

EXTRACTION OF DITHIOCARBAMATE CHELATES OF Ni(II), Cu(II), Zn(II)

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Received March 9, 1995

Accepted May 21, 1995

Extraction has been investigated of chelates of alkali salts of dithiocarbamic (DTC) acids derived from (R-) dimethyl-, diethyl-, dipropyl-, diisopropyl-, dibutyl-, diisobutyl-, dipentyl-, and dihexylamine, piperidine, and morpholine with Ni(II), Cu(II), and Zn(II) from aqueous solutions of various pH values into chloroform for various time intervals. The optimum conditions have been determined for the maximum extraction yields of the metal connected with the minimum extraction yields of excess DTC ligand. The extraction of DTC chelates of Ni(II), Cu(II), and Zn(II) is best accomplished in a reaction period of 4.5 min in strong acid region (Ni, Cu) or in alkaline region with buffers of pH 8.5–9.0 (Zn). The advantage of DTC as compared with many other reagents lies in the possibility of quantitative extraction of Ni(II) and Cu(II) from strong acid media since in this region the excess DTC ligand is completely decomposed to carbon disulfide and amine in short time, and thus it does not interfere with the subsequent spectrophotometric determination.

Key words: Extraction; Dithiocarbamate, spectrophotometric determination; Spectrophotometry.

Alkali salts of dithiocarbamic (DTC) acids form planar complexes with Ni(II) and deformed tetrahedral-octahedral chelates with Cu(II) and Zn(II)¹; their general formula is $M(R-C-S_2)_2$, where R is the residue of dialkylamine. Earlier papers dealt in detail with electronic spectra of DTC salts² and their chelates^{3,4} as well as with extraction of DTC acids. Also described⁵ is the possibility of separation of the mixture and the determination of individual planar Ni(II) chelates by means of gas chromatography. It was found that the spectrophotometric determination of metals in the form of their DTC chelates in UV region of spectrum necessitates elimination of the effect of excess ligand which interferes with the determination in the region of the absorption bands of ZnDTC (265 nm) and CuDTC (275 nm). The extraction conditions were published⁶ for the DTC acids concerning the reaction times and pH values of the aqueous phase which make this effect negligible.

A quantitative extraction of metals necessitates the knowledge of the time needed for formation of their extractable chelates and the extraction rate. As the rate of transition of nonpolar chelates from polar phase to nonpolar solvent is high⁷, the extraction yields at a given pH value are affected by the rates of formation and decomposition of the chelate $M^{2+} + 2 L^- \rightarrow ML_2$ as well as by the existence of side reactions of the metals with the buffer solution components.

The present paper is focused on finding the most suitable conditions for extraction of DTC chelates of Ni(II), Cu(II), and Zn(II) which would enable a quantitative extraction into chloroform when adopting 10^{-3} mol l⁻¹ reference solutions of DTC ligands in the form of salts of the dithiocarbamic acids. In this context it was necessary to study the dependence of formation of the DTC chelates on time and pH value of the aqueous phase as well as the effects of composition of buffer solutions and their pH on the extraction yields of DTC chelates of Ni(II), Cu(II), and Zn(II). The extraction was studied with the aim to develop spectrophotometric procedures for determination of Ni(II), Cu(II), and Zn(II) in the form of their DTC chelates in the chloroform extracts, which will be described elsewhere.

EXPERIMENTAL

Chemicals

The preparation of the DTC chelates of Ni(II), Cu(II), and Zn(II) which were extracted into chloroform started from sodium and potassium salts of the dithiocarbamic acids which were synthesized from dimethyl-, diethyl-, dipropyl-, diisopropyl-, dibutyl-, diisobutyl-, methylisopropyl-, dipentyl-, and dihexylamine, piperidine, and morpholine using a known procedure². Fresh aqueous solutions of these compounds of 10^{-3} mol l⁻¹ concentration were prepared before each measurement since they decompose on standing to give carbon disulfide and the corresponding amine.

Reference stock solutions of 10^{-2} mol l⁻¹ concentration were prepared from NiSO₄ · 7 H₂O, CuSO₄ · 5 H₂O, and ZnSO₄ · 7 H₂O of analytical purity grade (Lachema) by dissolving in water. Hydrochloric acid of p.a. purity grade was purified before use by distillation in a glass apparatus to remove heavy metals. The chloroform adopted for the extractions was distilled before use if necessary: it did not exhibit any absorption in the wavelength range about 255 nm. Deionized water with the electric resistance below 18 MΩ cm⁻¹ was adopted for preparation of the solutions.

All the other chemicals used in the work were products from Lachema and were of p.a. purity grade.

pH Values of aqueous solutions for extractions were adjusted with the use of buffer solutions according to Clark and Lubs modified with regard to the conventional NBS scale, acetate solutions according to Babko, and solutions according to Bates and Bayer.

Apparatus

The absorbances of chloroform extracts were measured in 1 cm quartz cells with a Specord M40 apparatus (Zeiss, Jena). The AAS determination of zinc was performed on a Perkin-Elmer AA spectrophotometer model 306.

Procedures

Table I presents the compounds studied.

The dependence of extraction yield on reaction time was studied as follows: 1 ml of aqueous solution of 10^{-3} mol l⁻¹ respective ion was mixed in a separating funnel with 5 ml buffer solutions of pH 3.0, 7.0, or 11.0. The mixture was treated with 5 ml aqueous 10^{-3} mol l⁻¹ NaEtDTC, and the turbid suspension of chelates Ni(EtDTC)₂, Cu(EtDTC)₂, and Zn(EtDTC)₂ formed was extracted – after a certain interval (0, 0.5, 1.0, 2.0, 4.0, 6.0, or 8.0 min) – with 20 ml chloroform for 30 s. The extracts

containing Ni and Cu chelates were left to clear up and transferred to a 25 ml calibrated flask, the volume was adjusted by adding chloroform, and the solution was measured spectrophotometrically against the reference solution. The Ni and Cu concentration in the extracts was determined from calibration dependences obtained with chloroform solutions of the respective solid standards of NiDTC and CuDTC containing the necessary amounts of Ni and Cu. The reference solutions for determination of Ni(II), Cu(II), and Zn(II) were treated analogously after extraction of NaEtDTC and buffer solution with chloroform. The absorbance of solutions was measured at 327 nm (NiDTC) and 437 nm (CuDTC). With regard to the proximity of the absorption band of DTC salts at 285 nm (ref.⁵) which overlaps the analytical absorption band of ZnDTC at 265 nm, Zn content was determined in another way. The extract containing ZnDTC was treated with HNO₃, evaporated, slightly annealed, and extracted, whereupon Zn was determined by means of the flame AAS.

The effect of pH upon the extraction of chelates at the optimum reaction time was investigated as follows: 1 ml 10⁻³ mol l⁻¹ Ni(II), Cu(II), and Zn(II) solution was mixed in a separating funnel with 5 ml buffer solution (pH in the interval from 2.2 to 10) or 5 ml 1.0, 0.1, or 0.01 mol l⁻¹ HCl. The mixture was treated with 5 ml aqueous alkali salt of DTC (10⁻³ mol l⁻¹ concentration) and was left to stand 4.5 min, whereupon the turbid suspension of chelates formed was extracted with 15 ml chloroform for 30 s. The extract was left to clear up, the chloroform layer was transferred into a 25 ml calibrated flask, and the aqueous layer was extracted once more with 5 ml for 30 s. The combined extracts were adjusted to 25 ml by addition of chloroform and after 45 min the absorbance was measured at 327 nm (NiDTC) and 437 nm (CuDTC); the content of Ni and Cu DTC chelates was obtained from the calibration dependences.

Calibration Dependences

The analytical calibration dependences for determination of Ni and Cu in the form of their DTC chelates in chloroform extracts were constructed from the absorbance values of reference chloroform

TABLE I
Metal chelates of dithiocarbamic acids (R-C-S₂)₂M, M = Ni(II), Cu(II), Zn(II)

R	Symbol
(CH ₃) ₂ N	Me
(C ₂ H ₅) ₂ N	Et
(C ₃ H ₇) ₂ N	Pr
(C ₄ H ₉) ₂ N	Bu
(C ₅ H ₁₁) ₂ N	Pe
(C ₆ H ₁₃) ₂ N	He
(CH ₃ , i-C ₃ H ₇)N	MeiPr
(i-C ₃ H ₇) ₂ N	iPr
(i-C ₄ H ₉) ₂ N	iBu
C ₅ H ₁₀ N	Pp
OC ₄ H ₈ N	Mo

solutions of the respective DTC chelates of Ni(II) and Cu(II) in the concentration range from 10^{-4} to 10^{-5} mol l^{-1} . The calibration dependence for the determination of Zn by AAS method was constructed in routine way using the medium of 1% HNO_3 solutions.

RESULTS AND DISCUSSION

The investigation of the most suitable reaction time for formation of DTC chelates of Ni(II), Cu(II), and Zn(II) showed that a quantitative extraction of CuDTC chelates can be achieved within 0.5–8.0 min (pH 3.0–10.0), that of NiDTC chelates within 4.0–8.0 min (pH 3.0–10.0), and that of DTC chelates of Zn(II) within 2.0–8.0 min (pH 6.0–11.0). For the optimum time of formation of DTC chelates of Ni(II), Cu(II), and Zn(II) we chose 4.5 min, which is sufficient also for quantitative extraction of Ni(II) and Cu(II) in strongly acidic media (pH 1–3).

The values of yields of extraction of Ni(II), Cu(II), and Zn(II) in the form of DTC chelates at various pH values in the optimum time interval of 4.5 min are presented in Table II. The pH dependences of extraction yields for the same reaction time are depicted in Figs 1–5.

Figure 1 presents the dependence of extraction yield of Ni(II) in the form of some chelates with DTC ligands upon the pH value of aqueous phase. From the dependence and from Table II it can be seen that the region of 100% extraction yields decreases in the following order of ligands: MeDTC, EtDTC, PrDTC, BuDTC, PeDTC, HeDTC. The decrease of the range of quantitative extraction from MeDTC to HeDTC agrees with the decreasing dissociation constants of the respective dithiocarbamic acids. The lowering extractability of Ni chelates in alkaline region is probably connected with formation of complexes and other compounds in aqueous phase as a result of competitive reactions of Ni(II) with anions of buffer solutions and/or with OH^- ions. The quantitative formation of the NiDTC chelates and, hence, their 100% chloroform extractability

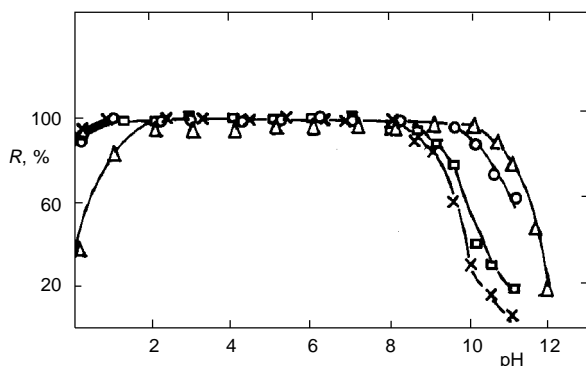


FIG. 1

pH Dependence of Ni extraction yields (R) for: Δ Ni(MeDTC)₂, \circ Ni(EtDTC)₂, \square Ni(PrDTC)₂, \times Ni(BuDTC)₂

with the ligands NaEtDTC, KPrDTC, NaBuDTC, KPpDTC, and NaiBuDTC at pH 1.0 of the aqueous phase can be connected with the rate of formation of the corresponding chelates (which must be much higher than the rate of decomposition of alkali salts⁵ giving carbon disulfide and amine) and with their low solubility in 0.1 M HCl within the time periods investigated. The solubility differences³ can probably be ascribed to

TABLE II
pH Regions of aqueous phase^a

Ligand	Ni(II)	Cu(II)	Zn(II)
NaMeDTC	1–10	1–10	3.5–8
NaEtDTC	1–9.5	1–10	5–11
KPrDTC	1–8	0.5–9	5–10.5
NaBuDTC	1–8	0–8	4.5–10
KPeDTC	3–8	0–8.5	5.5–9
KHeDTC	3.5–8	–	5.8–9
NaiPrDTC	3–10	1–8.5	4.5–9
NaiBuDTC	0–9	0.5–8.5	3–9
KMeiPrDTC	3–10	3–8.5	5–9
KPpDTC	0.5–9.5	0–9	4–9.5
KMoDTC	2–9	0–10	4–9

^a The pH regions in which the extraction yields of DTC chelates are above 99% within the reaction time of 4.5 min.

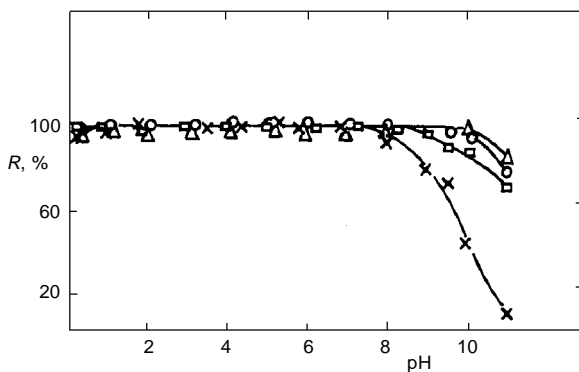


FIG. 2
pH Dependence of Cu extraction yields (*R*) for: Δ Cu(MeDTC)₂, \circ Cu(EtDTC)₂, \square Cu(PrDTC)₂, \times Cu(BuDTC)₂

steric and electronic effects of DTC ligands¹. This presumption can be supported by the fact that the ligands having high +I effects (dimethyl-, diisopropyl-) produce chelates which are extracted in acidic media less, and in alkaline media more, than the chelates with the structurally nearest ligands (DTC salts of diethylamine and dipropylamine). Similarly, steric effects can be presumed to operate in the formation of chelates with bulkier aliphatic DTC ligands (C₅ and C₆) whose rate is probably lower.

Figure 2 presents the dependence of extraction yield of Cu in the form of DTC chelates. The results – like those for the extraction of NiDTC – document the effect of alkyl substituent at nitrogen on the strength of dithiocarbamic acids and hence on the extractability of their chelates. Evidently, the region of quantitative extraction decreases in the order: Cu(MeDTC)₂, Cu(EtDTC)₂, Cu(PrDTC)₂, Cu(BuDTC)₂ like in the

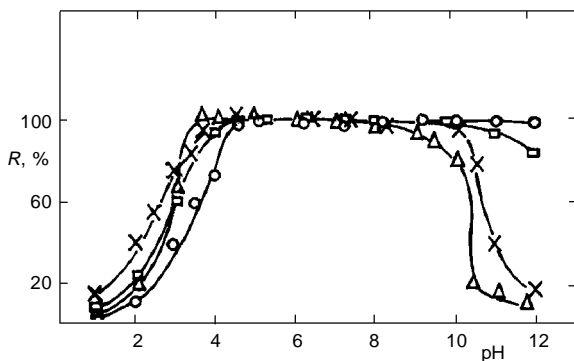


FIG. 3

pH Dependence of Zn extraction yields (*R*) for: Δ Zn(MeDTC)₂, \circ Zn(EtDTC)₂, \square Zn(PrDTC)₂, \times Zn(BuDTC)₂

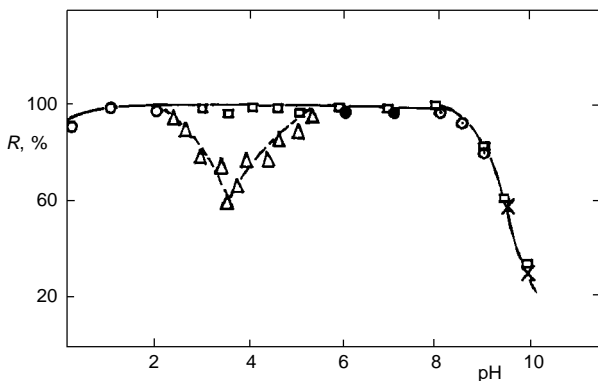


FIG. 4

pH Dependence of Ni extraction yields (*R*) in the form of Ni(EtDTC)₂ for various buffer solutions: \circ HCl: 1.0, 0.1, 0.01 mol l⁻¹; \square acetate; Δ phthalate; \bullet phosphate; \blacktriangle borate; \times carbonate

case of Ni(II) derivatives. From comparison of Figs 1 and 2 it can be deduced that the Cu chelates are more stable than Ni chelates in acidic region, which can be connected with the differences in volumes of the central atoms Cu and Ni and with the higher rate of formation of the CuDTC chelates. It can be presumed that the electronic effect and the effect on extractability of Cu(II) chelates are similar to those of NiDTC.

Figure 3 gives the pH dependences of extraction yield of some DTC chelates of Zn(II).

It can be seen that, in comparison with Ni and Cu chelates, the region of 100% extraction is shifted to higher pH values, which indicates a higher solubility (or slower formation) of the Zn(II) chelates and lower tendency of Zn(II) ion to form competing complexes and/or basic salts in alkaline region. The effect of alkyl substituents upon extractability of Zn(II) chelates is similar to those in the preceding cases.

Also the effect of composition of buffer solutions upon the extraction yields of DTC chelates was submitted to investigation. It was found that the acetate, phosphate, borate, and carbonate buffers do not influence the extraction yields whereas the phthalate buffer solutions negatively affect the extraction yields of DTC chelates of Ni(II) and Cu(II) within the pH region from 3.0 to 5.5 with the minimum at pH 3.5–4.0. This effect was observed with all the DTC chelates, being the strongest with the use of iBuDTC, iPrDTC, and MePrDTC ligands and the weakest with PpDTC and MoDTC. No such deviations were observed in the extraction of Zn(II) chelates. The decrease in extraction yield of Ni(II) and Cu(II) in the form of DTC chelates caused by the phthalate solutions can obviously be connected with the higher ability of the metal ions mentioned to form competing complexes with the phthalate ligand as compared with the corresponding ability of Zn(II), which generally possesses weaker chelation properties due to inability to form π bonds.

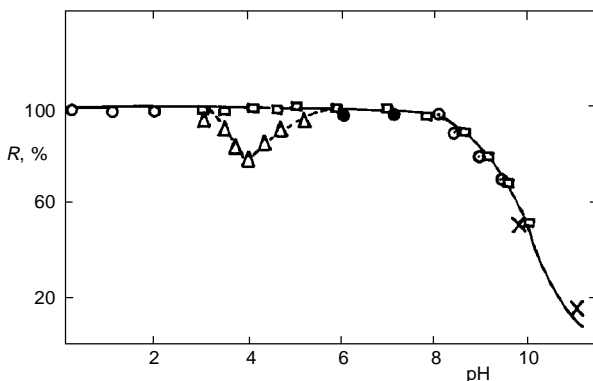


FIG. 5

pH Dependence of Cu extraction yields (R) in the form of $\text{Cu}(\text{EtDTC})_2$ for various buffer solutions: ○ HCl: 1.0, 0.1, 0.01 mol l^{-1} ; □ acetate; Δ phthalate; ● phosphate; ▲ borate; × carbonate

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