Brief Communications

Extraction of zinc(II) from aqueous alkali solutions by *ortho*-derivatives of phenols

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The ability of a series of *ortho*-functionalized phenol derivatives and of *N*-(2-hydroximinocyclohexyl)palmitohydroxamic acid to extract Zn^{2+} ions from aqueous alkali solutions (0.2—4.0 mol L^{-1}) in the presence of trialkylmethylammonium methylsulfate has been investigated. The most active extractants are chelating phenols containing N- and S-coordinating groups and chelates of the pyrocatechol series.

Key words: *ortho*-derivatives of phenol; zinc, extraction.

Previously we reported on the extraction of gallium(III) and aluminum(III) with pyrocatechol derivatives from aqueous alkali solutions.[1] We found that bulky substituents located in the *ortho*-position with respect to the hydroxyl groups decrease the extraction ability of pyrocatechols and have practically no effect on the selectivity of the extraction of metals. When derivatives of *o*-amino- or *o*-thiophenols, analogs of pyrocatechols, were used in the presence or in the absence of quaternary ammonium salts, no extraction of metals was observed. This fact made it possible to suggest that the presence of two neighboring hydroxyl groups in the molecule of an extracting agent is the crucial factor ensuring the extraction of trivalent metals from concentrated alkali solutions.

One could expect that in the case of bivalent metal ions, other rules will be followed. To verify this assumption, we have tested the ability of phenol derivatives **1**—**11** (see below) containing functional groups or bulky substituents in the *ortho*-position as well as of *N*-(2-hydroximinocyclohexyl)palmitohydroxamic acid (**12**) to extract zinc.

Experimental

Procedures for the synthesis of compounds **4**,[1] **2**,[2] **11**,[3] **10**,[4] **1** and **7**,[5] and **8** and **9**[6] were reported previously, and compounds **3**, **5**, **6**, and **12** were received from the Gidrotsvetmet Institute (Novosibirsk, Russia) and identified based on their ^1H NMR spectra.

Zinc was extracted from aqueous solutions of $ZnSO_4$ ($5 \cdot 10^{-3}$ mol L^{-1}) containing 0.2—4.0 mol L^{-1} of NaOH. The extractants were used as toluene solutions ($5 \cdot 10^{-3}$ mol L^{-1}) containing 10 % (v/v) of trialkylmethylammonium methylsulfate. The ammonium salt was added in order to suppress micelle formation.

An alkaline aqueous solution of $ZnSO_4$ was shaken with a toluene solution of an extractant (10 mL each) at 20 °C for 1 h. The aqueous phase was separated, and 1 mL of the solution was withdrawn and neutralized to pH 7. Distilled water was added to bring the volume of the sample to 10 mL and the remaining metal was analyzed by the atomic-absorption method on a Saturn-2 instrument. The aqueous solution after reextraction of the organic phase with 2 *M* HCl was analyzed in a similar way (with an accuracy of ±5 %).

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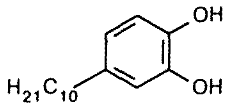
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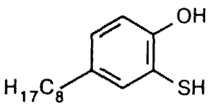
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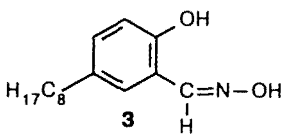
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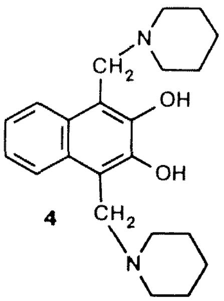
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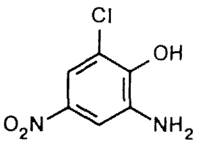
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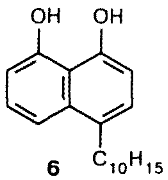
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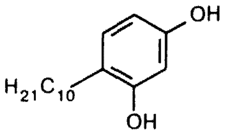
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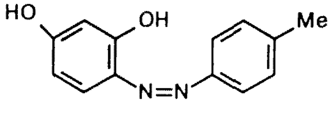
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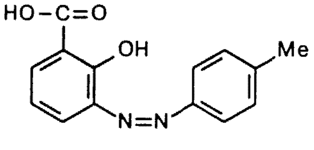
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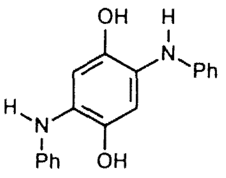
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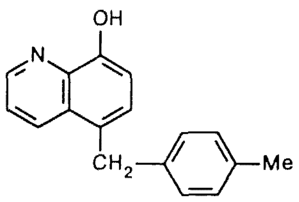
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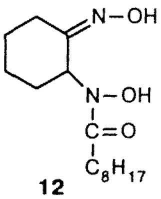
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Results and Discussion

4-Decylpyrocatechol **1** (Table 1) quantitatively extracts zinc over the whole range of the alkali concentrations studied, and extractants **2** and **11** are only slightly less efficient. Thus, unlike trivalent metals, bivalent metals such as zinc can be extracted from alkali solutions by *ortho*-derivatives of phenols containing various functional groups (—OH, —SH, —N=).

The presence of bulky substituens in proximity to the hydroxyl groups as, for example, in the molecule of extractant **4**, as well as the transfer of one of the hydroxyl groups from the *ortho*-position to the *meta*-position of the benzene ring (compound **7**) or to the *peri*-position of the naphthalene system (compound **6**) have a substantial effect on the efficiency of the extraction of zinc with this extractant (see Table 1).

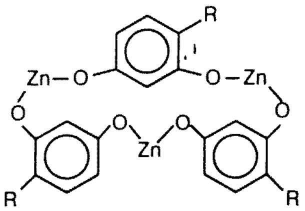
The decrease in the extraction ability in the case of compounds **4** and **6** may be due to steric effects and to the change in the geometry of the coordination ring in

Table 1. Extraction of zinc(II) from 0.2—4.0 *M* aqueous solutions of NaOH by *ortho*-derivatives of phenols in the presence of trialkylmethylammonium methylsulfate

Extractant	Degree of extraction of Zn (%) from NaOH solutions*					
	0.2 *M*	0.5 *M*	1 *M*	2 *M*	3 *M*	4 *M*
1		100	99	99	99	
2		98	98	97	89	
11		98	97	94	83	
12		99	90	68		
5	69		18	17	17	12
3	59		18	18	17	16
4		45	35	18	17	
6	46					
7	24		6	6	5	4
8			22	20		20
9	18		19	17		16
10		11	9	7	5	

* The contents of metal in aqueous phases were determined after the extraction and reextraction.

the complexes ZnQ or $Na_2[ZnQ_2]$ (where Q is the dianion of the extractant). The formation of complexes of this type with compound **7** is extremely hampered; in this case, a macrocyclic extraction complex of the composition Zn_3Q_3 or a complex with an even more complicated structure (see below) is most likely formed.



As noted above, the hydroxyquinoline derivative **11** is the most efficient in the series of nitrogen-containing chelating extractants. 4-Alkyl-2-aminophenols seem to be attractive model compounds of this type; however, the susceptibility of solutions of *o*-aminophenols to oxidation in air, especially in the presence of acids, hampers the use of these compounds as extractants. Other nitrogen-containing extractants studied by us proved to be inefficient, despite the presence of electron-donating and electron-withdrawing substituents.

In our opinion, the fact that zinc is extracted by acid **12**, whose structure is similar to that of oxime **3**, is of interest. These compounds differ both in the acidity of their hydroxyl groups and in the stereochemistry. Whereas in the case of oxime **3** both *E*- and *Z*-isomers are known, acid **12** exists mostly as the *E*-isomer (judging by its chemical properties). Note that at a concentration of NaOH of 0.5 mol L^{-1}, compound **12** is as good for extraction of zinc as compound **11**, but its extracting ability dramatically decreases as the concentration of the alkali increases.

Thus, it was shown that zinc can be efficiently extracted from alkaline solutions (0.2—4.0 mol L^{-1} of NaOH) with extractants containing various chelating groups (—OH, —SH, —N=). The efficiency of the extracting agents studied decreases in the following order: **1** > **2** > **11** > **12**.

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