L} has been determined by the following experimental procedure: v ml of a $HL-(B^+, Cl^-)$ toluene solution $(2 \cdot 10^{-2} M)$ are shaken with 50 ml of a $1 M$ NaCl solution at $25.0 \pm 0.2°C$. pH are noted before and after contacting the two phases. The following equations allow the K_{Cl-L} determination,

$$[\overline{HL}] \qquad = [\overline{HL}]_i - [\overline{B^+, L^-}],$$
$$[\overline{B^+, Cl^-}] = [\overline{B^+, Cl^-}]_i - [\overline{B^+, L^-}],$$
$$[\overline{B^+, L^-}] = \Delta[H^+] v \bar{v}^{-1},$$

where v and $\bar{v}$ are the aqueous and organic phase volumes, and i denotes initial concentrations.

HL Distribution and Dissociation

Constants of the equilibria "$\overline{HL} \rightleftarrows H^+ + L^-$" were determined by two-phase titration [25°C, toluene, (Na, H)ClO$_4$ 1 M] [14].

Cobalt Extraction and Analytical Procedures

The distribution measurements were performed in a thermostated vessel $(25.0 \pm 0.2°C)$ using a batch technique. Equal volumes of the organic and aqueous phases were shaken for at least 15 minutes, and separated by gravity. For each experimental point, aliquots of each phase were withdrawn and analyzed after suitable dilution (and stripping of Co for the organic aliquots) by atomic absorption, using an IL 453 spectrophotometer.
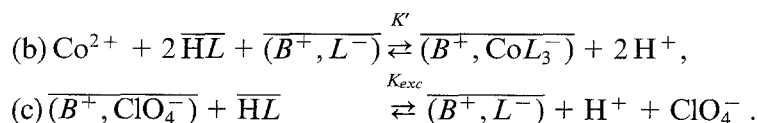
Results and Discussion

Some typical extraction curves $\log D$ vs. pH $(D = [\overline{Co}] [Co]^{-1})$, are given in Fig. 1. They are straight lines of slopes close to 3, in agreement with the extraction equilibrium

$$(a)\, Co^{2+} + 3\overline{HL} + \overline{(B^+, ClO_4^-)} \overset{K}{\rightleftarrows} \overline{(B^+, CoL_3^-)} + 3H^+ ClO_4^-$$
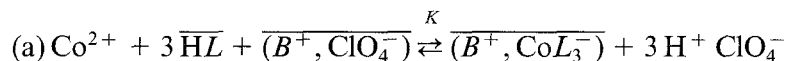
of constant K. The stoichiometry of the extracted species has been confirmed by the slopes of the curves $\log D$ vs. $\log [\overline{HL}]$ and $\log D$ vs. $\log [\overline{(B^+, ClO_4^-)}]$, ≈ 3 and ≈ 1 respectively. The $\log K$ values, determined from the experimental data, are given in Table 1.

Equilibrium (a) can be considered as the summation of equilibria (b) and (c) of constants K' and K_{exc}, respectively,

$$(b)\, Co^{2+} + 2\overline{HL} + \overline{(B^+, L^-)} \overset{K'}{\rightleftarrows} \overline{(B^+, CoL_3^-)} + 2H^+,$$
$$(c)\, \overline{(B^+, ClO_4^-)} + \overline{HL} \overset{K_{exc}}{\rightleftarrows} \overline{(B^+, L^-)} + H^+ + ClO_4^-.$$

$\log K_{exc}$ obtained from the experimental data (see the experimental section), and $\log K' = \log K - \log K_{exc}$, are also given in Table 1. The 4-acyl-pyrazol-5-ols have
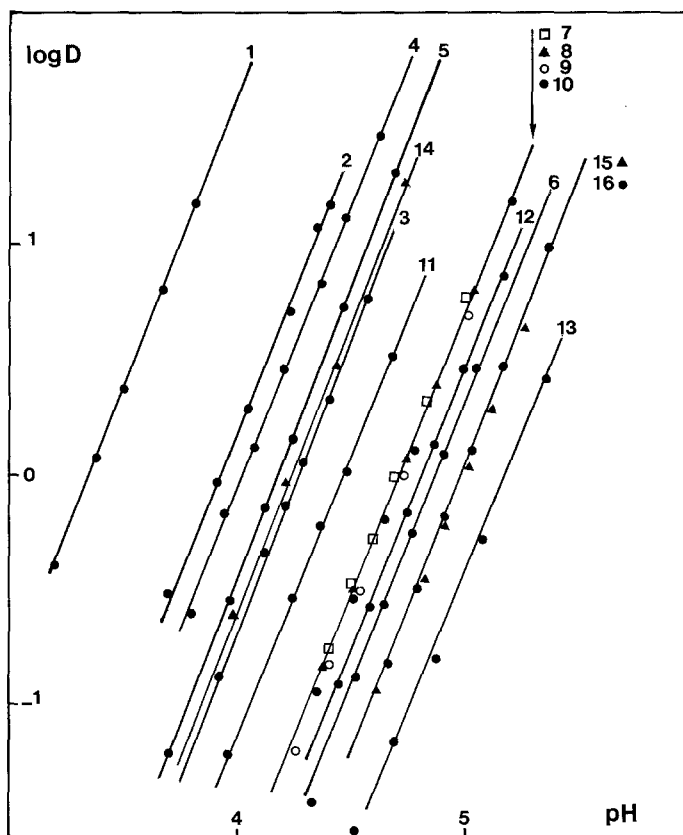
Fig. 1. Cobalt extraction from 1 M perchlorate medium with 4-acyl-pyrazol-5-ols (0.02 M) and (B^+, ClO_4^-) (0.02 M) in toluene; numbers correspond to the acyl-pyrazolols defined in Table 1

been classified following the decreasing values of log K' because they do not depend upon the nature of the inorganic anion. Equilibrium (b) is in fact the expected extraction equilibrium of cobalt from sulphate medium (ionic strenth 1 M) where $\overline{(B^+, L^-)}$ predominates in the extraction pH range, though, to be valid in sulphate medium, the calculated log K' should be systematically minimized owing to the $Co^{2+} - SO_4^{2-}$ interactions ($\approx - 0.55$ [5]).

1-Phenyl-3-methyl-4-acyl-pyrazol-5-ols

K' follows the order p,m-tri-MeO-benzoyl > $tert$.-butyl-benzoyl > benzoyl > 2-ethyl-hexanoyl > stearoyl = lauroyl = nonanoyl > isononanoyl > 2-thenoyl > cyclohexanoyl. K' is determined by three main factors: the two-phase acidity of $HL (\overline{HL} \rightleftarrows H^+ + L^-$ of constant K_a/K_d with K_a = dissociation constant and K_d = distribution constant of HL), the ability of L^- to form the CoL_3^- anion, and the stability and lipophilicity of the $\overline{(B^+, CoL_3^-)}$ ion pair. When the substitutent of the acyl group is a linear saturated alkyl chain, the length of the chain (from 8 to 17 C) has no noticeable effect on K', K, and K_{exc}.

The ramification of the chain has various effects on the three equilibrium constants:

— when acyl = isononanoyl, the effect is slightly negative on the three equilibrium constants, which can be explained by a little loss of lipophilicity of the extractant;

Table 1. Cobalt extraction and $\overline{(B^+, ClO_4^-)}/\overline{HL}$ anionic exchange constants; $HL = 1\text{-}R_1\text{-}3\text{-}R_3\text{-}4\text{-}acyl\text{-}$pyrazol-5-ol

No.	R_1	R_3	Acyl	$\log K$	$\log K_{exc}$[a]	$\log K'$
1	$p\text{-}NO_2\text{-}Ph$	Ph	lauroyl	-3.15	-6.35	3.20
2	Ph	Me	$p,m\text{-}$tri-$MeO\text{-}Ph$CO	-4.90	-7.45	2.55
3	Ph	Me	$tert.\text{-}$butyl-PhCO	-5.85	-7.80	1.95
4	Ph	Me	PhCO	-5.10	-7.00	1.90
5	Ph	Me	Ph-acetyl	-5.70	-7.20	1.50
6	Ph	Me	2-ethylhexanoyl	-7.60	-8.85	1.25
7	$p\text{-}MeO\text{-}Ph$	Ph	lauroyl	-7.15	-8.35	1.20
8	Ph	Me	stearoyl	-7.20	-8.35	1.15
9	Ph	Me	lauroyl	-7.25	-8.40	1.15
10	Ph	Me	nonanoyl	-7.25	-8.40	1.15
11	$p\text{-}Cl\text{-}Ph$	Me	lauroyl	-6.50	-7.60	1.10
12	Ph	Me	isononanoyl	-7.50	-8.45	0.95
13	$C_{12}H_{25}$	Me	lauroyl	-8.50	-9.25	0.75
14	Ph	Me	2-thenoyl	-5.85	-6.50	0.65
15	Ph	C_3H_7	lauroyl	-8.05	-8.45	0.40
16	Ph	Me	cyclohexanoyl	-8.00	-8.35	0.35
17	Ph	Me	Ph-propionyl	[b]	-7.75	[b]

[a] $K_{exc} = K_{ClO_4 - L}$
[b] No synergistic extraction

— when acyl = cyclohexanoyl, the effect on K_{exc} is slightly negative or null, and it is strongly negative on K' and K, which can be explained by a little loss of lipophilicity of the extractant and some difficulty to form the CoL_3^- anion (steric hindrance?);

— when acyl = 2-ethyl-hexanoyl, the negative effect on K is explained by the strong negative effect on K_{exc}, minimized by a possible stabilization of the extracted ion pair $\overline{(B^+, CoL_3^-)}$, which would also explain a slightly better value of K'.

The substitution of the alkyl groups by phenyl containing groups makes the acyl group more electron-attractive and increases the acid dissociation of HL (the pK_a of the 4-benzoyl-pyrazol-5-ol is ≈ 4 [12] whereas those of 4-alkoyl-pyrazol-5-ols are > 5 [13]). It follows that $\log K_{exc}$, $\log K'$ and $\log K$, respectively increase from -8.35 to -7.00, 1.15 to 1.90 and -7.25 to -5.10 from HL = lauroyl-pyrazolol to HL = benzoyl-pyrazolol.

Substitutions on the phenyl ring lead to various effects: the presence of three MeO-groups in *meta* and *para* positions on the phenyl ring decreases the acidity of HL by inductive electron-donation. Consequently K_{exc} decreases, whereas K and K' are respectively slightly and strongly increased by a better formation of CoL_3^- and perhaps a stabilization of the extracted ion pair $\overline{(B^+, CoL_3^-)}$. A *tert.*-butyl group in the *para* position on the phenyl ring increases the lipophilicity of HL and slightly decreases its acidity leading to a noticeable decrease of K_{exc} and K, whereas K' is slightly greater. When the phenyl group is separated from the

carbonyl by a methylene (phenylacetyl-pyrazolol), its electron-attractive effect is weakened leading to lower values of $\log K_a K_d^{-1}$ (from -7.4 to -7.9 [14]), $\log K_{exc}$ (from -7.0 to -7.2) and consequently of $\log K'$ (from 1.9 to 1.5) and $\log K$ (from -5.1 to -5.7). Replacing now the benzoyl of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-ol by 2-thenoyl leads to the following facts: $\log K_a$ slightly increases from -4.0 to -3.8 whereas $\log K_d$ decreases from 3.4 to 3.0 [12, 14]. It follows that $\log K_{exc}$ increases from -7.0 to -6.5. The loss of lipophilicity of HL explains the decrease of $\log K'$ (-1.25) (already observed in the extraction of InL_3 [15]) which is minimized for $\log K$ (-0.75) owing to the increase of $\log K_{exc}$ ($+0.5$).

Other 4-Acyl-pyrazol-5-ols

Two 3-phenyl-4-lauroyl-pyrazol-5-ols have been synthesized with a *para*-nitro-phenyl and a *para-MeO*-phenyl substituent on the 1-position of the pyrazole ring: the simultaneous substitutions of 1-phenyl by 1-*para-MeO*-phenyl and 3-methyl by 3-phenyl in the 1-phenyl-3-methyl-4-lauroyl-pyrazol-5-ol have rather poor effects on K_{exc}, K, and K'. However, replacing now 1-*para-MeO*-phenyl by 1-*para*-nitro-phenyl induces a great increase of $\log K_{exc}$ ($+2.0$) followed by great increases of $\log K'$ ($+2.0$) and $\log K$ ($+4.0$). The high acidity of HL is here the main cause of the high extraction observed.

Two other 3-methyl-4-lauroyl-pyrazol-5-ols with a lauryl and a *para*-chloro-phenyl in the 1-position of the pyrazole are now compared with the 1-phenyl-3-methyl-4-lauroyl-pyrazol-5-ol: replacing 1-phenyl by 1-lauryl decreases the acidic dissociation of HL and increases its lipophilicity. Large decreases of $\log K_{exc}$ (-0.85) and $\log K$ (-1.25) are observed, wheras the decrease of $\log K'$ is minimized owing to the better lipophilicity of the extractant. The substitution of 1-phenyl by 1-chlorophenyl has no noticeable effect on $\log K'$ but $\log K_{exc}$ is largely increased ($+0.8$) which favours $\log K$ ($+0.75$).

Another compound, the 1-phenyl-3-propyl-4-lauroyl-pyrazol-5-ol was prepared and compared to the 1-phenyl-3-methyl-4-lauroyl-pyrazol-5-ol: if, as expected, $\log K_{exc}$ remains unchanged, more surprising are the decreases of $\log K$ and $\log K'$ (-0.75). Perhaps some steric effect hinders the CoL_2 or CoL_3^- formation, but this explanation remains doubtful. In the same way, why no synergistic extraction of cobalt was observed with $HL = $ 1-phenyl-3-methyl-4-phenylpropionyl-pyrazol-5-ol?

Conclusions

Seventeen 4-acyl-pyrazol-5-ols (HL) have been compared in the synergistic extraction of cobalt(II) from perchlorate medium, in combination with aliquat 336 (B^+, ClO_4^-) in toluene. The importance of the anionic exchange occurring between $\overline{HL}$ and $\overline{(B^+, ClO_4^-)}$ has been emphasized and the corresponding conditional constants determined. They allowed to estimate the expected synergistic extraction constants from sulphate medium where $\overline{(B^+, L^-)}$ most probably is the predominating ammonium species. It has been shown that aromatic substituents in the 1 and 4 positions of the pyrazole ring favours the $\overline{(B^+, L^-)}$ formation and the extractions of cobalt from perchlorate and sulphate media. Electron-attractive substituents on these aromatic groups increase the effect. Nevertheless, the lipo-

philicity of the pyrazole substituents is also an important parameter of the extraction: indeed, the substitution of benzoyl in the 4-position of the pyrazole by 2-thenoyl slightly increases the HL acidity, but decreases its lipophilicity leading to poorer extractions. With some substituents, the CoL_2 or CoL_3^- formation can be hindered, weakening (4-cyclohexanoyl-pyrazolol, propyl in the 3-position of the 4-benzoyl-pyrazolol) or preventing (phenylpropionyl-pyrazolol) the synergistic extraction.

Acknowledgements

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