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Extraction of Zinc and Copper with Acetylenic Quaternary Ammonium Salts

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Abstract—Extraction of zinc(II) and copper(II) from HCl solutions with solutions of mono- and dialkynyl-substituted quaternary ammonium halides in chloroform and toluene is more efficient than the extraction with saturated quaternary ammonium salts and occurs by different mechanism. The dependences of the metal distribution factors on the HCl concentration have two maxima whose positions (absolute and relative) and relative intensities depend on the particular extractant, metal, and diluent.

There are only a few papers on recovery and purification of metal ions with unsaturated compounds; nevertheless, their results allowed development of very efficient methods for extractive concentration of osmium with α-olefins [1] and extractive chromatography of actinides with allyltrialkylammonium nitrate [2]. The effect exerted on the extraction by a triple bond capable of complexation with soft Lewis acids was not examined previously.

In [3] we described the extraction of Zn(II) from solutions of alkali metal halides in HCl with hept-2-ynyltrioctylammonium bromide and concluded that further studies in this direction would be promising.

Here we continue a study of the effect exerted by the structure of quaternary ammonium salts containing a triple bond in the β-position relative to the nitrogen atom, and also by the diluent on extraction of copper and zinc from HCl solutions. We chose the following ammonium salts:

$$[R_3NCH_2C{\equiv}CR']^+X^- \quad [(C_8H_{17})_2N(CH_2C{\equiv}CC_4H_9)_2]^+Br^-$$

Ia–**Ie** **II**

$$[(C_8H_{17})_3NCH_3]^+I^-$$

III

R = C_8H_{17}, R' = H, X = Br (**a**); R = C_8H_{17}, R' = C_4H_9, X = Br (**b**); R = C_8H_{17}, R' = C_4H_9, X = I (**c**); R = $C_{10}H_{21}$, R' = C_4H_9, X = Br (**d**); R = $C_{10}H_{21}$, R' = C_6H_{13}, X = Br (**e**).

The salts were prepared by quaternization of dioctylamine, trioctylamine, and tridecylamine with appropriate propargyl halides under very mild conditions following the previously developed procedure [4]. The reactions at room temperature are complete within 1–2 h in acetonitrile and 1–2 days in pentane; the yields of the quaternary ammonium salts are close to quantitative.

A principal difference of the examined extractants **Ia**–**Ie** and **II** from those described in the literature [5, 6] is the better steric accessibility of the nitrogen atom due to the linear structure of the CH_2–C≡C–CH_2 fragment. This is extremely important for the donor–acceptor bonding $R_4NX{:}\rightarrow MeX_n$ [7] between the anion X of the quaternary ammonium salt and the metal cation Me in the extractable complex.

First we studied how the distribution factors of Zn(II) and Cu(II) in extraction with quaternary ammonium salts (QASs) **Ia**, **Ib**, and **III** depend on the HCl concentration in the initial aqueous solution, varied from 0.75 to 9.0 M (Figs. 1, 2). These dependences appeared to be complex. In the extraction of the metals with solutions of **Ia** and **Ib** in chloroform and toluene, two local maxima are observed at HCl concentrations of 2–4 and 5–7 M. On the contrary, in extraction of Zn(II) with compound **III** containing no π bonds, the corresponding dependence is dome-shaped and has only one broad maximum at an HCl concentration of 3–5 M, in full agreement with published data on the extraction of Zn, Cu, Cd, and many other metals with ammonium salts containing saturated hydrocarbon substituents [8].

The composition of the Zn and Cu complexes extracted with **Ib** was determined by the equilibrium shift method [9]. The composition of the aqueous phase was kept constant (C^0_{HCl} 1, C^0_{Me} 0.02 M at

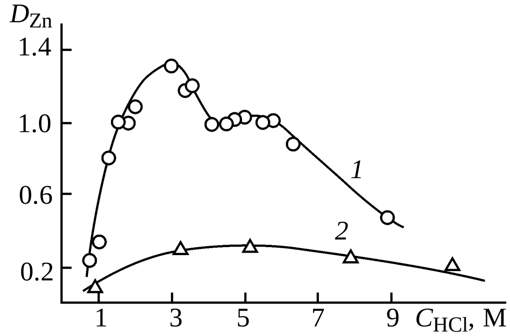


Fig. 1. Distribution factor of Zn(II) as a function of HCl concentration in the aqueous phase in extraction with (*1*) **Ib** and (*2*) **III**; diluent chloroform. C_{QAS} 0.05 and C_{Zn} 0.02 M; 25°C.

25°C), and the concentration of the quaternary ammonium salt in the organic phase was varied from 0.025 to 0.25 M. The dependences of the copper and zinc distribution factors on the concentrations of **Ib** in toluene and chloroform, respectively, are monotonically ascending (Fig. 3), and the corresponding log–log plots are straight lines with the slope close to unity (except the case of extraction of Zn with 0.075–0.25 M solutions of **Ib** in chloroform; in this range, the slope is close to 2, Fig. 3).

These data indicate that zinc and copper are extracted from 1 M HCl in the form of 1 : 1 metal–QAS complexes. With zinc, at a 3–4-fold and greater excess of the extractant, 1 : 2 complexes are formed. It should be emphasized that, according to published data [5–7], 1 : 1 adducts are not formed in extraction of copper and zinc with saturated ammonium salts.

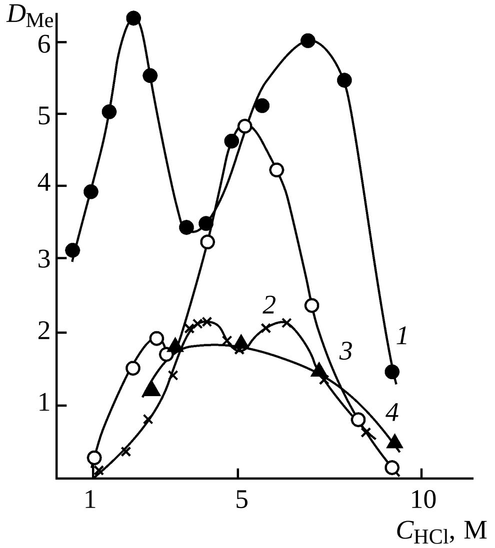


Fig. 2. Distribution factors of metals as functions of HCl concentration in the aqueous phase. Metal: (*1*) Zn and (*2–4*) Cu; extractant: (*1, 2*) **Ia**, (*3*) **Ib**, and (*4*) **Id**; diluent toluene; C_{QAS} 0.05 and C_{Me} 0.02 M; 25°C.

Thus, two maxima appearing in the metal extraction curves may be caused by changes in the composition of the extractable species, associated to certain extent with the presence of a triple bond in the extractant molecule.

On the one hand, it could be expected that, at HCl concentration higher than 5 M, the addition of HCl across the π bond of the quaternary ammonium salt would become more probable. However, in this case, the metal distribution factors should decrease owing

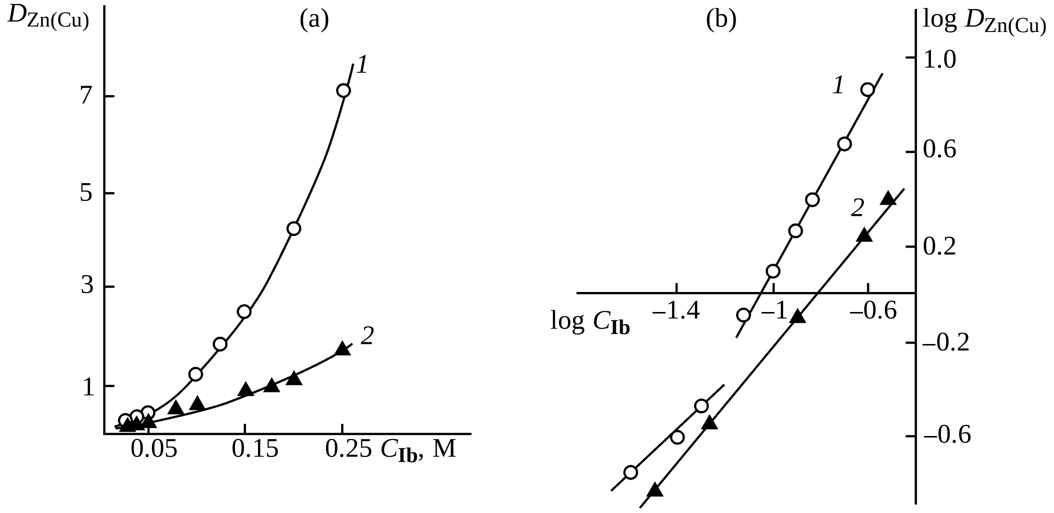


Fig. 3. Distribution factors of (*1*) Zn(II) and (*2*) Cu(II) as functions of the concentration of hept-2-ynyltrioctylammonium bromide **Ib** in (*1*) chloroform and (*2*) toluene at 25°C: (a) linear and (b) logarithmic coordinates. C_{HCl} 1 and C_{Me} 0.02 M.

Table 1. Distribution factors *D* of Zn(II) and Cu(II) in extraction from aqueous HCl with 0.05 M solutions of quaternary ammonium salts in chloroform and toluene at 25°C

Extractant	[HCl], M	Solvent	D_{Zn}	D_{Cu}	Σσ* [4, 12, 13]
Ia	3.5	Chloroform	0.69	–	+0.37
	3.5	Toluene	3.56	2.06	–
	5.0	"	4.63	1.82	–
Ib	3.5	Chloroform	1.19		+0.09
	3.5	Toluene	[a]	2.5	
	5.0	"		4.85	
Ic	3.5	Chloroform	0.57	–	+0.09
Id	3.5	Toluene	[a]	1.85	+0.09
	5.0	"		1.90	
Ie	3.5	Chloroform	1.62		+0.09
	3.5	Toluene	[a]		
	5.0	"	–	1.62	–
II	3.5	Chloroform	0.83		+0.7
	3.5	Toluene	10.47		
	5.0	"		2.05	
III	3.5	Chloroform	0.29		–0.39
1-Octyne	3.5	"	[b]		
	3.5, 5.0	Toluene	[b]	[b]	

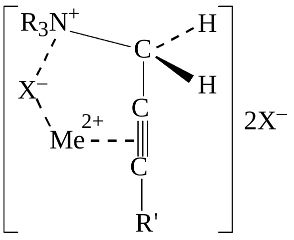
[a] The Me^{2+} content in the aqueous phase after the extraction was below the detection limit. [b] The Me^{2+} content in the organic phase after the extraction was below the detection limit.

to an increase in the substituent volume upon transition from the *sp* to sp^2 or sp^3 state, and also to the acceptor power of the chlorine atom appearing in the substituent (negative inductive effect), rather than pass through a second maximum.

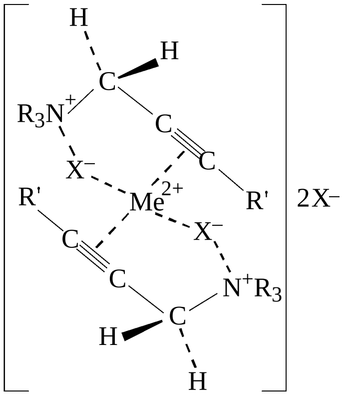
Furthermore, it is indicated in the literature [5, 10] that the extraction of metals with saturated quaternary ammonium salts decreases at high HCl concentrations because of the growing competition of the extraction of the acid itself.

On the other hand, the triple bond capable of formation of donor–acceptor complexes with cations of soft (concept of hard and soft acids and bases [11]) acids could enhance the extraction of Zn and Cu. However, as shown by our experiments, 1-octyne forms stable complexes with Zn and Cu ions neither in aqueous nor in organic phase. In the organic phase, we detected no metal ions (complexometric titration, Table 1), and in the aqueous phase phase, after twofold washing with the diluent, 1-octyne was not detected by the reaction with an ammonia solution of CuCl, which is a very sensitive qualitative reaction for a terminal triple bond [14].

Thus, the second maximum (Figs. 1, 2) is apparently due to the unique structure of the quaternary ammonium salt containing a triple bond in the β-position relative to the nitrogen atom. The extractants that we studied are presumably capable to form under the experimental conditions complexes of types **IV** and/or **V**, rather than common double salts $[R_4N^+X^-Me^{2+}X^- \cdot N^+R_4](X^-)_2$ (**VI**) formed by addition and/or anion exchange [5, 15] involving only the ammonium nitrogen atom in saturated quaternary ammonium salts.



IV



V

Adducts **IV** and **V**, similarly to other chelate compounds (e.g., those formed by Cu^{2+} with glycols or α-amino acids [16]), can show increased thermodynamic stability due to intramolecular interaction of the closely located fragments of the quaternary ammonium salts with the metal ion. Apparently, the stability of these adducts should largely depend on the HCl concentration, and the presence of two maxima suggests the realization of at least two major mechanisms of extraction of zinc and copper from acid solutions with acetylenic salts.

As expected, the metal distribution factors in extraction with **Ia**–**Ie**, as in extraction with common quaternary ammonium salts, strongly depend on the diluent. Replacement of chloroform by toluene sharply increases the extractability of Zn(II) and Cu(II), especially in the range of the maximum at high HCl concentrations (Figs. 1, 2). In particular, in toluene salt **Ib** virtually quantitatively extracts zinc from 3.5 M HCl and extracts copper from 5.0 M HCl with D_{Cu} 4.85, whereas in chloroform salt **Ib** does not extract copper at all, and the maximal distribution factor of zinc is as low as 1.3 (Table 1).

This relationship can be accounted for as follows. First, $CHCl_3$, being somewhat more electrophilic than toluene, better solvates the halide anion, reducing its nucleophilicity toward the metal ion and thus decreasing the extractive power of the quaternary ammonium salt. Second, toluene, whose polarizability is much higher than that of chloroform, should better dissolve molecular complexes of acetylenic quaternary ammonium bases with soft (readily polarizable [11]) Lewis acids Zn^{2+} and Cu^{2+}.

It is interesting that the positions (absolute and relative) and relative heights of the maxima in the plots of the distribution factors vs. HCl concentration depend on the structure of the compound and on the kind of the metal and diluent (Figs. 1, 2). In particular, salt **Ia** in toluene approximately equally extracts the metal from solutions with low and high HCl concentrations (in the points of maxima). Salt **Ib** in toluene extracts copper much better at high acid concentrations, and in chloroform it extracts zinc much better at low acid concentrations, with the second maxima being ill-defined. With **Id**, the curve becomes dome-shaped, similarly to the curves observed with saturated quaternary ammonium salts.

The concept considering quaternary ammonium salts as nucleophilic agents forming donor–acceptor bonds with the metal cation through the anion in extraction [5] allows the strength of the extractable complexes to be correlated with the inductive and steric effects of substituents at the N atom.

We showed that the acetylenic salts extract Zn and Cu better than does salt **III**, which is due, in particular, to the steric factors. It follows from construction of molecular models [17] that the effective volume of the $RC{\equiv}CH_2$ group is somewhat smaller than that of the CH_3 group (if R is not too bulky). As alkynyl groups, exhibiting negative inductive effect, should decrease the nucleophilicity of the anion, the abnormally high extractability of the acetylenic quaternary ammonium salts also suggests that the triple bond directly participates in the formation of molecular complexes of types **IV** and/or **V**. At the same time, the contribution of species **VI** (with no π,ν interaction of the triple bond with the metal ion) to extraction with acetylenic quaternary ammonium salts is hardly significant.

Our further experiments were aimed to reveal how the degree of extraction depends on the extractant structure.

In chloroform (Fig. 1, Table 1), the zinc distribution factors (C_{HCl} 3.5 M) grow with an increase in the length of substituents at the nitrogen atom and triple bond, considerably exceeding the distribution factors observed with the saturated analog **III**:

Ie > **Ib** > **II** > **Ia** > **III**.

This trend is consistent with a decrease in the solubility of the extractable metal complexes in the aqueous phase in going to more hydrophobic extractants, and also with a decrease in the acceptor power of alkynyl substituents (σ^* +0.76 for $HC{\equiv}CH_2$ [12, 18] and +0.48 for $C_4H_9C{\equiv}CCH_2$ and $C_6H_{13}C{\equiv}CCH_2$ [4]).

In toluene, the most promising extractant is **Ib** (Fig. 2, Table 1). For copper, a further increase in the length of substituents at the nitrogen atom (**Id**) or triple bond (**Ie**) leads to a decrease in the distribution factor (C_{HCl} 5.0 M):

Ib > **II** > **Id** > **Ia** > **Ie**.

However, this order may depend on the HCl concentration. For example, at C_{HCl} 3.5 M, salt **Ia** extracts Cu better than does **Id**. With zinc, no such fine distinctions were found. In toluene, all the examined acetylenic quaternary ammonium salts with the molecular weight equal to or exceeding that of **Ib** virtually quantitatively extract Zn from HCl solutions, i.e., this diluent levels the extractive properties of these salts.

One of possible factors responsible for such a dependence of the distribution factors on the length of hydrocarbon substituents in quaternary ammonium salts is association; its role increases with a decrease in the diluent polarity [7, 19]: nitrobenzene < chloroform < benzene < toluene < xylene < CCl_4 < alkanes.

In more polar [20] chloroform (μ 1.87 D, ε 4.70), the association of quaternary ammonium salts is somewhat weaker than in toluene (μ 0.36 D, ε 2.38), and, despite the hindering effect exerted by electrophilic $CHCl_3$, which tends to specifically interact with halide anions, on the formation of molecular complexes with metal cations, the distribution factors grow with an increase in the length of substituents at the N atom, owing to a decrease in the solubility of the adducts in water.

In less polar toluene, an increase in the association of quaternary ammonium salts with an increase in their hydrophobicity results in a decrease in the active active concentration of the free extractant and hence in the worse extraction of copper. This effect becomes more pronounced with a decrease in the HCl concentration.

This trend is, apparently, responsible for the fact that salt **Ia** in toluene, despite much stronger acceptor properties of the alkynyl substituent, extracts copper from 5 M HCl better than does **Ie**, and from 3.5 M HCl, also better than does **Id**. As for zinc, all the quaternary ammonium salts with long-chain alkynyl groups in toluene are moch more efficient extractants

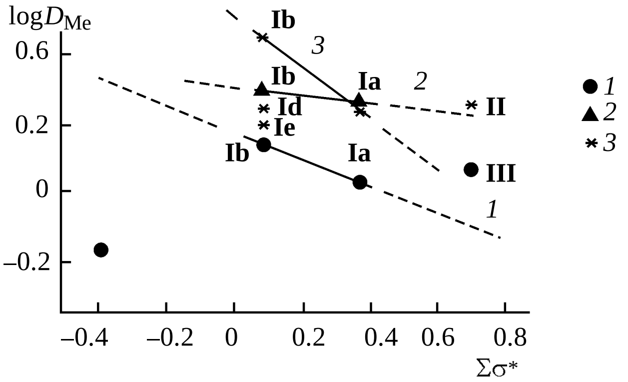


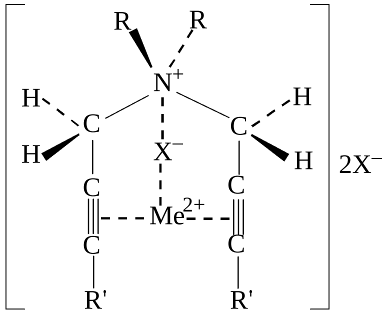
Fig. 4. Distribution factors of Zn(II) and Cu(II) in extraction from aqueous HCl with quaternary ammonium salts at 25°C, as functions of the Taft inductive constants (Σσ*). C_{QAS} 0.05 and C_{Me} 0.02 M. (*1*) Zn(II), chloroform, C_{HCl} 3.5 M; (*2*) Cu(II), toluene, C_{HCl} 3.5 M; and (*3*) Cu(II), toluene, C_{HCl} 5.0 M. The numbering of the quaternary ammonium salts is the same as in the text and in Table 1. Dashed lines are drawn through the points for the most structurally similar compounds **Ia** and **Ib**, with the aim to emphasize the effect of growing hydrophobicity of quaternary ammonium salts (Σσ* and E_N remain constant) at varied diluent polarity.

than **Ia** (in chloroform, the trend is similar) and virtually completely extract zinc from the aqueous phase.

Presumably, complexes of quaternary ammonium salts with zinc ions are associated in the organic phase more strongly than complexes with copper ions (especially in toluene). Since association of extractable complexes enhances the transfer of metals to the organic phase, the distribution factor of zinc is higher. A similar assumption was made to account for, e.g., higher distribution factors of Pt, compared to Pd, in extraction with solutions of quaternary ammonium salts in toluene [19].

Figure 4 shows the correlation of the distribution factors of copper and zinc with the Taft inductive constants (Σσ*) of substituents at the ammonium nitrogen atom. The fact that the extraction is not described by a common straight line in the $\log D_{Me}$–Σσ* coordinates suggests the significant role of some factors other than electronic effects. Despite a limited data set (dashed lines), we can speak of significant deviations of the points for **III** (downward) and **II** (upward) from straight lines *1* and *3*, suggesting different mechanisms of formation of donor–acceptor complexes of metal halides with quaternary ammonium salts in the series of saturated, monoacetylenic, and diacetylenic derivatives. It is clearly seen from Fig. 4 that, whereas in chloroform $\log D$ increases with increasing length of substituents at the N atom (increasing hydrophobicity of the quaternary ammonium salt) compared to **Ib**, in less polar toluene $\log D$, on the contrary, decreases.

The abnormally high (from the viewpoint of electronic factors) extractive power of **II** (Fig. 4, Table 1) should be particularly noted. Despite the presence of two electron-withdrawing substituents, it extracts zinc more efficiently than does **Ia**, and in extraction of copper it is inferior only to **Ib**. This is apparently caused also by the fact that in **II**, compared to the other salts studied, the quaternary nitrogen atom is the most accessible sterically. Furthermore, the second triple bond creates prerequisites for formation of still more stable (compared to **IV** and **V**) chelate complexes, e.g., of type **VII**:



VII

Thus, the efficiency of extraction with acetylenic quaternary ammonium salts largely depends on their structure.

The simultaneous influence of the inductive and steric effects of substituents in amines on their nucleophilic reactivity can be quantitatively estimated with the extended Taft equation [4, 17]

$$\log k = \log k_0 + \rho^*\Sigma\sigma^* + \delta E_N.$$

As the constant E_N characterizing the steric effects in an amine $R^1R^2R^3N$ is used the Taft constant E_S for the isosteric hydrocarbon substituent $R^1R^2R^3C$. This equation can be applied to describing extraction processes [5] involving salts of primary, secondary, and tertiary amines as nucleophilic agents.

As the steric effect is telescopic [13] (introduction of the next radical exerts a greater steric effect than introduction of the previous radical), its role in processes involving quaternary ammonium salts is particularly significant. Unfortunately, steric constants for quaternary ammonium salts are lacking. Therefore, to compare the steric accessibility of the nitrogen atom in quaternary ammonium salts, we took the E_N values for tertiary amines with linear substituents (Table 2). Some of these values were calculated by us previously from data on the quaternization kinetics.

Table 2 shows that, starting from tributylamine **VIIIc**, an increase in the length of the alkyl chain does not longer affect the steric accessibility of the nitrogen atom in the saturated tertiary amine. At the same time, comparison of E_N for **VIIIa**, **IXa**, and **IXb** shows that the steric constants of the CH_3 and $CH_2C{\equiv}CR$ groups are virtually equal, taking into account that the error in their determination is 0.1–0.2 unit. However, a shift of the triple bond away from the nitrogen atom by even one or two carbon atoms (compounds **IXa**, **IXb**, **Xa**, **Xb**) results in that the steric effect of γ- and δ-acetylenic amines becomes the same as that of the corresponding saturated analogs (**VIIIb**–**VIIId**).

These data confirm our assumption that the steric accessibility of the nitrogen atom in quaternary ammonium salts **Ia**–**Ie** and **III** should be similar. Therefore, the higher extractive power of the salts with acetylenic substituents can be rationalized only by assuming principally different complexation mechanisms (e.g., those involving chelation). Also, from this standpoiont, a significant dependence of the distribution factors of zinc and copper in extraction with **Ib**, **Id**, and **Ie** on the diluent can be rationalized only by different effects of solvation of quaternary ammonium salts and molecular complexes formed by them; such an attempt was made in this paper.

Thus, acetylenic quaternary ammonium salts that we studied (especially **Ib**, **Id**, and **Ie**) under definite conditions extract zinc from aqueous HCl much more efficiently than do tributyl phosphate [21] (traditionally used extractant) and ammonium salts with saturated substituents at the nitrogen atom [5]. The acetylenic quaternary ammonium salts also show promise for extraction of copper from hydrochloric acid solutions, taking into account the fact that the results of this study were obtained at low (0.05 M) concentrations of the extractants in the organic phase.

The relatively high extractive power of the salts studied, and also the simplicity of procedures for the recovery of Zn(II) and Cu(II) with these salts allow these procedures to be recommended for analytical practice.

Of considerable interest is also the fact that acetylenic quaternary ammonium salts efficiently extract rare-earth elements, according to our preliminary data. Doubtless advantages of these extractants are very fast (within several minutes) attainment of the extraction equilibrium and phase separation, and also considerably lower concentrations of the extractant in the organic phase, as compared to the published systems.

Our further studies are aimed to elucidate the composition and structure of molecular complexes of copper and zinc ions with acetylenic quaternary ammonium salts, as influenced by the extractant structure, kind of diluent, and concentration of HCl or metal halide (salting-out agent) in the aqueous phase, and to gain insight into the extraction mechanism.

Table 2. Steric constants E_N of tertiary β-, γ-, and δ-acetylenic and saturated amines [4]

Comp. no.	Amine	$-E_N$
VIIIa	$(CH_3)_2NCH_3$	1.54[a]
VIIIb	$(CH_3)_2NC_5H_{11}$	2.2
VIIIc	$(C_4H_9)_2NC_4H_9$	4.5[a]
VIIId	$(C_4H_9)_2NC_7H_{15}$	4.4
VIIIe	$(C_8H_{17})_2NC_8H_{17}$	4.5
IXa	$(CH_3)_2N(CH_2)_3C{\equiv}CC_4H_9$	2.6
IXb	$(C_4H_9)_2N(CH_2)_3C{\equiv}CC_4H_9$	4.5
Xa	$(CH_3)_2N(CH_2)_2C{\equiv}CC_4H_9$	2.6
Xb	$(C_4H_9)_2N(CH_2)_2C{\equiv}CC_3H_7$	4.5
XIa	$(CH_3)_2NCH_2C{\equiv}CCH{=}CH_2$	1.8[a]
XIb	$(CH_3)_2NCH_2C{\equiv}CC_2H_5$	1.8
XIc	$(C_4H_9)_2NCH_2C{\equiv}CC_4H_9$	3.7
XId	$(C_8H_{17})_2NCH_2C{\equiv}CC_5H_{11}$	3.7

[a] Data from [17].

EXPERIMENTAL

The procedure for preparing quaternary ammonium salts and tertiary amines containing triple bonds in the β-position relative to the nitrogen atom was described in [4, 22].

Extraction of zinc with solutions of quaternary ammonium salts and 1-octyne in appropriate organic diluent was performed at 25°C, with equal volumes of the organic and aqueous phases. The initial concentration of Zn(II) and Cu(II) was kept constant and equal to 0.02 M. The extraction equilibrium with quaternary ammonium salts is attained within 1 min. The equilibrium concentrations of Zn(II) and Cu(II) were found by complexometric titration with Xylenol Orange indicator at pH 5. The acid concentration was determined by titration with KOH (Methyl Orange indicator) [23].

The concentration dependences and diluent effects were studied at 25°C.

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