Sodium Dibutyldiselenocarbamate. Analytical Application to the Extraction Spectrophotometry of Heavy Metals

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Synopsis. Sodium dibutyldiselenocarbamate is soluble in water, and the form of its dibutyldiselenocarbamic acid is extractable by methylene dichloride; more than 99% of the reagent exists in the methylene dichloride phase in the pH region of 4—10. The reagent readily forms extractable chelates with Au^{III}, Co^{II}, Cu^{II}, Hg^{II}, Ni^{II}, Pd^{II}, and Zn^{II} while it gives considerable white precipitates with Ag^{I} and Hg^{II} in the pH region of 1—7. Each chelate in methylene dichloride absorbs at wavelengths lower than 400 nm. The peak of the copper(II) chelate with the molar absorbtivity of 1.50×10^4 at 442 nm is not affected by the spectra of the reagent and other metal chelates, and it can be used for the selective spectrophotometric determination of copper(II) up to 0—10 μg/cm³.

It is well known that heavy-transition metals form more stable complexes with chelating ligands which have π-acceptor donor atoms with unfilled $p\pi$ or $d\pi$ orbitals, like sulfur and selenium elements. However, scarcely no information on the solvent-extraction reagents with a selenium donor atom has been reported.[1,2] In a previous paper, the present author reported the synthesis of new monoseleno analogs of β-diketone, 1,1,1-trifluoro-4-(2-thienyl)-4-hydroseleno-3-buten-2-one and its analytical utility as an extraction-spectrohotometric reagent for heavy metals.[3] Now that author has investigated a selenium containing a chelating reagent of dithiocarbamate, sodium dibutyldiselenocarbamate, in the anticipation of enhanced stability and selectivity in reactions with heavy-transition metals; the investigation has been undertaken with analytical applications in view

Experimental

Apparatus. A model 323 Hitachi Recording Spectrophotometer; a model 239 Hitachi Digital Spectrophotometer; a Hitachi-Horiba glass electrode pH meter ,model M-5; an Iwaki shaking machine, model KM; a Kubota centrifuge machine, and a Yanagimoto Micro Melting-point Apparatus, Model MP-J2, were used.

Preparation of Metal Solution. The solution of the copper(II) ion was prepared by dissolving $CuSO_4\cdot5H_2O$ of a guaranteed-grade reagent in a slightly acidic hydrochloric acid solution to make a 10^{-1} M† aqueous solution. The concentration of the copper(II) ion was standardized complexometrically, and the solution was diluted as required with distilled water. The other guaranteed-grade metal salts of Ag^{I}, Au^{III}, Bi^{III}, Cd^{II}, Co^{II}, Cu^{II}, $Fe^{II,III}$, Hg^{II}, In^{III}, Ir^{III}, Mn^{II}, Ni^{II}, Pb^{II}, Pd^{II}, Pt^{II}, Rh^{III}, Sn^{II}, Tl^{I}, $UO_2{}^{II}$, $VO_2{}^{I}$, and Zn^{II} were also dissolved in distilled water or in an acidic hydrochloric or nitric acid solution to make a 10^{-1} M aqueous stock solution of each metal ion.

Synthesis of Sodium Dibutyldiselenocarbamate. Carbon diselenide was synthesized by the similar method of Barnard and Woodbridge.[4] It turns from a clear lemon-yellow color to orange within a couple of weeks and finally to black as solid-carbon diselenide polymers form; it is used as soon as possible for the synthesis of sodium dibutyldiselenocarbamate. Sodium dibutyldiselenocarbamate was synthesized by a slight modification of the method of Barnard and Woodbridge.[4]

$$[CH_3(CH_2)_3]_2NH + CSe_2 + NaOH \longrightarrow [CH_3(CH_2)_3]_2N-C(=Se)SeNa + H_2O \qquad (2)$$

Carbon diselenide (2.11 g, 0.0124 M) in dioxane (20 cm³) was added to a solution of sodium hydroxide (0.5 g, 0.0124 M) and dibutylamine (1.6 g, 0.0124 M) in water (20 cm³) at −10 °C for 30 min while being stirred in an atmosphere of nitrogen. In order to avoid possible insoluble impurities coming from the polymerization of carbon diselenide, the solution was filtered once, and the sodium salt of dibutyldiselenocarbamate thus prepared was separated by extraction with methylene dichloride. The methylene dichloride solution was dried over anhydrous sodium sulfate, and the product was recovered by the evaporation of the excess solvent under low pressure. The sodium dibutyldiselenocarbamate thus obtained was an orange-red oily substance, which showed a melting point of 50—60 °C. The reagent was sealed in a brown-colored bottle in a nitrogen atmosphere and stored in a refrigerator kept at 5 °C.

Extraction Procedure. To an aqueous solution containing 10^{-6}—10^{-2} M metal ions we added 10^{-2} M acetic acid (in the pH region of 0—7) or 10^{-2} M boric acid (in the pH region of 7—13); its pH was adjusted to the desired value by means of a 0.1—1 M sodium hydroxide or hydrochloric acid solution. Ten cm³ of this solution and 10 cm³ of 3×10^{-5} M sodium dibutyldiselenocarbamate in methylene dichloride were then introduced into a 50-cm³ glass-stoppered centrifuge tube; the mixture was equilibrated for 1—30 min, after which the phases were separated by centrifugation. Metal complexes of dibutyldiselenocarbamate are also readily extractable in such organic solvents as chloroform, benzene, carbon tetrachloride, and isobutyl methyl ketone. In general, halogen-substituted hydrocarbons with large dielectric constants are superior for the extraction of metal complexes.

Results and Discussion

Sodium dibutyldiselenocarbamate is soluble in water to give a pH of 11.30 and is extractable with methylene dichloride; it is, in fact, remarkably stable in this solvent. However, sodium dibutyldiselenocarbamate is unstable in an acid medium, and the decomposition of the reagent gradually proceeds below pH 4. From the experimental results on the variation of the percentage of the extraction of sodium dibutyldiselenocarbamate (2×10^{-5} M) from an aqueous solution into methylene dichloride as a function of the pH, it was found that more than 99% of the reagent was in the

† 1 M = 1 mol dm⁻³.

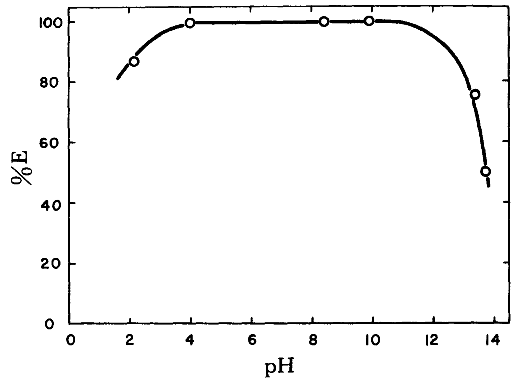

Fig. 1. Variation in the percentage extraction of 2×10^{-5} M dibutyldiselenocarbamic acid from an aqueous solution into methylene dichloride as a function of pH.

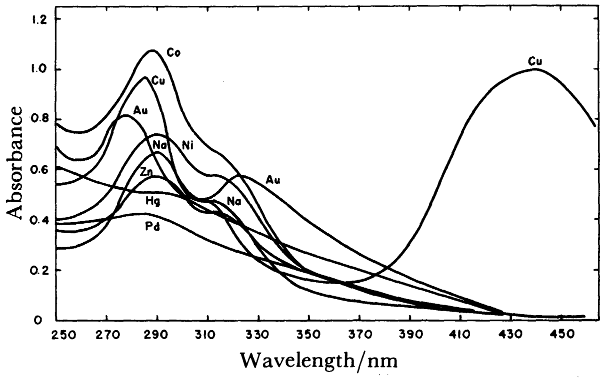

Fig. 2. Absorption spectra of 3×10^{-5} M sodium dibutyldiselenocarbamate and of 1.5×10^{-5} M its metal chelates in methylene dichloride.

methylene dichloride phase in the pH region of 4—10 within 5 min (Fig. 1). The pH value of an aqueous phase corresponding to a 50% extraction of the ligand was 13.7. The sodium dibutyldiselenocarbamate (10^{-3} M) readily forms extractable chelates into methylene dichloride with many metals (trace—10^{-2} M), such as Au^{III}, Co^{II}, Cu^{II}, Hg^{II}, Ni^{II}, Pd^{II}, and Zn^{II}, in the pH region of 1—7 within 30 min. Each metal chelate in methylene dichloride absorbs at wavelengths lower than 400 nm (Fig. 2), shows its own specific color, and has absorption maxima (λ_{max}/nm), as is shown in Table 1, together with the results for dibutyldithiocarbamate. The electronic spectra of metal complexes of dibutyldiselenocarbamate closely resemble those of the corresponding dibutyldithiocarbamate in intensity and position, except for a general red shift, that is, a slight shift to longer wavelengths. Ag^{I} and Hg^{II} give white precipitates. The reaction of the sodium dibutyldiselenocarbamate with Bi^{III}, Cd^{II}, $Fe^{II,III}$, In^{III}, Ir^{III}, Mn^{II}, Pb^{II}, Pt^{II}, Rh^{III}, Sn^{II}, UO_2^{II}, VO_2^{I}, and Tl^{I} is not observed distinctly. The molar absorptivity at the λ_{max} of sodium dibutyldiselenocarbamate and its copper(II) chelate, expressed in cm^2 l mol^{-1}, is 2.37×10^4 (288.5 nm) and 1.69×10^4 (311 nm) for the ligand and 6.66×10^4 (283.2 nm), 3.00×10^4 (308 nm), and 1.50×10^4 (440 nm) for the complex respectively. The peak of the copper chelate at 442 nm is not affected by the spectra of the ligand and other metal chelates, is stable at least for several hours, and can be used for the selective-extraction spectrophotometric determination of copper(II) up to 0—10 μg/cm^3 without such treatment as masking the foreign cations. The results reveal that dibutyldiselenocarbamate has analytical potentiality as diethyldithiocarbamate, one of the most useful agents.[2,7]

Table 1. Extraction of metals with sodium dibutyldiselenocarbamate in methylene dichloride in the pH region of 1—7

Metal[a]	Color	λ_{max}/nm	Remarks
Na^{I}	Colorless	288.5, 311[b) (281)	
Ag^{I}	Colorless		ppt.
Au^{III}	Bright-brown	275.5, 319.8[b] (275, 319)	
Co^{II}	Bright-brown	288.5, 315[b] (259, 285)	
Cu^{II}	Yellow-green	283.2, 308,[b] 440 (273, 287,[b] 430)	
Hg^{II}	Colorless	290[b] (252, 276)	ppt.
Ni^{II}	Yellow	289.5, 311.5[b] (261, 280)	
Pd^{II}	Orange-brown	283.0 (275)	
Zn^{II}	Yellow	288.5, 313.0[b] (266, 282[b])	

a) The reaction of sodium dibutyldiselenocarbamate with Bi^{III}, Cd^{II}, $Fe^{II,III}$, In^{III}, Ir^{III}, Mn^{II}, Pb^{II}, Pt^{II}, Rh^{III}, Sn^{II}, Tl^{I}, UO_2^{II}, and VO_2^{I} was not observed distinctly. b) Shoulder.
The values in brackets are the absorption maxima of metal dibutyldithiocarbamates. Sodium dibutyldithiocarbamate (mp 33—34 °C) was synthesized by using the method of Klapping and Van der Kerk.[5,6]

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