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Effect of Aniline Derivatives on the Extraction of Cobalt with 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one in Toluene

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Summary. The effect of aniline derivatives [4-methylaniline = 4-toluidine, 3,4-dimethylaniline = 3,4-xylidine, N,N-dimethylaniline and tribenzylamine (*Am*)] on the extraction of cobalt from sulphate, nitrate and perchlorate aqueous media of $1.0\,M$ ionic strength with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (H*L*) in toluene, has been quantitatively studied. With both primary amines a synergic effect was found owing to the $Am\mathrm{H}\cdot\mathrm{Co}L_3$ ion pair extraction. The $Am\mathrm{H}\cdot\mathrm{Co}L_3$ average formation constant, from $\mathrm{Co}L_2$ and $Am\mathrm{H}\cdot L$, was $\log K_s = 3.7$ and 3.8 for *Am* = 4-toluidine and 3,4-xylidine respectively. With N,N-dimethylaniline and tribenzylamine which are poorly protonated in the cobalt extraction *pH* range (4–6), no noticeable synergism was observed.

Keywords. Aniline derivatives; Cobalt; 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one; Solvent extraction; Synergic effect.

Die Wirkung von Anilin-Derivaten auf die Extraktion von Kobalt mit 1-Phenyl-3-methyl-4-benzoylpyrazol-5-on in Toluol

Zusammenfassung. Der Einfluß von Anilin-Derivaten [4-Methylanilin = 4-Toluidin, 3,4-Dimethylanilin = 3,4-Xylidin, N,N-Dimethylanilin und Tribenzylamin (*Am*)] auf die Extraktion des Kobalts in wäßrigem Medium mit einer Sulfat-, Nitrat- und Perchloratkonzentration von $1.0\,M$ mit 1-Phenyl-3-methyl-4-benzoylpyrazol-5-on (H*L*) in Toluol wurde quantitativ untersucht. Für beide primären Amine wurde ein synergetischer Effekt beobachtet, der sich auf die Ionenpaarextraktion des $Am\mathrm{H}\cdot\mathrm{Co}L_3$ zurückführen läßt. Die durchschnittlichen Bildungskonstanten von $\mathrm{Co}L_2$ und $Am\mathrm{H}\cdot L$ sind $\log K_s = 3.7$ und 3.8 für *Am* = 4-Toluidin bzw. 3,4-Xylidin. N,N-Dimethylanilin und Tribenzylamin sind im *pH*-Bereich von 4—6 nur geringfügig protoniert. Dies ist der *pH*-Bereich der Kobalt-Extraktion, wobei hier kein wesentlicher synergetischer Effekt beobachtet wurde.

Introduction

When the usual coordination number of a metal cation M^{m+} is equal to $(2m + 2)$, the formation of an anionic metal complex $ML_{m+1}{}^-$ with a chelating anion L^- is possible. Then it is less hydrated than the neutral complex ML_m and it can be

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synergically extracted as $\overline{B\cdot ML_{m+1}}$ ion pairs by the chelating acidic extractant $\overline{\mathrm{H}L}$ in presence of an anion-exchanger $\overline{B.X}$. This was observed particularly in the extraction of actinides [1], rare earths [2, 3], divalent transition metals (Zn, Co, Ni, Cd) [4] and alkali or alkaline earth metals [5] with mixtures of 4-acylpyrazol-5-ones and high molecular weight amines or quaternary ammonium salts. Under the experiment conditions of the cited papers, the amines of sufficient basicity were largely protonated by the inorganic acid H*X* or by the extractant $\overline{\mathrm{H}L}$: It followed that they could not act as neutral solvating synergists, as did tribenzylamine in the extraction of cobalt with 2-thenoyltrifluoroacetone (H*TTA*) in toluene [6]. The present paper deals precisely with the extraction of cobalt with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (H*PMBP* or H*L*) and amines of low basicity (*Am*): tribenzylamine, 4-methylaniline, 3,4-dimethylaniline and N,N-dimethylaniline. The extraction of cobalt with carboxylic acids and 3,4-dimethylaniline was previously studied [7].

Materials and Methods

Chemicals. H*PMBP* was prepared and purified according to Jensen [8]. Other reagents—N,N-dimethylaniline and 4-methylaniline "puriss" from Fluka, 3,4-dimethylaniline 98% from "Aldrich" and tribenzylamine 98% from "Merck"—were used without further purification.

Extraction and Analytical Procedure. The organic solutions were pre-equilibrated with aqueous solutions, free of metal, analogous to those used in the metal extraction procedure. The total inorganic anion concentrations in the aqueous phases were kept equal to 1.0*M* (ClO_4^- or NO_3^-) or 0.33*M* (SO_4^{2-} + HSO_4^-). The initial total metal concentration was $1.7\cdot 10^{-3}M$.

Liquid-Liquid Behaviour of the Extractants

Inorganic Acid Extraction with Amines (Am) in Toluene. An organic solution of amine at various concentration is shaken at 25°C with an aqueous solution of 1.0*M* ionic strength fixed by the sodium salt of the inorganic acid, at $pH \sim 2$. The *pH* is measured before and after extraction. The *pH* variation allows to estimate the acid extraction. Typical experimental data are given in Table 1; $x = 100\,[Am\mathrm{H}^+]/\overline{[Am]}_i$. The concentration is given in mol/l at an organic/aqueous volume ratio = 1 : 1.

Interaction Between $\overline{Am}$ *and* $\overline{\mathrm{H}L}$. A 0.33 *M* sulphate aqueous solution at $pH \sim 7$ is equilibrated with an equal volume of organic solution containing a) H*PMBP* 0.02*M*, b) H*PMBP* 0.01 *M* and c) H*PMBP* 0.02*M*, *Am* 0.01*M*. The final *pH* are measured and compared in Table 2.

Note. Overlined symbols refer to the organic phase, *i* denotes initial concentrations before contacting the phases.

Results and Discussion

Extraction of Cobalt(II) from 0.33M Sulphate Medium with H*PMBP + Am in Toluene*

Synergic Extraction with Am = 3,4-Dimethylaniline. The experimental data, given in Tables 1 and 2, allow to conclude that the formation of $\overline{(Am\mathrm{H})_2SO_4}$ or $\overline{Am\mathrm{H}\cdot HSO_4}$ species, under the conditions of cobalt extraction (pH = 3 to 5), is negligible, and that most of amine is protonated by H*PMBP*.

Table 1. Extraction of inorganic acids with amines

Am	H_2SO_4			$HClO_4$			HNO_3		
	$[\overline{Am}]_i$	*pH*	*x*	$[\overline{Am}]_i$	*pH*	*x*	$[\overline{Am}]_i$	*pH*	*x*
3,4-Dimethylaniline	0	2.02	—	0	1.93	—	0	1.97	—
	0.01	2.07	10	0.010	2.64	95	0.010	2.77	89
	0.02	2.15	12	0.015	3.41	76	0.015	3.30	62
	0.03	2.23	12	0.020	3.77	58	0.020	3.60	52
4-Methylaniline	0	2.02	—	0	1.93	—	0	1.97	—
	0.01	2.07	10	0.010	2.65	95	0.010	2.73	91
	0.02	2.15	12	0.015	3.47	76	0.015	3.45	62
	0.03	2.23	12	0.020	3.84	58	0.020	3.76	53
N,N-Dimethylaniline	0	2.03	—	0	1.83	—	0	1.99	—
	0.01	2.08	10	0.005	1.99	90	0.01	2.32	55
	0.02	2.14	10	0.010	2.21	86	0.02	2.62	52
	0.03	2.20	10	0.015	2.51	77	0.03	2.82	44
Tribenzylamine	0	2.04	—	0	1.83	—	0	1.97	—
	0.01	2.04	0	0.005	1.99	90	0.01	2.01	10
	0.03	2.04	0	0.010	2.19	83	0.03	2.10	9
	0.08	2.04	0	0.030	2.98	46	0.04	2.15	9

Table 2. $\overline{\mathrm{H}PMBP}$ and $\overline{Am}$ interaction

		Solution	*pH*	Interaction
	0.01*M*	H*PMBP*	5.62	
	0.02*M*	H*PMBP*	5.44	
	0.02*M*	H*PMBP*		
+	0.01*M*	3,4-Dimethylaniline	5.60	Strong
+	0.01*M*	4-Methylaniline	5.61	Strong
+	0.01*M*	N,N-Dimethylaniline	5.46	Weak
+	0.01*M*	Tribenzylamine	5.44	Weak

Experimental curves, $\log D$ vs. *pH* ($D = [\overline{\mathrm{Co}}]/[\mathrm{Co}]$) at various $[\overline{\mathrm{H}L}]_i$ and $[\overline{Am}]_i$, are given in Fig. 1. They are straight lines of slopes 1.7 to 1.9. The difference with the entire value 2 can be explained by the formation of the metal extracted species which decreases the free extractant concentrations. Assuming that $[\overline{Am\mathrm{H}\cdot L}] = [\overline{Am}]_i - [\overline{\mathrm{Co}}]$ and $[\overline{\mathrm{H}L}] = [\overline{\mathrm{H}L}]_i - [\overline{Am}]_i - 3\,[\overline{\mathrm{Co}}]$, the curves of Figs. 2 and 3—$\log D$ vs. $\log [\overline{\mathrm{H}L}]$ and $\log D$ vs. $\log [\overline{Am\mathrm{H}\cdot L}]$ at constant $[\overline{Am}]_i$ and $[\overline{\mathrm{H}L}]_i$, respectively, and constant *pH*—have been obtained. They are straight lines of slopes close to 2 and 1, respectively. Thus, the synergic extraction can be described by equilibrium (1):

$$\mathrm{Co}^{2+} + 2\,\overline{\mathrm{H}L} + \overline{Am\mathrm{H}\cdot L} \overset{K_{3,1}}{\rightleftarrows} \overline{Am\mathrm{H}\cdot \mathrm{Co}L_3} + 2\,\mathrm{H}^+. \qquad (1)$$

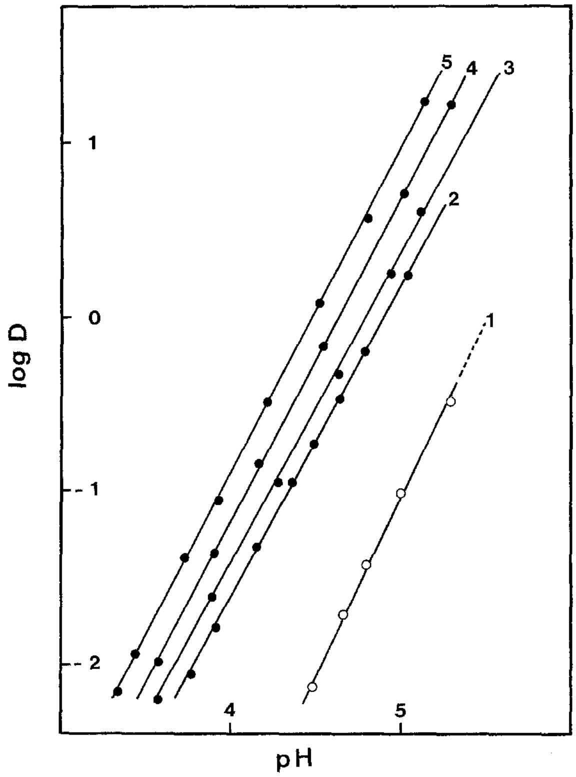

Fig. 1. Cobalt extraction from 0.33*M* sulphate medium with H*PMBP* + 3,4-dimethylaniline in toluene: log *D* vs. *pH*. $\overline{[HL]}_i - \overline{[Am]}_i = 0.02M$, $\overline{[Am]}_i = 0$ (*1*), 0.0033*M* (*2*), 0.0066*M* (*3*), 0.01*M* (*4*), 0.02*M* (*5*)

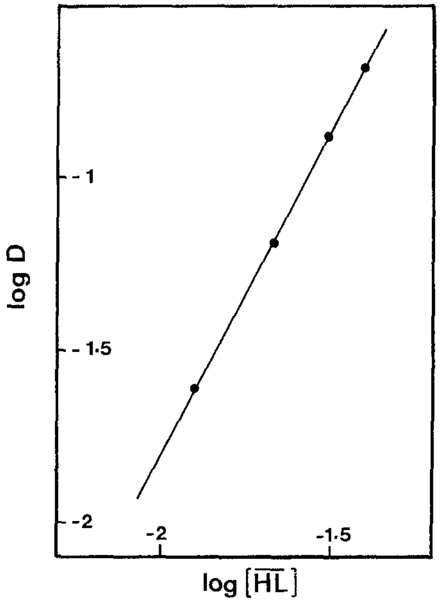

Fig. 2. Cobalt extraction from 0.33*M* sulphate medium with H*PMBP* and 3,4-dimethylaniline in toluene: log *D* vs. log $\overline{[HL]}$ at $pH = 4.0$, $\overline{[Am]}_i = 0.01M$, $\overline{[HL]} = \overline{[HL]}_i - \overline{[Am]}_i - 3\overline{[Co]}$

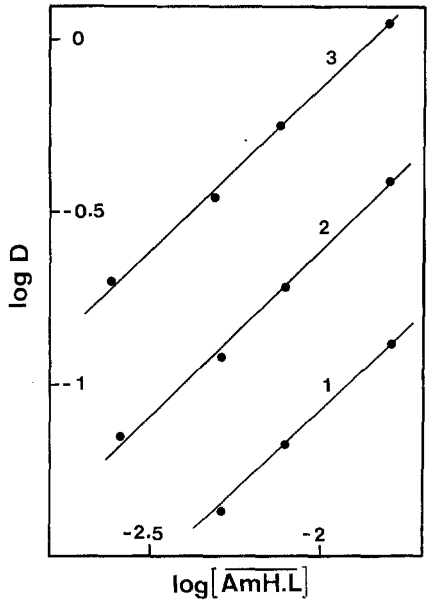

Fig. 3. Cobalt extraction from 0.33*M* sulphate medium with H*PMBP* and 3,4-dimethylaniline in toluene: log *D* vs. log $\overline{[AmH \cdot L]}$ at $pH = 4.0$ (*1*), 4.25 (*2*), 4.5 (*3*), $\overline{[HL]}_i - \overline{[Am]}_i = 0.02M$, $\overline{[AmH \cdot L]} = \overline{[Am]}_i - \overline{[Co]}$

In absence of amine, the extraction equilibrium is

$$\mathrm{Co}^{2+} + 2\,\overline{\mathrm{H}L} \overset{K_{2,0}}{\rightleftarrows} \overline{\mathrm{Co}L_2} + 2\,\mathrm{H}^+ \tag{2}$$

with $\log K_{2,0} = -7.60$, and the synergic equilibrium is

$$\overline{\mathrm{Co}L_2} + \overline{Am\mathrm{H}\cdot L} \overset{K_s}{\rightleftarrows} \overline{Am\mathrm{H}\cdot\mathrm{Co}L_3}\,. \tag{3}$$

A rough value of $K_{3,1}$ was first determined with the assumption that $[\overline{Am\mathrm{H}\cdot L}] = [\overline{Am}]_i - [\overline{\mathrm{Co}}]$. Then, equilibrium (4) was also considered,

$$\overline{Am} + \overline{\mathrm{H}L} \overset{K(Am\mathrm{H}\cdot L)}{\rightleftarrows} \overline{Am\mathrm{H}\cdot L}\,, \tag{4}$$

and a first value of $K(Am\mathrm{H}\cdot L)$ was obtained from the four following equations

$$K_{3,1} = D[\mathrm{H}^+]^2[\overline{\mathrm{H}L}]^{-2}[\overline{Am\mathrm{H}\cdot L}]^{-1}, \tag{5}$$

$$[\overline{\mathrm{H}L}]_i = [\overline{\mathrm{H}L}] + [\overline{Am\mathrm{H}\cdot L}] + 3[\overline{\mathrm{Co}}], \tag{6}$$

$$[\overline{Am}]_i = [\overline{Am}] + [\overline{Am\mathrm{H}\cdot L}] + [\mathrm{Co}], \tag{7}$$

$$K(Am\mathrm{H}\cdot L) = [\overline{Am\mathrm{H}\cdot L}][\overline{Am}]^{-1}[\overline{\mathrm{H}L}]^{-1}. \tag{8}$$

An iterative calculation $[K(Am\mathrm{H}\cdot L) \rightarrow K_{3,1} \rightarrow K(Am\mathrm{H}\cdot L) \rightarrow \ldots]$ led to the final values $\log K_{3,1} = -3.80$, $\log K(Am\mathrm{H}\cdot L) = 2.30$ and $\log K_s = 3.80$ ($\Delta \log K < 0.1$).

Extraction with Other Amines. A comparison of the extractions of cobalt with H*PMBP* and the different amines is given in Fig. 4. The synergic extraction

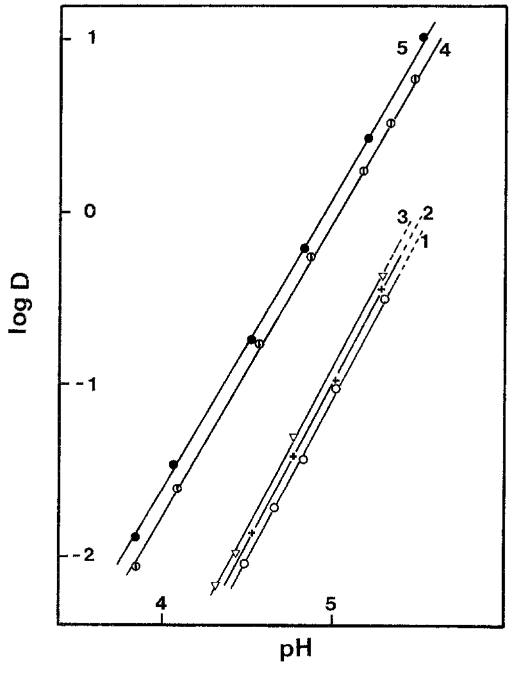

Fig. 4. Cobalt extraction from $0.33M$ sulphate medium with $\overline{\mathrm{H}PMBP}$ and $Am([\overline{\mathrm{H}L}]_i = 0.02M)$. *1*: $[\overline{Am}]_i = 0$, *2* to *5*: $[\overline{Am}]_i = 0.01M$. Am = tribenzylamine (*2*), N,N-dimethylaniline (*3*), 4-methylaniline (*4*), 3,4-dimethylaniline (*5*)

performed with Am = 4-methylaniline is slightly lower than the one performed with Am = 3,4-dimethylaniline [$\log K_{3,1} = -3.90$, $\log K_s = 3.70$, $\log K(Am\mathrm{H}\cdot L) = 2.30$] whereas the extractions performed with N,N-dimethylaniline and tribenzylamine are close to the extraction with HL alone. If one considers the $\overline{Am}$-$\overline{\mathrm{H}PMBP}$ interactions (Table 2), it is clear that a noticeable synergism is only obtained with the amines having strong interactions with H$PMBP$. In other words, N,N-dimethylaniline and tribenzylamine, which are mainly in the neutral form "$\overline{Am}$" in the organic phase, do not form the $\overline{\mathrm{Co}L_2Am}$ synergic species, as do $\overline{\mathrm{Co}(TTA)_2}$ and $\overline{Am}$ = tribenzylamine in toluene with $\log K_s = 3.26$ [6].

Extraction of Cobalt(II) From 1.0 M $\mathrm{NaClO_4}$ *and* $\mathrm{NaNO_3}$ *Media with* H*PMBP* + *Am in Toluene*

As it is generally observed [4], the extractions of $\mathrm{HNO_3}$ and $\mathrm{HClO_4}$ with amines are much higher than with $\mathrm{H_2SO_4}$ (Table 1). It follows that the formation of $\overline{Am\mathrm{H}\cdot X}$ salts ($X = \mathrm{NO_3}$, $\mathrm{ClO_4}$) cannot be neglected. Assuming arbitrarily that the ammonium salts are only monomers, rough HX extraction constants [equilibrium (9)] have been determined from the experimental data, and are given in Table 3,

$$\overline{Am} + \mathrm{H}^+ + X^- \overset{K(Am\mathrm{H}\cdot X)}{\rightleftarrows} \overline{Am\mathrm{H}\cdot X}. \qquad (9)$$

Typical extraction curves, $\log D$ vs. pH, of cobalt from perchlorate and nitrate media with H$PMBP$ + Am mixtures in toluene are shown in Figs. 5 and 6. Such curves were obtained at various $\overline{\mathrm{H}PMBP}$ and $\overline{Am}$ concentrations ($0.02M < [\overline{\mathrm{H}L}]_i < 0.04M$ and $0.0033M < [\overline{Am}]_i < 0.01M$). Taking into account equilibria (4) and (9), $\log K_{3,1}$ has been calculated for each experimental point. The average $\log K_{3,1}$ values are given in Table 4.

As it has been found in the cobalt extraction from suphate medium, no synergism is observed in the extractions from nitrate and perchlorate media with H$PMBP$ and tribenzylamine or N,N-dimethylaniline. The magnitude of the synergic effect obtained with 3,4-dimethylaniline and 4-methylaniline is quite similar for the three aqueous media, and it is largely lower than those previously determined with Am = n-dodecylamine [9] and tri-n-octyl amine [4] ($\log K_s = 5.15$ and 6.10, respectively). The differences can be explained by the lower lipophilicities together with the lower basicities of the aniline derivatives. In no case, the synergic extraction of cobalt with mixtures of H$PMBP$ and amines could be explained by the formation

Table 3. HX extraction constants [$\log K(Am\mathrm{H}\cdot X)$]

	$\mathrm{ClO_4}$	$\mathrm{NO_3}$
3,4-Dimethylaniline	3.9	3.6
4-Methylaniline	4.0	3.8
N,N-Dimethylaniline	3.0	2.4
Tribenzylamine	2.9	1.1

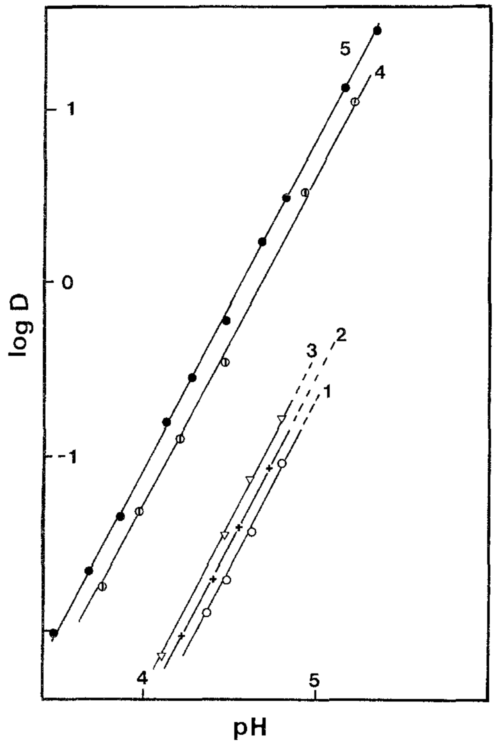

Fig. 5. Cobalt extraction from 1.0 M perchlorate medium with $\overline{\mathrm{H}PMBP}$ and $Am([\overline{\mathrm{H}L}]_i = 0.02M)$. *1*: $[Am]_i = 0$, *2* to *5*: $[Am]_i = 0.01M$. Am = tribenzylamine (*2*), N,N-dimethylaniline (*3*), 4-methylaniline (*4*), 3,4-dimethylaniline (*5*)

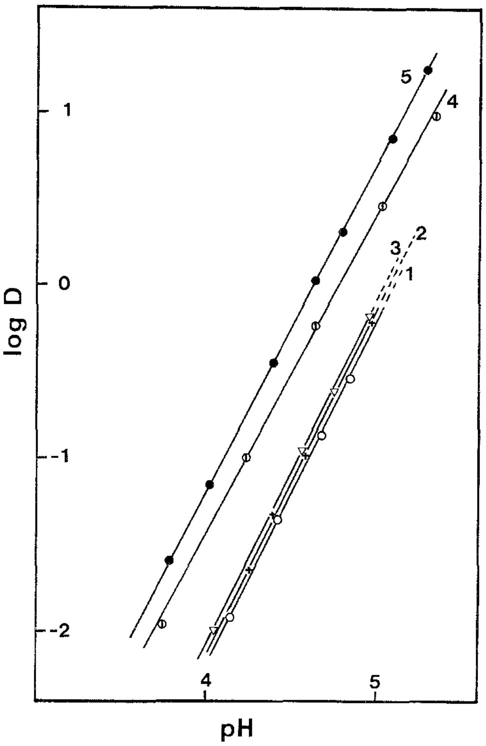

Fig. 6. Cobalt extraction from 1.0 M nitrate medium with $\overline{\mathrm{H}PMBP}$ and $Am([\overline{\mathrm{H}L}]_i = 0.02M)$. *1*: $[Am]_i = 0$, *2* to *5*: $[Am]_i = 0.01M$. Am = tribenzylamine (*2*), N,N-dimethylaniline (*3*), 4-methylaniline (*4*), 3,4-dimethylaniline (*5*)

Table 4. Cobalt extraction constants

		SO_4	NO_3	ClO_4
$\log K_{3,1}$	3,4-Dimethylaniline	− 3.80	− 3.15	− 3.25
	4-Methylaniline	− 3.90	− 3.40	− 3.30
$\log K_{2,0}$		− 7.60	− 6.80	− 7.20
$\log K_s$	3,4-Dimethylaniline	3.80	3.65	3.95
	4-Methylaniline	3.70	3.40	3.90

of $\overline{\mathrm{Co}(PMBP)_2Am_x}$ type complexes. The formation of $\overline{Am\mathrm{H}\cdot\mathrm{Co}L_3}$ ion pairs was always the cause of the synergism observed.

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References

[1] Bacher W., Keller C. (1973) J. Inorg. Nucl. Chem. **35**: 2949
[2] Sasaki Y., Freiser H. (1983) J. Inorg. Chem. **22**: 2289
[3] Dukov I. L., Genov L. Ch. (1986) Solvent Extr. Ion Exch. **4**: 999
[4] Brunette J. P., Lakkis Z., Lakkis M., Leroy M. J. F. (1985) Polyhedron **4**: 577
[5] Brunette J. P., Pléa M., Leroy M. J. F. (1984) Solvent Extr. Ion Exch. **2**: 1009
[6] Khalifa S. M., Aly H. F. (1980) J. Inorg. Nucl. Chem. **42**: 1189
[7] Kopacz S., Kalembkiewicz J. (1986) J. Chem. Anal. (Warsaw) **31**: 645
[8] Jensen B. S. (1959) Acta Chem. Scand. **13**: 1668
[9] Kalembkiewicz J., Brunette J. P., Leroy M. J. F. (1988) Solvent Extr. Ion Exch. **6**: 919

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