EXTRACTION OF IRON, COBALT, NICKEL AND COPPER WITH DIBENZYL SULFOXIDE SOLUTION IN TOLUENE

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The dependence of the distribution ratio of the metal on the concentration of hydrochloric or nitric acid was examined for Fe, Co, Ni, and Cu extraction with 0·05M solution of dibenzylsulfoxide in toluene. Iron is extracted considerably more than the other metals, and is better extracted from hydrochloric acid than from nitric acid. The separation factor $\alpha_{Fe/M}$ (for 8M-HCl) is of the order of 10^4; this is not sufficient for a separation of trace quantities of iron from Co, Ni, and Cu, but even at lower concentrations of HCl (*e.g.*, 5M) the value is high enough for extraction chromatographic separation. The composition of the iron solvate extracted from HCl or LiCl medium was determined to be $HFeCl_4.2\,B$ (B = dibenzyl sulfoxide).

From our previous study[1] it follows that the extraction of metals from aqueous solutions in the form of solvates with dibenzyl sulfoxide proceeds better from hydrochloric or nitric acid medium than from perchloric acid medium, and that toluene suits better than tetrachloromethane as the solvent.

For a utilization of a dibenzyl sulfoxide solution as the stationary phase in extraction chromatography (RPPC), the distribution of the metals to be separated has first to be studied in the static arrangement of the system constituted by the mobile and the stationary phases of the RPPC. In the present work we are concerned with the possibility of separation of iron, cobalt, nickel, and copper, which is of importance not only from the analytical, but also from the technological point of view.

Extraction of salts of the above metals with dibenzyl sulfoxide solution has not been so far subject to quantitative study. Dibenzyl sulfoxide has only been suggested for extraction-photometric determination of iron in the presence of thiocyanate[2]. Extraction of salts of the metals in question with other sulfoxides, particularly aliphatic ones, has been described[3-5] and the mechanism of this extraction has also been suggested[4,6,7]. The extraction ability of dibenzyl sulfoxide for various ions and the possibility of its application as the stationary phase in RPPC can be assessed from the results of paper chromatography in the system dibenzyl sulfoxide solution–hydrochloric[8] or nitric[9] acid solution.

The aim of the present work was to determine the quantitative data on the extraction of iron(III), cobalt, nickel, and copper with dibenzyl sulfoxide solution in toluene from nitric or hydrochloric acid medium.

EXPERIMENTAL

Chemicals and Apparatus

Dibenzyl sulfoxide solutions were prepared by dissolving in toluene a weighed amount of a preparation 99·7% purity (determined by potentiometric titration with perchloric acid in acetic anhydride[10]). The standard solution of iron was prepared by the dissolution of metallic iron (p.a., Merck) in the acid of interest, evaporation of the excess of the latter, and dissolution of the residue in 0·01M-HCl or 0·01M-HNO_3. This solution was labelled with $^{59}FeCl_3$ so that after dilution to volume its activity was ~2000 Bq/ml. The copper standard solution was prepared by dissolving a known amount of electrodeposited copper in the corresponding acid and successive treatment as with iron. The cobalt standard solution was prepared by dissolving $CoSO_4.7\,H_2O$ in 0·01M-HCl or 0·01M-HNO_3. The standard solution of nickel was obtained from a weighed amount of nickel diacetyldioximate on mineralization and dissolution in the corresponding acid. The other chemicals were *p.a.* purity.

The iron in the organic and aqueous phases was determined radiometrically. Copper, cobalt, and nickel were determined directly in the organic phase in the presence of dibenzyl sulfoxide, which is more appropriate for the determination of the metal distribution ratio — regarding the low D values — than the analysis of the aqueous phase. Copper was determined by the exchange reaction with lead diethyldithiocarbaminate. Cobalt was determined with 2-furilmonoxime in conditions reported in the paper[11]; for the neutralization of the extracted acid, however, 0·2 ml of pyridine had to be added to a 1 ml aliquot of the organic phase of the acid concentration in the aqueous phase 1—6 mol l^{-1}. For the direct determination of nickel in the organic phase (in the presence of dibenzyl sufloxide), a procedure was worked out using sodium diethyldithiocarbaminate; optimization was applied making use of the simplex method[12].

The extraction was accomplished in ground-in test tubes on a rotary apparatus (60 rpm) at 20°C and $V_{org} = V_{aq}$. The extraction equilibrium in the system metal solution in acid–dibenzyl sulfoxide solution in toluene was found to establish within 5 minutes of agitating; the shaking duration of 15 min was therefore applied to all the extraction mixtures. The absorbances of the solutions were measured on a spectrophotometer VSU 2P (Zeiss, Jena). The gamma radiation was measured by means of a scintillation probe with a well crystal and an automat NZQ 715 (Tesla, Liberec).

RESULTS AND DISCUSSION

THE EFFECT OF HYDROCHLORIC OR NITRIC ACID IN THE AQUEOUS PHASE ON THE METAL EXTRACTION

The effect of the hydrochloric acid concentration on the extraction of the metals studied was investigated in the acid concentration region 1 – 9 mol l^{-1}, with the dibenzyl sulfoxide (DBSO) concentration in toluene 0·05 mol l^{-1} and the initial concentration of iron in the aqueous phase $8 \,.\, 10^{-4}$ mol l^{-1}, the initial concentration of copper, cobalt, and nickel $1{\cdot}0 \,.\, 10^{-2}$ mol l^{-1}. The considerably lower initial concentration of iron(III) could be applied owing to the higher sensitivity of the radiometric determination of the iron concentration in the equilibrium phases. The dependence $D_M = f(c_{HCl})$ found is apparent from Table I.

The effect of nitric acid was examined in the range 1–8 mol l^{-1}; $c_{\mathrm{DBSO}} = 0{\cdot}05$ mol l^{-1}, $c_{\mathrm{Fe}} = 8 \,.\, 10^{-3}$ mol l^{-1}, and $c_{\mathrm{Cu,Co,Ni}} = 0{\cdot}01$ mol l^{-1}. The dependence $D_{\mathrm{M}} = f(c_{\mathrm{HNO_3}})$ is only given for the extraction of iron(III):

$c_{\mathrm{HNO_3}}$, mol l^{-1}:	1·0	3·0	4·0	5·0	6·0	7·0	8·0
D_{Fe}:	—	—	0·0008	0·014	0·20	0·32	0·65

The extraction of the remaining metals is negligible in the whole studied region of nitric acid concentrations.

The extraction recovery of iron and partly also of the other metals examined during the extraction from nitric acid medium can be raised by employing a salting-out agent ($NaNO_3$). For instance, during the extraction of iron at pH 6, $c_{\mathrm{Fe}} = 8 \,.\, 10^{-4}$ mol l^{-1}, and $c_{\mathrm{DBSO}} = 0{\cdot}05$ mol l^{-1}, the following variation of D_{Fe} with the concentration of the salting-out agent was found:

$c_{\mathrm{NaNO_3}}$, mol l^{-1}:	0·5	1·0	2·0	3·0	4·0	5·0
D_{Fe}:	0·09	0·19	0·30	0·35	0·39	0·39

Also on increasing the pH at a constant concentration of nitrate, the D_{Fe} value is raised (data for c_{DBSO} and c_{Fe} as above):

pH:	2·0	3·0	4·0	5·0	6·0
D_{Fe}:	0·001	0·02	0·21	0·33	0·41

The data obtained thus indicate that a better extraction of the metals in question can be achieved from hydrochloric acid than from nitric acid.

EXTRACTION SCHEME

Because of the low extraction recoveries of all the metals studied from nitric acid medium, the extraction scheme of the solvated nitrates could not be elucidated. It can be only inferred from the D_{M} values increasing with the pH in the presence of nitrates that during the extraction with an aromatic sulfoxide, too, hydroxide-salts are extracted according to the equation

$$\mathrm{M}^{z+} + (z - m)\,\mathrm{NO}_3^- + h\,\mathrm{H_2O} + n\,\overline{\mathrm{B}} \rightleftharpoons$$
$$\rightleftharpoons \overline{\mathrm{M(OH)}_m\,(\mathrm{NO}_3)_{z-m}\,(h - m)\,\mathrm{H_2O}\,.\,n\,\mathrm{B}} + m\,\mathrm{H}^+\,, \qquad (A)$$

where B stands for dibenzyl sulfoxide and the bars denote the species in the organic phase. This extraction scheme has been assumed by Nikitin and coworkers[5,13] for the extraction of Fe(III) and Cu(II), Co(II), and Ni(II) with aliphatic or petroleum sulfoxides from nitrate medium. The recovery of extraction of the hydroxido salts solvated by aliphatic or petroleum sulfoxides is, however, higher than that of the dibenzyl sulfoxide-solvated hydroxido salts.

As can be seen from Table I, nickel, cobalt and copper virtually are not extracted from hydrochloric acid medium of less than 4M-HCl, iron is little extracted (with 0·05M-DBSO in toluene). When more than 4M-HCl is employed, the distribution ratio of all the ions under study rises, still iron is extracted essentially more than nickel, cobalt, or copper (*e.g.*, from 7M-HCl, 96% Fe, 0·1% Ni, 01·% Co, and 0·09% Cu at $V_{org} = V_{aq}$),

The extraction scheme for the extraction from hydrochloric acid medium has been studied only for the distribution of iron, because the recovery of Cu, Co, and Ni is too low. For the extraction with other (mainly aliphatic) sulfoxides, iron was found to be extracted from hydrochloric acid medium as the solvate $FeCl_3.2\,B$ and as a solvate of the complex chloro-acid $HFeCl_4.2\,B$ (see[4,14–16]). We studied the effect of the concentration (activity) of hydrochloric acid and of lithium chloride, respectively, on the iron distribution ratio. The activity coefficients requisite for the calculation of the activities were taken from[17].

TABLE I

Dependence of the Metal Distribution Ratio on the Hydrochloric Acid Concentration in the Aqueous Phase

c_{HCl} mol l^{-1}	D_{Fe}	$10^4 D_{Ni}$	$10^4 D_{Co}$	$10^4 D_{Cu}$
1·0	—	—	—	—
2·0	0·0005	—	—	—
3·0	0·0032	—	—	—
4·0	0·0022	—	—	—
4·5	0·0055	—	—	—
5·0	0·178	3·12	2·04	1·35
5·5	0·83	—	—	—
6·0	2.51	6·97	7·14	4·04
6·5	7·78	—	—	—
7·0	25·1	10·2	8·50	9·44
7·5	37·5	—	—	—
8·0	52·5	19·4	11·9	10·7
9·0	74·1	27·9	18·2	13·1

The extraction of Fe(III) from hydrochloric acid medium can be assumed to proceed generally according to the equation

$$(m-3)\,\mathrm{H}^+ + \mathrm{FeCl}_i^{(3-i)+} + (m-i)\,\mathrm{Cl}^- + n\,\overline{\mathrm{B}} \rightleftharpoons \overline{\mathrm{H}_{m-3}\mathrm{FeCl}_m.n\,\mathrm{B}} \qquad (B)$$

with the equilibrium thermodynamic (extraction) constant

$$K_{\mathrm{ex}} = [\mathrm{H}_{m-3}\mathrm{FeCl}_m.n\,\mathrm{B}]_{\mathrm{org}}\, y_{\mathrm{org}} / [\mathrm{H}^+]_{\mathrm{aq}}^{(m-3)}\, [\mathrm{FeCl}_i^{(3-i)+}]_{\mathrm{aq}}\, [\mathrm{Cl}^-]_{\mathrm{aq}}^{(m-i)}\,.$$
$$.\,[\mathrm{B}]_{\mathrm{org}}^n\, y_{\mathrm{Fe}} y_{\mathrm{H}}^{(m-3)} y_{\mathrm{Cl}}^{(m-i)} y_{\mathrm{B}}^n\,. \qquad (1)$$

For the Fe(III) concentration applied (10^{-4} mol l^{-1}), y_{Fe} can be assumed to approach unity. Furthermore, the ratio of the activity coefficients of the species in the organic phase ($y_{\mathrm{org}}/y_{\mathrm{B}}^n$) can be regarded constant. For the equilibrium concentration $[\mathrm{B}]_{\mathrm{org}}$ we have

$$[\mathrm{B}]_{\mathrm{org}} = c_{\mathrm{B}} - [\mathrm{BH}^+]_{\mathrm{aq}} - [\mathrm{B.HCl}]_{\mathrm{org}} - n[\mathrm{Fe}]_{\mathrm{org}}\,, \qquad (2)$$

where c_{B} denotes the total (initial) concentration of dibenzyl sulfoxide in the organic phase. The last three terms in the relation (*2*) can be neglected with respect to c_{B}, since the transfer of dibenzyl sulfoxide from toluene into the aqueous solution of hydrochloric acid is negligible[1], the extraction of HCl into the DBSO solution in toluene is also low[16], and with the applied concentration of Fe(III) ($8 \,.\, 10^{-4}$ mol l^{-1}) and the D_{Fe} values found (Table I, Fig. 1) and $n < 4$, the amount of dibenzyl sulfoxide bonded in the solvate is also negligible as compared with the initial amount of dibenzyl sulfoxide. Thus $[\mathrm{B}]_{\mathrm{org}} \approx c_{\mathrm{B}}$.

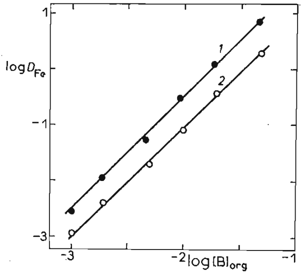

FIG. 1

Dependence of log D_{Fe} on log $[\mathrm{B}]_{\mathrm{org}}$

B = dibenzyl sulfoxide; extraction of Fe(III) from *1* 6·5M-HCl, *2* 7·0M-LiCl + + 0·01M-HCl.

Taking into account all the above assumptions we obtain

$$K'_{\mathrm{ex}} = \frac{[\mathrm{H}_{m-3}\mathrm{FeCl}_m . n\,\mathrm{B}]_{\mathrm{org}}}{[\mathrm{B}]^n_{\mathrm{org}}\,[\mathrm{FeCl}_i^{(3-1)+}]_{\mathrm{aq}}\,a_{\mathrm{H}}^{(m-3)}\,a_{\mathrm{Cl}}^{(m-i)}}\,. \qquad (3)$$

Supposing that in a hydrochloric acid concentration region a single iron containing species exists in each of the two phases, we have

$$[\mathrm{H}_{m-3}\mathrm{FeCl}_m . n\,\mathrm{B}]_{\mathrm{org}}/[\mathrm{FeCl}_i^{(3-i)+}]_{\mathrm{aq}} = D_{\mathrm{Fe}}\,, \qquad (4)$$

and if furthermore $a_{\mathrm{H}^+} = a_{\mathrm{Cl}^-} = a_{\pm\mathrm{HCl}}$, then on substituting from Eq. (*4*) in Eq. (*3*) and converting to the logarithmic form we obtain

$$\log D_{\mathrm{Fe}} = \log K'_{\mathrm{ex}} + n \log [\mathrm{B}]_{\mathrm{org}} + (2m - i - 3) \log a_{\pm\mathrm{HCl}}\,. \qquad (5)$$

The dependence of $\log D_{\mathrm{Fe}}$ on $\log [\mathrm{B}]_{\mathrm{org}}$ was examined for $a_{\pm\mathrm{HCl}} = \mathrm{const}$ ($c_{\mathrm{HCl}} = 6{\cdot}5\ \mathrm{mol\ l^{-1}}$) or $a_{\pm\mathrm{LiCl}} = \mathrm{const}$ ($c_{\mathrm{LiCl}} = 7{\cdot}0\ \mathrm{mol\ l^{-1}}$). The results obtained are shown in Fig. 1. The slope od both curves of Fig. 1 is 2, hence the extracted iron containing species is a disolvate. This was borne out by the dependence of D_{Fe} on the original iron concentration in the aqueous phase (Fig. 2): from this dependence it follows that in the iron-saturated organic phase the iron concentration is

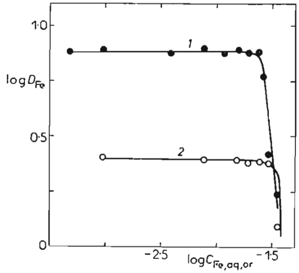

FIG. 2

Dependence of $\log D_{\mathrm{Fe}}$ on $\log c_{\mathrm{Fe,aq,or}}$

Extraction of Fe(III) from *1* 6·5M-HCl, *2* 7·0M-LiCl + 0·01M-HCl.

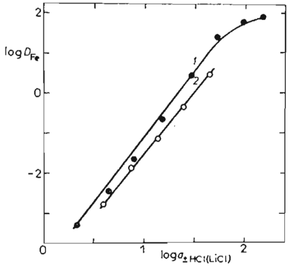

FIG. 3

Dependence of $\log D_{\mathrm{Fe}}$ on $\log a_{\pm\mathrm{HCl}}$ or $\log a_{\pm\mathrm{LiCl}}$

Extraction of Fe(III) from *1* HCl, *2* LiCl + 0·01M-HCl.

0·023 mol l^{-1}, so that for $c_B = [B]_{org} = 0·05$ mol l^{-1} the B : Fe ratio is approximately 2·1. Thus the species $H_{m-3}FeCl_m.2$ B is extracted.

The m value was found from the dependence of $\log D_{Fe}$ on $\log a_{\pm HCl}$ for $[B]_{org} =$ = const and from the dependence of $\log D_{Fe}$ on $\log a_{\pm LiCl}$ for c_{HCl} = const and $[B]_{org}$ = const. For the former dependence

$$\log D_{Fe} = \log K''_{ex} + (2m - i - 3) \log a_{\pm HCl}\,, \qquad (6)$$

where $K''_{ex} = K'_{ex}[B]^n_{org}$. In the concentration region of 2–6M-HCl the slope of this dependence is 3·2 (Fig. 3). The distribution diagram of the Fe(III) chloro complex in dependence on the chloride ion concentration indicates that in the aqueous phase the $FeCl_2^+$ species (*i.e.*, $i = 2$) predominates in the above conditions. Since $(2m - i - 3) \approx 3$, m equals 4. Thus in the mentioned region of hydrochloric acid concentrations, the species $HFeCl_4.2$ B prevails in the organic phase on the extraction with dibenzyl sulfoxide solution in toluene. At higher concentrations of hydrochloric acid (>7 mol l^{-1}) the slope of the dependence (*6*) lowers, but the composition of the extracted species is probably preserved, since in the aqueous phase the proportion of the $FeCl_3$ species increases and thus for, *e.g.*, the slope 2 and i = 3 we have again $m = 4$.

The dependence of $\log D_{Fe}$ on $\log a_{\pm LiCl}$ was examined again for a constant concentration of HCl (0·01 mol l^{-1}) and $[B]_{org}$ = const, so that Eq. (*6*) applies to this dependence, too, if $a_{\pm LiCl}$ is inserted instead of a_{HCl}. For the curve *2* in Fig. 3 the slope of 3·1 was obtained. In the lithium chloride concentration region used (3–7 mol l^{-1}) the ion $FeCl_2^+$ predominates in the aqueous phase, so $i = 2$ and $m = 4$. Thus the species $HFeCl_4.2$ B is extracted also in the presence of LiCl (and HCl).

This conclusion concerning the composition of the solvate in which iron is transferred to the organic phase during the extraction with dibenzyl sulfoxide solution is in accordance with the results of the paper[14], but contrasts with the observations and conclusions of McDowell and Harmon[4], who obtained the slope of 4 for the extraction from solution in hydrochloric acid or from lithium chloride in the presence of hydrochloric acid (1M) and the slope of 3 for the extraction from solution in lithium chloride (with $c_{HCl} = 0·1$ mol l^{-1}). These differences in the slope may be due to the different values of the activity coefficients employed; the true cause of the difference, however, lies probably in the fact that McDowell and Harmon assumed during the interpretation of the slopes found the occurrence of the Fe^{3+} ion in the aqueous phase, which at $c_{HCl} > 1$ mol l^{-1} is not justified, as follows from the distribution diagram of the iron chloro complexes.

It can be concluded that for the separation of the ions under study by extraction with dibenzyl sulfoxide solution, hydrochloric acid medium suits better than nitric acid medium, and that iron can be separated from cobalt, nickel, and copper by extraction with 0·05M solution of dibenzyl sulfoxide in toluene from aqueous solution of more than 8M-HCl, with the value of the separation factor for the separation of Fe from Co, Ni, Cu $\alpha \approx 10^4$. This acid concentration, however, is not convenient from the practical point of view, and moreover, the sulfoxide decomposes at this concentration[1,17]. At lower hydrochloric acid concentration (*e.g.*, 5 mol l^{-1}) the separation factor for the separation of Fe from Co, Ni, Cu is still high enough (~ 50) for their sharp chromatographic separation during their extraction chromatographic treatment.

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