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Synergistic Extraction of Cadmium and Cobalt with Mixtures of 4-Stearoyl-Pyrazol-5-ol and Tri-*n*-octylamine in Toluene

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Summary. The synergistic extraction of cobalt and cadmium (M^{2+}) from 1 *M* sodium perchlorate medium with mixtures of 1-phenyl-3-methyl-4-stearoyl-pyrazol-5-ol (H*PMSP*) and tri-*n*-octylammonium perchlorate ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$) in toluene, at 25°C, has been studied. Co and Cd are extracted as $M(PMSP)_2$ species with H*PMSP* alone ($\log_{12} = -7.4$ and -9.4, respectively), and as [$TOA\mathrm{H}^+$, $M(PMSP)_3{}^-$] species in the presence of ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$). At high ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$) concentrations, the synergistic equilibrium is:

$$M^{2+} + 3\,\overline{\mathrm{H}PMSP} + \tfrac{1}{2}(\overline{TOA\mathrm{H}^+,\mathrm{ClO_4}^-})_2 \rightleftharpoons [\overline{TOA\mathrm{H}^+, M(PMSP)_3{}^-}] + 3\,\mathrm{H}^+ + \mathrm{ClO_4}^-$$

of constant $\log K_{131} = -7.10$ and -9.45 (M = Co and Cd, respectively). Owing to the anionic exchange between H*PMSP* and ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$) ($\log K_{exc} = -4.0$) that occurs at highest *pH* range, the synergistic extraction of cadmium, at low ammonium concentrations, is better described by:

$$\mathrm{Cd}^{2+} + 2\,\overline{\mathrm{H}PMSP} + (\overline{TOA\mathrm{H}^+, PMSP^-}) \rightleftharpoons [\overline{TOA\mathrm{H}^+,\mathrm{Cd}(PMSP)_3{}^-}] + 2\,\mathrm{H}^+$$

of constant $\log K_{121} = -4.65$.

Keywords. 4-Acyl-pyrazol-5-ols; Tri-*n*-octylamine; Tri-*n*-octylammonium perchlorate; 1-Phenyl-3-methyl-4-stearoyl-pyrazol-5-ols; Solvent extraction; Synergistic effect.

Synergistische Extraktion von Kadmium und Kobalt mit Mischungen von 4-Stearoyl-pyrazol-5-ol und Tri-*n*-octylamin in Toluol

Zusammenfassung. Es wurde die synergistische Extraktion von Kadmium und Kobalt (M^{2+}) aus 1 *M* Natriumperchlorat-Lösungen mit Mischungen von 1-Phenyl-3-methyl-4-stearoyl-pyrazol-5-ol (H*PMSP*) und Tri-*n*-octylammoniumperchlorat ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$) in Toluol bei 25°C untersucht. Co^{2+} und Cd^{2+} werden mit H*PMSP* allein als $M(PMSP)_2$ Spezies extrahiert ($\log K_{12} = -7.4$ bzw. -9.4), in Gegenwart von ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$) hingegen als [$TOA\mathrm{H}^+$, $M(PMSP)_3{}^-$]. Bei hohen ($TOA\mathrm{H}^+$, $\mathrm{ClO_4}^-$)-Konzentrationen läßt sich das synergistische Gleichgewicht wie folgt schreiben:

$$M^{2+} + 3\,\overline{\mathrm{H}PMSP} + \tfrac{1}{2}(\overline{TOA\mathrm{H}^+,\mathrm{ClO_4}^-})_2 \rightleftharpoons [\overline{TOA\mathrm{H}^+, M(PMSP)_3{}^-}] + 3\,\mathrm{H}^+ + \mathrm{ClO_4}^-$$

mit den Konstanten $\log K_{131} = -7.10$ bzw. -9.45 für Co^{2+} bzw. Cd^{2+}. Wegen des im höchsten *pH*-

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Bereich auftretenden Anionenaustauschs zwischen H*PMSP* und $(TOAH^+, ClO_4^-)$ ($\log K_{exc} = -4.0$) wird die synergistische Extraktion von Kadmium bei geringen Ammoniumkonzentrationen besser folgendermaßen beschrieben:

$$Cd^{2+} + 2\,\overline{HPMSP} + \overline{(TOAH^+, PMSP^-)} \rightleftharpoons \overline{[TOAH^+, Cd(PMSP)_3^-]} + 2\,H^+$$

mit der Konstanten $\log K_{121} = -4.65$.

Introduction

Among the 4-acyl-pyrazol-5-ols (noted H*L*), 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-ol (H*PMBP*) has been extensively studied, alone or in combination with other reagents, as a cation-exchanger extractant ([1–3] and included references). Obviously, H*PMBP* is a good acidic chelating reagent owing to its low pK_a (~ 4), but its industrial applications are limited by the low solubility of its metal complexes and also by the strong and nearly irreversible extraction of iron(III): these drawbacks can be partly cancelled by substituting 4-benzoyl by the more lipophilic groups 4-lauroyl and 4-stearoyl. The respective H*PMLP* and H*PMSP*, less acidic than H*PMBP*, extract iron(III) very slowly allowing a good selectivity in the copper extraction [4, 5]. Thus, in this paper, the synergistic extraction of metal cations ($M^{2+} = Co^{2+}$, Cd^{2+}) with mixtures of H*PMSP* and tri-*n*-octylammonium salts, in toluene, is studied to extend the previous work performed with H*PMBP* in combination with various ammonium salts [6–14].

Materials and Methods

Chemicals and Solutions

H*PMSP* was synthesized according to Jensen [15]. Organic solutions of tri-*n*-octylamine (*TOA*) (Fluka Chemical) in toluene were pre-equilibrated with 1 *M* perchloric acid before their use in distribution measurements. The ionic strength of the aqueous phase was kept equal to 1 *M*. The total initial Co and Cd aqueous concentrations were 1.7 and $0.9 \cdot 10^{-3}$ *M*, respectively.

Metal Distribution and Analytical Procedure

The distribution measurements were performed in a thermostated vessel (25.0 ± 0.2°C) using a batch technique. Equal volumes of organic and aqueous phases were shaken for at least 30 min and separated by gravity. For each experimental point, aliquots of both phases were withdrawn and analyzed, after suitable dilution (and stripping of metal for the organic aliquots), by atomic absorption, using a 2380 Perkin Elmer spectrophotometer.

Anionic Exchange Between H*PMSP and* $(TOAH{\cdot}ClO_4)$

The constant of the anionic exchange between H*PMSP* and $(TOAH \cdot ClO_4)$ has been estimated from the *pH* variations observed by contacting 1 *M* perchlorate aqueous solutions at $pH = 2$ with toluene solutions of *TOA* and H*PMSP* mixtures [12].

Results and Discussion

Extraction of Cadmium

Cadmium distribution curves log *D* vs. *pH* ($D=[\overline{M}]/[M]$) at constant $[\overline{HPMSP}]_i$ and various $[\overline{(\mathrm{TOAH}\cdot \mathrm{ClO_4})}]_i$ are shown in Fig. 1 ("*i*" denotes initial concentrations). For $[\overline{(\mathrm{TOAH}\cdot \mathrm{ClO_4})}]_i=0$, the curve is a straight line of slope 2 according to the well-established equilibrium (1):

$$M^{2+} + 2\overline{HL} \overset{K_{12}}{\rightleftharpoons} \overline{ML} + 2\,\mathrm{H}^+ \qquad (1)$$

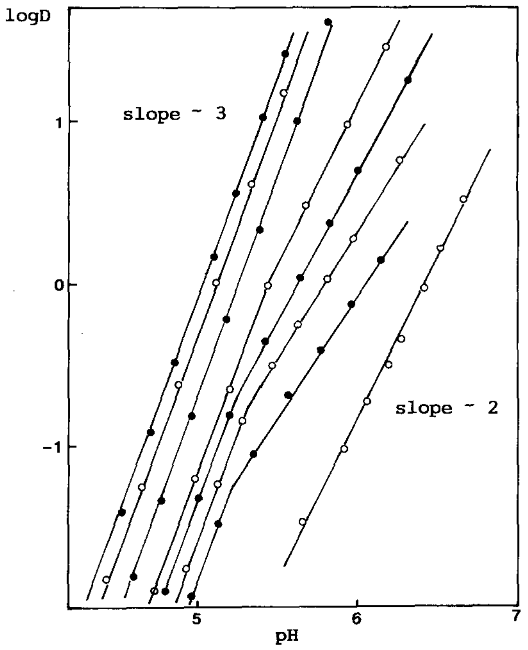

Fig. 1. Extraction of cadmium from 1 *M* perchlorate medium with mixtures of H*PMSP* (0.02 *M*) and (*TOA*H · ClO$_4$) in toluene. From right to left, $[(\overline{TOA\mathrm{H}\cdot \mathrm{ClO_4}})]_i\cdot 10^4=0$, 2, 4, 8, 16, 66, 400, 1 000 *M*

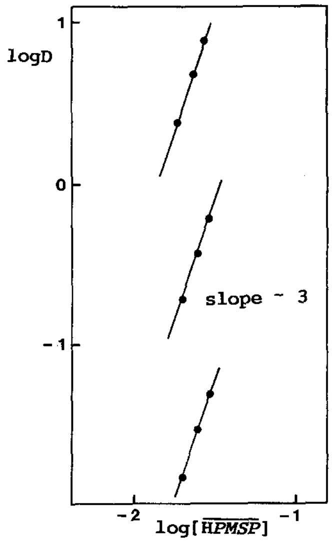

Fig. 2. Extraction of cadmium from 1 *M* perchlorate medium with mixtures of H*PMSP* and (*TOA*H · ClO$_4$) (0.0066 *M*) in toluene, from bottom to top, at $pH=4.6$, 5.0, 5.4

A third phase formation was observed with H*PMBP*, in the same experimental conditions, which is not found with H*PMSP*. $\log K_{12} = -9.40$ and -8.20 for $\text{H}L = \text{H}PMSP$ and H*PMBP* [16]. As previously observed in the extraction of magnesium [9], the higher lipophilicity of H*PMSP* compared to H*PMBP* is not sufficient to counterbalance its lower acidity ($pK_a > 5.1$).

In the presence of $\overline{(TOA\text{H}\cdot\text{ClO}_4)}$, a synergistic effect is observed. Two different $[\overline{(TOA\text{H}\cdot\text{ClO}_4)}]_i$ ranges have to be considered: $[\overline{(TOA\text{H}\cdot\text{ClO}_4)}]_i > 1.6\cdot 10^{-3}\,M$ (case A) and $[\overline{(TOA\text{H}\cdot\text{ClO}_4)}]_i \leqslant 1.6\cdot 10^{-3}\,M$ (case B).

In case A, the curves $\log D$ vs. pH are straight lines of slope ~ 3; so are the curves $\log D$ vs. $\log[\overline{\text{H}PMSP}]$ at constant pH and $[\overline{(TOA\text{H}\cdot\text{ClO}_4)}]_i$ (Fig. 2) which is in agreement with the extraction of $\text{Cd}(PMSP)_3^-$ moieties. Owing to the electroneutrality of extracted species, one can assume that $[\overline{TOA\text{H}\cdot\text{Cd}(PMSP)_3}]$ is extracted. Nevertheless, the curves $\log D$ vs. $\log[\overline{(TOA\text{H}\cdot\text{ClO}_4)}]$ (Fig. 3) are straight lines of slope ~ 0.5 which agrees with equilibrium (2), where $\log K_{131} = -9.45 \pm 0.06$,

$$M^{2+} + 3\,\overline{\text{H}L} + \tfrac{1}{2}\overline{(TOA\text{H}\cdot\text{ClO}_4)_2} \overset{K_{131}}{\rightleftharpoons} \overline{(TOA\text{H}\cdot ML_3)} + 3\,\text{H}^+ + \text{ClO}_4^- \qquad (2)$$

better than with equilibrium (3), where $\log K'_{131} = -8.5 \pm 0.2$.

$$M^{2+} + 3\,\overline{\text{H}L} + \overline{(TOA\text{H}\cdot\text{ClO}_4)} \rightleftharpoons \overline{(TOA\text{H}\cdot ML_3)} + 3\,\text{H}^+ + \text{ClO}_4^- \qquad (3)$$

In case B, the slope of the curves $\log D$ vs. pH tends towards 3 at lowest pH and 2 at highest pH: there, it is interesting to consider the anionic exchange equilibrium (4) where $\log K_{exc} = -4.00$ (see Materials and Methods).

$$\overline{(TOA\text{H}\cdot\text{ClO}_4)} + \overline{\text{H}PMSP} \rightleftharpoons \overline{(TOA\text{H}\cdot PMSP)} + \text{H}^+ + \text{ClO}_4^- \qquad (4)$$

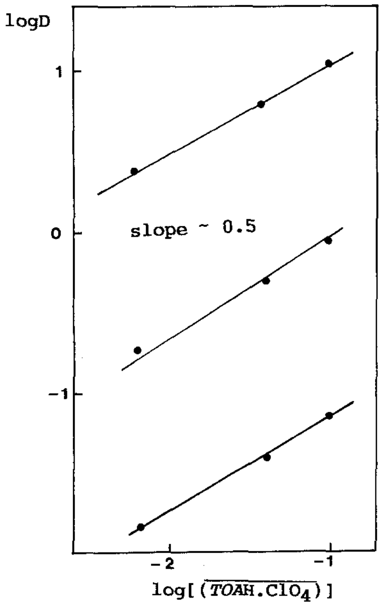

Fig. 3. Extraction of cadmium from 1 M perchlorate medium with mixtures of H*PMSP* (0.02 M) and $(TOA\text{H}\cdot\text{ClO}_4)$ in toluene from bottom to top, at $pH = 4.6$, 5.0, 5.4

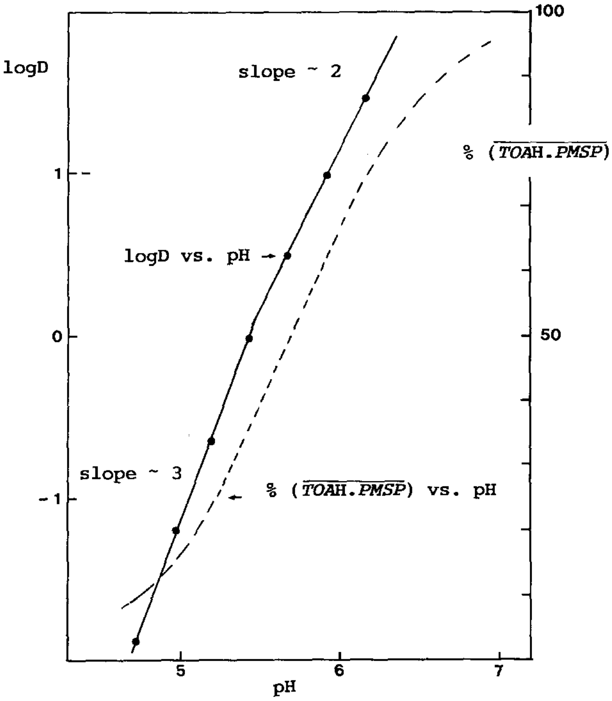

Fig. 4. Extraction of cadmium from 1 *M* perchlorate medium with mixtures of H*PMSP* (0.02 *M*) and ($\overline{TOA\text{H}\cdot\text{ClO}_4}$) (0.0016 *M*) in toluene: log*D* and $[(\overline{TOA\text{H}\cdot PMSP})]/[(\overline{TOA\text{H}\cdot\text{ClO}_4})]_i$ vs · *pH*

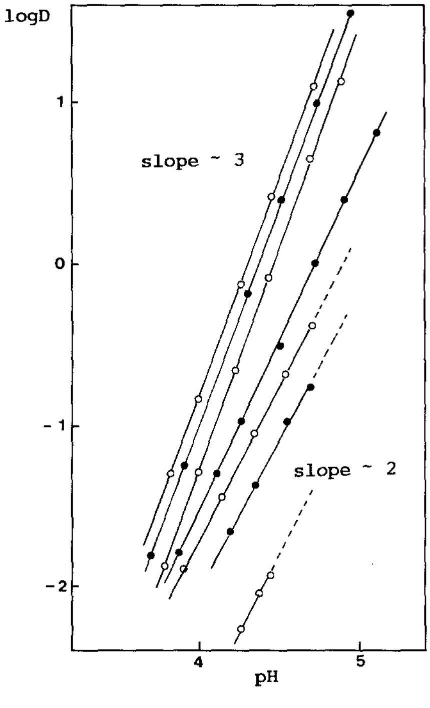

Fig. 5. Extraction of cobalt from 1 *M* perchlorate medium with mixtures of H*PMSP* (0.02 *M*) and ($\overline{TOA\text{H}\cdot\text{ClO}_4}$) in toluene. Broken lines = third phase formation. From right to left, $[(\overline{TOA\text{H}\cdot\text{ClO}_4})]_i\cdot 10^4 = 0$, 2, 4, 16, 66, 400, 1000 *M*

It follows that, at low ($\overline{TOA\text{H}\cdot\text{ClO}_4}$) concentrations, in the cadmium extraction *pH* range, noticeable quantities of ($\overline{TOA\text{H}\cdot PMSP}$) are formed (Fig. 4): then, at highest *pH*, the cadmium extraction is well described by Eq. (5), of constant $\log K_{121} = -4.65 \pm 0.06$.

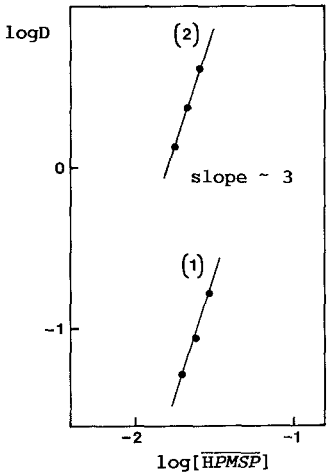

Fig. 6. Extraction of cobalt from 1 *M* perchlorate medium with mixtures of H*PMSP* and (*TOA*H · ClO$_4$) (0.0066 *M*) in toluene, at *pH* = 4.0 (1) and 4.5 (2)

$$M^{2+} + 2\overline{HL} + \overline{(TOAH \cdot L)} \overset{K_{121}}{\rightleftharpoons} \overline{(TOAH \cdot ML_3)} + 2\,H^+ \qquad (5)$$

Equilibria (2) or (3) explain the slope 3 of the curves at lower *pH*. Eq. (6), which results from the difference between Eq. (5) and (1), describes the synergistic effect:

$$\overline{ML_2} + \overline{(TOAH \cdot L)} \overset{K_{syn}}{\rightleftharpoons} \overline{(TOAH \cdot ML_3)} \qquad (6)$$

with $\log K_{syn} = 4.75 \pm 0.15$, which is close to $4.90 = \log K'_{131} - \log K_{12} - \log K_{exc}$ [taking arbitrarily (*TOA*H, ClO$_4$) in the monomeric form]. Thus, the replacement of

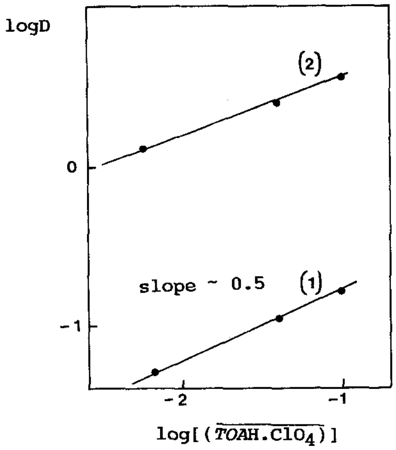

Fig. 7. Extraction of cobalt from 1 *M* perchlorate medium with mixtures of H*PMSP* (0.02 *M*) and (*TOA*H · ClO$_4$) in toluene, at *pH* = 4.0 (1) and 4.5 (2)

Table 1. Equilibrium constants

	Cadmium		Cobalt	
	H*PMSP*	H*PMBP* [10]	H*PMSP*	H*PMBP* [10]
$\log K_{12}$	-9.40 ± 0.05	-8.15	-7.40 ± 0.05	-7.25
$\log K_{131}$	-9.45 ± 0.06	–	-7.10 ± 0.07	–
$\log K'_{131}$	-8.50 ± 0.20	-6.60	-6.05 ± 0.20	-4.90
$\log K_{syn}$	4.90 ± 0.25 4.75 ± 0.15	5.50	5.35 ± 0.25	6.30

H*PMBP* by H*PMSP* leads to a weaker synergistic effect ($\log K_{syn} = 5.50$ with H*L* = H*PMBP* [10]).

Extraction of Cobalt

Typical distribution curves $\log D$ vs. *pH*, vs. $\log\overline{[\mathrm{H}PMSP]}$ and vs. $\log\overline{[(TOA\mathrm{H} \cdot \mathrm{ClO_4})]}$ are given in Figs. 5, 6, and 7. At high $\overline{(TOA\mathrm{H} \cdot \mathrm{ClO_4})}$ concentrations ($> 1.6 \cdot 10^{-3} M$), the experimental data can be explained by the same equilibria as those describing the cadmium extraction. The equilibrium constants are summarized in Table 1, in comparison with those related to H*PMBP* [10] which are systematically higher. Nevertheless, it is interesting to note that better selectivities are found with H*PMSP* than with H*PMBP* between the Cd and Co extractions. At low $\overline{(TOA\mathrm{H} \cdot \mathrm{ClO_4})}$ concentrations ($\leq 1.6 \cdot 10^{-3} M$), the slope of the curves $\log D$ vs. *pH* decreases from 3 to below 2 with decreasing $\overline{[(TOA\mathrm{H} \cdot \mathrm{ClO_4})]}$ which cannot be explained by the $\overline{(TOA\mathrm{H} \cdot PMSP)}$ formation which is (negligible in the Co extraction *pH* range. Moreover, a third phase appears when $\overline{[\mathrm{Co}]} = [\overline{(TOA\mathrm{H} \cdot \mathrm{ClO_4})}]_i$ (Fig. 8), which may correspond to the stoichiometry of the extracted species, likely $(TOA\mathrm{H} \cdot \mathrm{Co}L_3)$ and/or $ML_2(TOA\mathrm{H} \cdot \mathrm{ClO_4})$.

Conclusions

Cadmium and cobalt are synergistically extracted from 1 *M* perchlorate medium with mixtures of 4-stearoyl-pyrazol-5-ol and tri-*n*-octylamine as $[TOA\mathrm{H}^+, M(PMSP)_3{}^-]$ ion pairs. The extractions and the synergistic effects are systematically lower than those achieved with 4-benzoyl-pyrazol-5-ol, less lipophilic but more acidic than H*PMSP*, but the selectivity between the Co and Cd extractions is improved with the latter. The main equilibria which describe the synergistic extraction of metal cations with mixtures of 4-acyl-pyrazol-5-ols and lipophilic ammonium salts are summarized in Fig. 9: the effects of aggregation phenomena remain difficult to evaluate, so they are neglected.

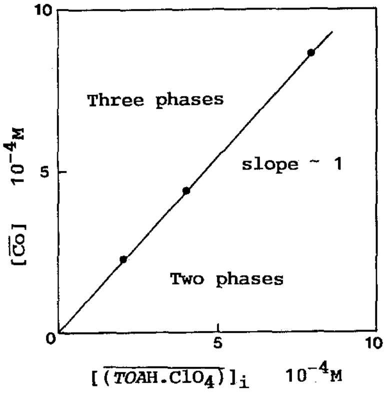

Fig. 8. Extraction of cobalt from 1 M perchlorate medium with mixtures of H*PMSP* (0.02 M) and $\overline{(TOA\mathrm{H}\cdot \mathrm{ClO}_4)}$: $\overline{[\mathrm{Co}]}$ (third phase formation edge) vs. $[\overline{(TOA\mathrm{H}\cdot \mathrm{ClO}_4)}]_i$

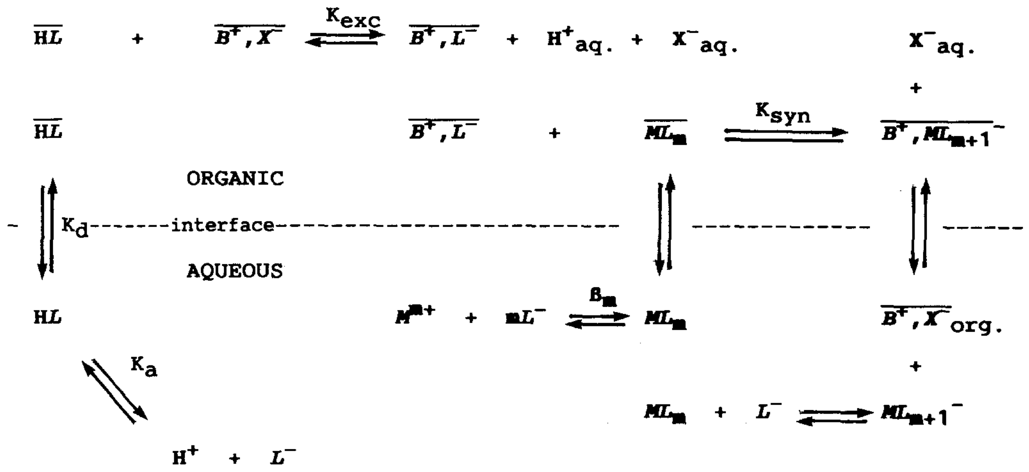

Fig. 9. Simplified scheme of the synergistic extraction of metal cations (M^{m+}) with mixtures of 4-acyl-pyrazol-5-ols (H*L*) and lipophilic ammonium salts (B^+, X^-) (X^- = inorganic anion that does not complex M^{m+})

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