EXTRACTION OF DITHIOCARBAMIC ACIDS FROM SOLUTIONS OF THEIR SALTS

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
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The extraction of dithiocarbamic acids with chloroform from aqueous phase containing their alkali salts has been investigated with regard to the fact that absorbing strongly in the 200—310 nm range, the acids interfere with the spectrophotometric determination of metals whose dithiocarbamate ligands exhibit their analytical absorption bands in that region. The amount of the dithiocarbamic acids formed depends on the kinetics of their formation and decomposition reactions and on the pH of the aqueous phase. The stability of the acids in chloroform extracts is highly time dependent. The maximum extraction of the acids (R_2NCS_2H) is attained at the following pH (R, pH): CH_3 5·0, C_2H_5 5·9, C_3H_8 6·3, C_4H_9 6·8, C_5H_{11} 6·9, C_6H_{13} 6·9, iso-C_3H_7 7·2, iso-C_4H_9 6·9; for $(CH_3, iso-C_3H_7)NCS_2H$ 7·3, ⟨N⟩NCS_2H 7·2, O⟨N⟩NCS_2H 5·2.

Alkali dithiocarbamates[1] are crystalline substances, well soluble in water but very low-soluble in organic solvents[2]. Nondissociated dithiocarbamic acids are fairly well soluble in chloroform and other organic solvents and can be extracted with them[3—5]. Their sodium and potassium salts have found wide application as reagents for spectrophotometric determination of metals[5—12]. Metal chelates of dithiocarbamic acids[13—15] are insoluble in water and well soluble in nonpolar solvents. Their extractability is affected by a number of factors, dependent on the properties of the solution extracted[9], the ligand, and the nature of the central atom and the chelate[7,9,16,17].

The aim of the present work was to examine the extraction of dithiocarbamate ligands from the point of view of their application to spectrophotometric determination of metals, with regard to the fact that in the photometric determination the ligand is used in excess and so it may be co-extracted with the metal chelate and interfere with the determination in the UV spectral region.

EXPERIMENTAL

The extractions were carried out using aqueous solutions of alkali salts of dithiocarbamic acids and of 1-piperidine- and 4-morpholinecarbodithioic acids (Table I) of the concentration ~ 10^{-3}

mol l^{-1}. The chloroform employed as the extractant was purified by rectification and filtration over a silica gel column; its absorbance at 250 nm did not exceed 0·3.

Buffers were set up according to Clark and Lubs (adjusted with respect to the conventional NBS scale[18]; pH 2 to 10), according to Babko[1]; (pH 3 to 11), and according to Bates and Bower[18] (pH 10 to 12).

The solutions were prepared in deionized water. All the chemicals were of reagent grade purity (Lachema, Brno).

The absorption spectra of the extracts and of the DTC metal chelates (DTC stands for dithiocarbamate salts, chelates, and ligands) were scanned on a Specord UV VIS spectrophotometer (Zeiss, Jena) using 1 cm quartz cells. The pH values of the aqueous phases (extraction mixtures and buffers) over the pH 2·2 to 12 range were measured on an OP-201/2 pH-meter (Radelkis, Budapest) fitted with a glass and a saturated calomel electrode.

Two procedures were applied to the preparation of the chloroform extracts of dithiocarbamic acids. In the first procedure, 5 ml of an aqueous solution of alkali DTC, concentration 1 mmol . . l^{-1}, was mixed with 5 ml of the buffer (pH 2·2 to 12) or of hydrochloric acid (1·0, 0·1, or 0·01 mol . . l^{-1}), and after a preselected period — 0, 2, or 4 min — the mixture was extracted for half a minute with 20 ml of chloroform. (The time of contact of the DTC salt with the buffer before the extraction together with the time of extraction makes the total reaction period of the protolytic and decomposition reactions of the ligands.) After the extract had cleared up, the chloroform layer was transferred into a 25 ml volumetric flask and brought to volume with chloroform. The

TABLE I

The pH values of the aqueous phases at which the absorbances of the extracts are below 0·05, for the reaction period 4·5 min; c(acid) $\approx$ 1 mmol l^{-1}

Dithiocarbamic acid	Acid region of low extraction	Alkaline region of low extraction	pH of maximum extraction
$(CH_3)_2NCS_2H$	0—3·2	7·7—12	5·0
$(C_2H_5)_2NCS_2H$	0—3·7	8·8—12	5·9
$(C_3H_7)_2NCS_2H$	0—2·5	9·7—12	6·3
$(C_4H_9)_2NCS_2H$	0—2·8	11—12	6·8
$(C_5H_{11})_2NCS_2H$	—	9·8—12	6·9
$(C_6H_{13})_2NCS_2H$	—	9·8—12	6·9
$(iso\text{-}C_3H_7)_2NCS_2H$	2—4	11—12	7·2
$(iso\text{-}C_4H_9)_2NCS_2H$	0—2	11—12	6·9
$CH_3(iso\text{-}C_3H_7)NCS_2H$	2·2—3·8	11—12	7·3
O͡‿NCS$_2$H	1·5—3	10—12	5·2
⬡NCS$_2$H	0—3	10—12	7·2

absorption spectrum of the solution was measured against a blank prepared in the same way but without using the ligand. In the second procedure, the chloroform extract was obtained by a two-minute extraction of 10 ml of the aqueous solution of alkali DTC with 25 ml of chloroform at pH 4 to 7. The extract was diluted with chloroform to 50 ml.
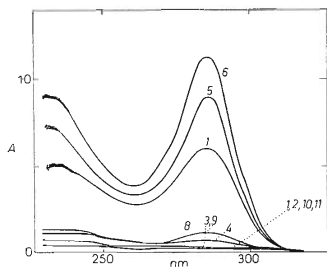

FIG. 1

Absorption spectra of chloroform extracts from $(C_2H_5)_2NCS_2Na$ for various pH values and the reaction period 4·5 min. The numbers labelling the curves denote the pH values
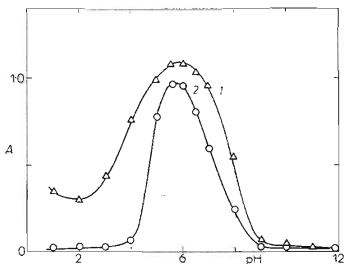

FIG. 2

Dependence of the absorbance of chloroform extracts from $(C_2H_5)_2NCS_2Na$ at 284 nm on pH. Reaction period 1 0·5 min, 2 4·5 min
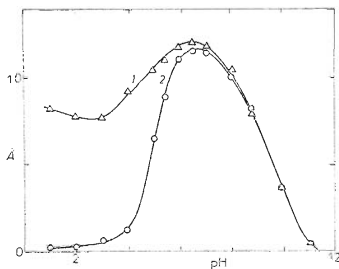

FIG. 3

Dependence of absorbance of chloroform extracts from $(C_4H_9)_2NCS_2Na$ at 284 nm on pH. Reaction period 1 0·5 min, 2 4·5 min
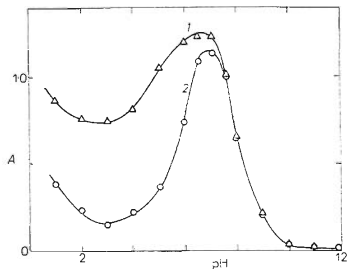

FIG. 4

Dependence of absorbance of chloroform extracts from $(C_5H_{11})_2NCS_2K$ at 284 nm on pH. Reaction period 1 0·5 min, 2 4·5 min

RESULTS AND DISCUSSION

The results of investigation of the extraction performed according to the first procedure are presented in Figs 1–4 in the form of dependences of the extract absorbances on the pH of the aqueous phase, and are evaluated in Table I.

The absorption spectra of the chloroform extracts of alkali DTC (Fig. 1) exhibit a characteristic absorption band[1] due to the N—C=S group at 285 nm, coinciding with the analytical bands of most DTC chelates (Fig. 5), lying at 250–300 nm. As Eqs (1)–(5) indicate, the dissolution and decomposition of the DTC ligands is associated with the formation of extractable compounds of a single type, *viz.* low-polar nondissociated dithiocarbamic acids. Thus it is reasonable to attribute the observed absorption band to the acids; based on the band intensity it is then possible to evaluate the content of the acid in the extract in dependence on the pH of the aqueous phase.
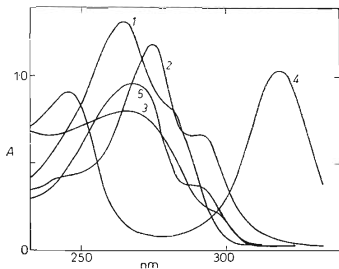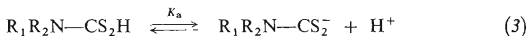
$$R_1R_2N—CS_2Na \longrightarrow R_1R_2N—CS_2^- + Na^+ \tag{1}$$

$$R_1R_2N—CS_2^- + H_2O \underset{v_1}{\rightleftarrows} R_1R_2N—CD_2H + OH^- \tag{2}$$

$$R_1R_2N—CS_2H \overset{K_a}{\rightleftarrows} R_1R_2N—CS_2^- + H^+ \tag{3}$$

FIG. 5

Absorption spectra of ethanolic solutions of dithiocarbamic chelates. Substance (c, mol l^{-1}): *1* [((C$_2$H$_5$)$_2$NCS$_2$)$_2$Zn] (8 . 10^{-5}), *2* [((C$_5$H$_{11}$)$_2$NCS$_2$)$_2$Cu] (7 . 10^{-5}), *3* [((C$_3$H$_7$)$_2$NCS$_2$)$_2$Pb] (5 . 10^{-5}), *4* [((C$_4$H$_9$)$_2$. NCS$_2$)$_2$Ni] (6 . 10^{-5}), *5* [((C$_2$H$_5$)$_2$. NCS$_2$)$_2$Cd] (4 . 10^{-5})
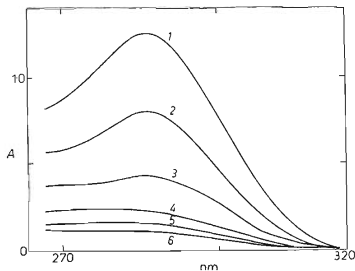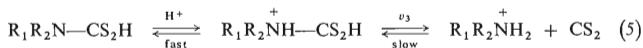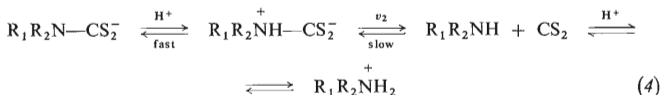
FIG. 6

Changes in the absorption spectrum of a chloroform extract from (C$_2$H$_5$)$_2$NCS$_2$Na in dependence on time. Time after preparation (min): *1* 0, *2* 10, *3* 20, *4* 30, *5* 40, *6* 60

$$R_1R_2N{\longrightarrow}CS_2^- \underset{fast}{\overset{H^+}{\rightleftharpoons}} R_1R_2\overset{+}{N}H{\longrightarrow}CS_2^- \underset{slow}{\overset{v_2}{\longrightarrow}} R_1R_2NH + CS_2 \overset{H^+}{\rightleftharpoons}$$

$$\rightleftharpoons R_1R_2\overset{+}{N}H_2 \tag{4}$$

$$R_1R_2N{\longrightarrow}CS_2H \underset{fast}{\overset{H^+}{\rightleftharpoons}} R_1R_2\overset{+}{N}H{\longrightarrow}CS_2H \underset{slow}{\overset{v_3}{\rightleftharpoons}} R_1R_2\overset{+}{N}H_2 + CS_2 \tag{5}$$

$\big($Eq. (4): ref.[10], Eq. (5): ref.[20]$\big)$.

The pH corresponding to the maximum extraction is related to the acid strength, the pH trend being decreasing with increasing acid strength. As the data of Table I suggest, the weakest is methylisopropyldithiocarbamic acid, the strongest, dimethyl-dithiocarbamic acid; this obviously is a consequence of the hyperconjugation and inductive effects, owing to which a replacement of the substituent at the nitrogen atom is associated with changes in the electron density at the nitrogen atom and at the S—H bond. In the acid range, a decrease in the pH is accompanied by a lowering and subsequently by an increase in the acid extraction, obviously due to a dependence of the v_1, v_2 and v_3 reaction rates on pH.

Comparing the results for the reaction periods 0·5 and 4·5 min we find the amount of the dithiocarbamic acids higher for the shorter period for all pH values. As Figs 2—4 show, in the ranges of pH 0 to 3 and 9 to 12 the amount of the dithiocarbamic acid extracted after the reaction period 4·5 min is low enough to permit a spectro-photometric determination with the use of compensation by a reference solution.

The formation and decomposition of dithiocarbamic acid can be observed visually in the case of $(C_4H_9)_2NCS_2^-$. If to this DTC is added 0·1M or 0·01M-HCl, $(C_4H_9)_2$.NCS$_2$H first separates, but within 4 min the acid decomposes and the solution clears up. This is consistent with Fig. 3, in which the extract in the pH 1—2 range exhibits an intense absorption in 0·5 min, but a negligible absorption in 4·5 min owing to the occurrence of reactions (4) and (5).

In the case of $(C_5H_{11})_2NCS_2^-$ and $(C_6H_{13})_2NCS_2^-$, the corresponding acids — insoluble in water — are formed instantly in strongly acidic solutions; the cloudiness is steadier than that of $(C_4H_9)_2NCS_2H$. The absorption spectra of the extracts from $(C_5H_{11})_2NCS_2K$ and $(C_6H_{13})_2NCS_2K$ solutions exhibit a band at 285 nm even if strongly acidic solutions are used and the reaction periods are several minutes. The dependence of the absorbance on pH in the alkaline region is similar to that observed with $(C_4H_9)_2NCS_2Na$.

Fig. 6 shows a part of the absorption spectrum of the chloroform extract from a solution of $(C_2H_5)_2NCS_2Na$, obtained by the second procedure, in dependence on time. These results along with additional experiments performed indicate that the chloroform extracts of dithiocarbamic acid are rather unstable, their halflives lying within the range of 15 to 20 min.

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