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Extraction of Zinc with Hept-2-ynyltrioctylammonium Bromide

V. P. Andreev, S. G. Tunina, V. V. Usov, and L. A. Remizova

Karelian State Pedagogical University, Petrozavodsk, Karelia, Russia
Petrozavodsk State University, Petrozavodsk, Karelia, Russia
St. Petersburg State University, St. Petersburg, Russia

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Abstract — Extraction of zinc(II) with hept-2-ynyltrioctylammonium bromide from solutions of sodium and potassium halides and hydrochloric acid was studied. Extraction of zinc in the form of $(R_4X)^+ZnX_3^-$ and $(R_4X)_2^+ZnX_4^{2-}$ complexes (where X is halide anion) follows from the log–log plots. Hept-2-ynyltrioctylammonium bromide is a promising extracting agent for Zn(II).

Quaternary ammonium bases are widely used in industry for extraction of a number of rare and radioactive elements [1,2]. However, salts with unsaturated substituents (especially with those containing triple bonds) are poorly studied. At the same time, substitution of alkyl groups with hydrocarbon groups containing double bonds increases the solubility of quaternary ammonium bases [3] and their complexes [4] in low-polar solvents and hence can increase the distribution coefficient of the metal extracted from aqueous solution. In addition, in accordance with the concept of soft and hard Lewis acids and bases [5], metal cations, especially those exhibiting properties of soft acids, and their compounds can form complexes of various strength with π bonds [6, 7]. Indeed, efficient procedures were developed for extraction concentration of osmium with α-olefins [8] and extraction-chromatographic separation of actinides with allyltrialkylammonium nitrate [9].

In this work we studied extraction of zinc with hept-2-ynyltrioctylammonium bromide $[(C_8H_{17})_3 \cdot NCH_2C{\equiv}CC_4H_9]^+Br^-$ (**I**) containing the triple bond at the β position with respect to the nitrogen atom. It should be noted that structurally related compounds can be readily prepared by quaternization of amines with appropriate alkynyl bromides [10].

The nitrogen atom in **I** is less sterically hindered than in the extracting agents studied previously. This is due to the linear structure of the $CH_2C{\equiv}CCH_2$ fragment caused by the *sp* hybridization of the carbon atoms forming the triple bond. The accessibility of the nitrogen atoms is the critical factor, since the metal cation (Me) is extracted in the form of complexes $R_4NA{\rightarrow}MeA_n$ in which the nitrogen atom of the quaternary ammonium base (A) is coordinated to the metal [11].

We studied extraction of Zn(II) with salt **I** form solutions containing halide anions exhibiting the strongest salting-out properties with respect to Zn [1, 6]. First we studied zinc extraction from hydrochloric acid solutions, since this acid is most frequently used to recover zinc from ores. Special experiments showed that zinc is poorly extracted from sulfuric acid solutions and is not extracted from nitric acid solutions (see table). As in the case of heteroaromatic *N*-oxides [12], we used chloroform as a diluent.

The extraction stoichiometry was determined by the equilibrium shift method [13]. The concentration of the extracting agent was varied from 0.025 to 0.25 M at the constant composition of the aqueous phase (C_{HCl}^{in} 1, C_{Zn}^{in} 0.02 M at 298 K). The zinc distribution coefficient monotonically increases with increasing concentration of salt **I** in the examined concentration range of the extracting agent (Fig. 1a). In the log–log plot there are two linear sections with the slopes close to 1 (at the concentration of **II** from 0.025 to 0.05 M) and 2 (at the concentration of **I** from 0.05 to 0.25 M). This suggests formation of zinc complexes with one and two formula units of the quaternary ammonium salt. The composition of zinc complexes formed by addition and/or anion substitution in the extraction system [1, 14, 15] can be described by the formulas

$$[R_4N]^+[ZnBr_nCl_m]^-,\ n + m = 3,$$
$$[R_4N]_2^+[ZnBr_nCl_m]^{2-},\ n + m = 4.$$

The dependence of the zinc distribution coefficient on the hydrochloric acid concentration in the initial aqueous solution, ranging from 0.75 to 9.0 M, is shown in Fig. 2. It should be noted that, in the case of salt **I**, this dependence passes through two maxima

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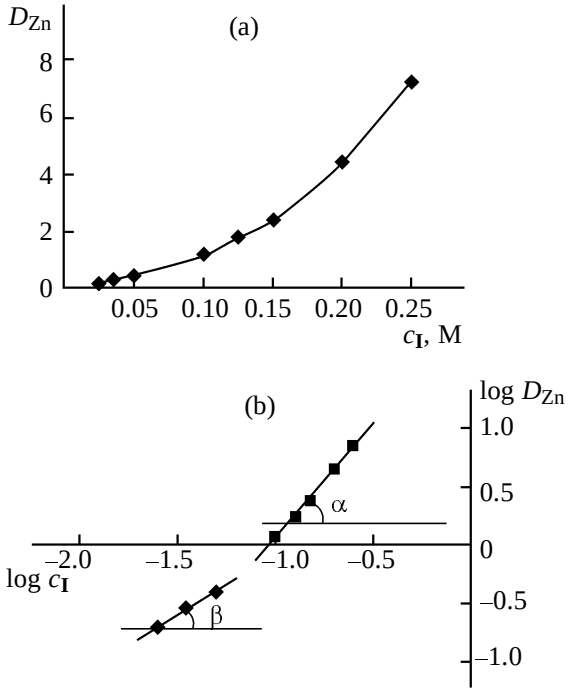

Fig. 1. Distribution coefficient of Zn(II) as a function of the concentration of hept-2-ynyltrioctylammonium bromide **I** in chloroform at 25°C: (a) common and (b) log–log plot; c_{HCl} 1, c_{Zn} 0.02 M.

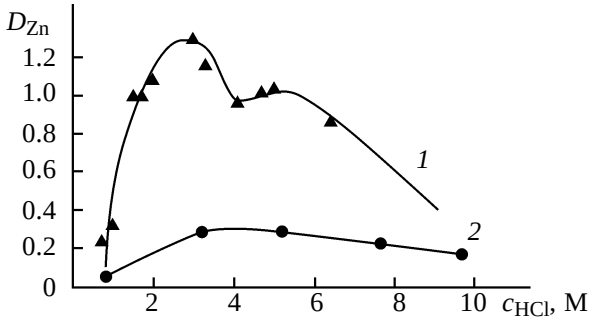

Fig. 2. Distribution coefficient of Zn(II) between the aqueous phase and chloroform solution of (*1*) hept-2-ynyltrioctylammonium bromide and (*2*) methyltrioctylammonium iodide at 25°C as a function of the HCl concentration in the aqueous phase; $c_{R_4N^+Hlg^-}$ 0.05, c_{Zn} 0.02 M.

at the HCl concentration of ~3 and 5 M, and then D_{Zn} sharply decreases with increasing acid concentration in the aqueous phase. The dependence for methyltrioctylammonium iodide **II** is dome-shaped with a single maximum at the HCl concentration of about 5 M, which agrees with the published data on zinc extraction from hydrochloric acid solutions with quaternary ammonium salts containing saturated hydrocarbon substituents. The decrease in D_{Zn} with increasing C_{HCl} is due to competing extraction of HCl with the quaternary ammonium salt [1, 14]. In addition, the zinc distribution coefficients in the system with salt **II** are substantially lower than those in the system containing salt **I**. It should be noted that, in double salts formed in extraction of metal ions with quaternary ammonium salts, the salt anion is coordinated to the metal. Hence, zinc extraction with salt **II** should be higher than that with salt **I**, since the nucleophilicity of the iodide anion of salt **II** is higher than that of bromide anion contained in salt **I**. However, the experimental results are opposite. These data and the fact that oct-1-yne (difficulty soluble in water and readily soluble in organic solvent) virtually does not extract zinc (see the table) indicate that the steric accessibility of the nitrogen atom of the base for the halide anion of $ZnCl_2$, rather than the interaction of zinc cation with the π bond and even the nucleophilicity of the anion of the quaternary ammonium salt, is the critical factor in formation of adducts of quaternary ammonium salts with zinc halides in the extraction systems.

Unusually complex shape of the D_{Zn} vs. C_{HCl} dependence for salt **I** can be due to the presence of the triple bond in its molecule. Probably, the second

Zinc(II) distribution coefficients (D_{Zn}) between the electrolyte and 0.05 M solutions of hept-2-ynyltrioctylammonium bromide **I**, methyltrioctylammonium iodide **II**, and oct-1-yne and 0.2 M solution of 4-[(*E*)-2-(4-methoxyphenyl)vinyl]pyridine-1-oxide (**III**) at 25°C or ambient temperature

Extracting agent	Electrolyte, *c*, M	Solvent	D_{Zn}
I	KCl, 3	Chloroform	0.19
	KBr, 3	〃	0.32
	NaCl, 3	〃	0.89
	NaBr, 3	〃	1.46
	NaBr, 3	Toluene	[a]
	HCl, 1[b]	Chloroform	0.34
	HCl, 1[b]	Benzene	29
	HCl, 1[b]	Toluene	21[c]
	H_2SO_4, 1[b]	〃	0.090
	HNO_3, 1[b]	〃	0.000
Oct-1-yne	HCl, 1[b]	Chloroform	0.000
II	HCl, 1[b]	〃	0.080
III	NaCl, 3	〃	0.075 [12]
	KBr, 3	〃	4.0 [12]
	NaBr, 3	〃	[a]

[a] The Zn^{2+} content in the aqueous phase after extraction is lower than the detection limit. [b] At 25°C. [c] D_{Cu} 1.64.

maximum appears owing to chemical reactions, e.g., HCl addition to the triple bond. It is known that the reactivity of acetylene derivatives with respect to electrophilic agents is lower than that of olefins owing to high electronegativity of the carbon atom with *sp* hybridization. These reactions are catalyzed by mercury, copper, iron, and nickel cations which probably form π complexes with the triple bond [16, 17]. In our catalytic system, Zn^{2+} cations can exhibit similar properties. We found that the HCl loss in the aqueous phase is negligible only at its initial concentration ranging from 0.75 to 3 M. This is an indirect evidence that HCl extraction competes with addition of this acid to the triple bond of cation of salt **I** at lower pH.

Usually the extraction power is determined in various diluents, since it is strongly affected by the nature of the diluent. We studied the extraction of Zn with solutions of salt **I** in low-polar solvents such as chloroform, benzene, toluene, and hexane. Salt **I** is almost insoluble in hexane. The extraction properties in other diluents strongly differ. In going form chloroform to benzene and toluene, the zinc distribution coefficient increases by a factor of several tens, whereas copper extraction in toluene solutions of **I** is much lower (see table).

This phenomenon can be explained in the terms of the concept of the solvent effect on the nucleophilicity of the reaction center of the salt. Electrophilic diluents such as $CHCl_3$ form weak donor–acceptor (in particular, hydrogen) bonds with the salt anion [18] and decrease its nucleophilicity with respect to the metal cation, thus decreasing the extraction power.

Benzene and toluene, unlike chloroform, exhibit mainly nucleophilic properties (the presence of readily polarizable π-electron system favors interaction of the benzene ring with electrophilic agents) and weakly solvate the nucleophilic centers of the quaternary ammonium salt. Hence, the extraction in the presence of these diluents is more efficient.

We also studied the influence of salting-out agents on zinc extraction with quaternary ammonium salts. Previously we found [12] that Zn(II) and Cu(II) are efficiently extracted with 4-[(*E*)-2-(4-methoxyphenyl)-vinyl]pyridine-1-oxide (**III**) from solutions of alkali metal halides. In this work we performed similar experiments with salt **I** to compare the extraction power of these two compounds with respect to copper and zinc cations.

Our results show (see table) that zinc extraction with both pyridine oxide **III** and salt **I** from bromide solutions is higher than from chloride solutions containing the same alkali metal cation.

This fact can be explained in terms of the general concept describing the influence of hydration of metal halide complexes formed in the aqueous phase on their extraction into the organic phase. The extraction of a metal complex into the organic phase increases as its hydration decreases. Better extraction of zinc bromides as compared to zinc chlorides is known [19] to be due to different hydration of these compounds. Zinc(II) is extracted from concentrated bromide solutions with salt **I** in the form of complexes $ZnBr_n^{2-n}$ (n = 1–4 [20]) which are poorly hydrated as compared to chloride or chloride–bromide complexes $ZnCl_mBr_n^{2-(m+n)}$ extracted from chloride solutions. In addition, Zn(II) extraction with salt **I** depends on the size of the supporting electrolyte cation. It is known that the energy of hydration of cations increases with a decrease in their radius. Since small cations are readily hydrated, the fraction of water molecules involved in hydration of the extractable species decreases in the presence of these cations, which favors extraction of these compounds into the organic phase [20–22].

Thus, the extraction power of salt **I** (see table) decreases in the following series of supporting electrolytes: NaBr > NaCl > KBr > KCl.

To supplement our previous data on zinc extraction with solutions of **III** [12], we studied Zn(II) extraction from 3 M NaBr solutions. The Zn(II) extraction, as in the case of salt **I**, is the most efficient from solutions containing NaBr as a supporting electrolyte. It was found that the extraction power of **III** is more sensitive than that of salt **I** to the nature of the cation and especially the anion of the electrolyte and decreases in the order NaBr > KBr > NaCl.

The strong difference in the effect of supporting electrolyte on the extraction with salt **I** and pyridine oxide **III** can be due to different natures of these extracting agents and hence different structures of their complexes with zinc halides. However, it should be noted that both extracting agents contain multiple bonds and their coordinating centers are sterically accessible. Molecules of **III** contain the double bond and have the planar structure providing their compact arrangement around a metal cation.

Thus, salt **I** is a promising extracting agent for zinc and is much more efficient than conventional tributyl phosphate [23, 24]. It should be noted that the residual zinc content after its extraction from 3 M NaBr and HCl solutions with dilute solutions of salt **I** in toluene is below the detection limit (see the table).

In subsequent works we are going to study com-

plexation of salt **I** and pyridine oxide **III** with other metal cations.

EXPERIMENTAL

The quaternary ammonium salts containing the triple bond at the β-position with respect to the nitrogen atom were prepared by the procedure in [10], and 4-[(*E*)-2-(4-methoxyphenyl)vinyl]pyridine-1-oxide (**III**), by the procedure in [25].

Zinc was extracted with solutions of salts **I** and **II**, oct-1-yne, and **III** in an appropriate organic solvent at room temperature (16–20°C) and 25°C, with phase volumes being the same. The initial concentration of Zn(II) and Cu(II) was kept constant at a level of 0.02 M. The extraction equilibrium with the quaternary ammonium salts and oct-1-yne was attained in 1 min, and with compound **III**, in 3 min. The equilibrium concentrations of Zn(II) and Cu(II) were determined by complexometric titration at pH 5 using Xylenol Orange as an indicator [12]. The acid concentration was determined by titration with a KOH solution with the same indicator [26].

The concentration dependences and the solvent effcet were studied at 25°C.

REFERENCES

1. Shmidt, V.S., *Ekstraktsiya aminami* (Extraction with Amines), Moscow: Atomizdat, 1970.
2. Mikhailichenko, A.I., Mikhlin, E.B., and Patrikevich, Yu.B., *Redkozemel'nye metally* (Rare-Earth Metals), Moscow: Metallurgiya, 1987.
3. Shmidt, V.S., Shesterikov, V.N., and Mezhov, E.A., *Usp. Khim.*, 1967, vol. 36, no. 12, p. 2167.
4. Sinitsyn, N.M., Buslaeva, T.M., Ukraintseva, M.I., and Samarova, L.V., *Zh. Neorg. Khim.*, 1985, vol. 30, no. 3, p. 725.
5. Becker, H., *Einführung in die Elektronentheorie organish-chemischer Reaktionen*, Berlin: Wissenschaften, 1964, 2nd ed.
6. Zolotov, Yu.A., *Ekstraktsiya v neorganicheskom analize* (Extraction in Inorganic Analysis), Moscow: Mosk. Gos. Univ., 1988.
7. Dneprovskii, A.S. and Temnikova, T.I., *Teoreticheskie osnovy organicheskoi khimii* (Theoretical Foundations of Organic Chemistry), Leningrad: Khimiya, 1991.
8. Torgov, V.G., Yatsenko, V.T., Gudkov, V.A., and Shul'man, R.S., *Zh. Anal. Khim.*, 1999, vol. 54, no. 10, p. 1057.
9. Astafurov, V.I., Plekhanov, V.V., and Frolova, V.M., Abstracts of Papers, *7-ya Vserossiiskaya konferentsiaya "Organicheskie reagenty v analiticheskoi khimii"* (7th Russian Conf. "Organic Reagents in Analytical Chemistry"), Saratov, 1999, p. 252.
10. Andreev, V.P., Vuks, E.M., Kochetkova, E.V., Remizova, L.A., and Favorskaya, I.A., *Zh. Org. Khim.*, 1979, vol. 5, no. 3, p. 464.
11. Frolov, Yu.G. and Ochkin, A.V., *Nekotorye teoreticheskie voprosy ekstraktsii aminami* (Some Theoretical Aspects of Extraction with Amines), Moscow: Atomizdat, 1969.
12. Andreev, V.P. and Tunina, S.G., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 4, p. 600.
13. Shmidt, V.S. and Mezhov, E.A., *Radiokhimiya*, 1970, vol. 12, no. 1, p. 38.
14. Mazurenko, E.A., *Spravochnik po ekstraktsii* (Handbook on Extraction), Kiev: Tekhnika, 1972.
15. Pyartman, A.K., Kovalev, S.V., Keskinov, V.A., and Khokhlova, N.V., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 10, p. 1750.
16. Roberts, J., and Ceserio, M., *Basic Principles of Organic Chemistry*, New York: Benjamin, 1964.
17. *Conprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*, Barton, D., and Ollis, W.D., Eds., Oxford: Pergamomn, 1979, vol. 1.
18. Steiner, T., *Chem. Commun.*, 1997, no. 8, p. 727.
19. Zolotova, Yu.A., *Ekstraktsiya galogenidnykh kompleksov* (Extraction of Halide Complexes), Moscow: Nauka, 1973.
20. Rozen, A.M. and Krupnov, B.V., *Usp. Khim.*, 1996, vol. 65, no. 11, p. 1052.
21. Prokuev, V.A., Stebeneva, L.I., and Belousov, E.A., *Zh. Neorg. Khim.*, 1986, vol. 31, no. 1, p. 165.
22. Tunina, S.G. Andreev, V.P., Ershova, N.Yu., and Nizhnik, Ya.P., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 12, p. 1985.
23. Prokuev, V.A., *Zh. Neorg. Khim.*, 1996, vol. 41, no. 11, p. 1896.
24. Prokuev, V.A., *Zh. Neorg. Khim.*, 1989, vol. 34, no. 8, p. 2091.
25. Andreev, V.P., Batotsyrenova, E.G., Ryzhakov, A.V., and Rodina, L.L., *Khim. Geterotsikl. Soedin.*, 1998, no. 8, p. 1093.
26. Alekseev, V.N., *Kolichestvennyi analiz* (Quantitative Analysis), Moscow: Khimiya, 1972.