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A Nephelometric Analysis of Mercury(II) with Potassium Salt of α,α'-Bis(dithiocarboxyoxy)-*p*-xylene

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Potassium salt of α,α'-bis(dithiocarboxyoxy)-*p*-xylene (abbreviated as K_2-XDX) was synthesized as a chelating agent with *p*-xylene-α,α'-diol, carbon disulfide, and potassium hydroxide. Since a mercury(II)–XDX chelate complex suspension scattered pearl-blue light strongly because of the formation of a colloidal solution, the nephelometric analysis of small amounts of mercury(II) was undertaken. The calibration curve was found to be linear in the two ranges of 0.03—1.00 and 0.50—25.00 $\mu g\ cm^{-3}$ of the mercury(II) ion respectively, but no suitable masking agents for interfering metal ions were found. The mole ratio of mercury(II) to XDX in the complex was found to be 1 to 1. These data for the complex suggested that XDX and mercury(II) combined alternately to form the $(\text{–Hg–XDX–})_n$ complex. The molecular weight of this complex could be calculated as about 2×10^7 from the Zimm plot on the basis of the light-scattering method.

The formation of chelate complexes between a number of metals and dithiocarbonic acid derivatives is well known. Since the derivatives with a dithiocarboxyoxy group as a functional group can readily be prepared, and since they have a good reactivity with many metal ions, they have been used for other analytical studies as well as for absorptiometric analysis.[1–7] If the two hydrogen atoms of dihydroxy-compounds can be replaced by some functional groups, we can assume that the dithiocarbonic acid derivatives react with each of the different kinds of metal ions to form polynuclear metal complex salts in which a successive and alternate arrangement of metal and ligand is found. Provided that these chelate complexes become large and colloidal in form, those solutions may be used in the nephelometric determination of trace amounts of the metal ions.

According to the above-mentioned idea, potassium salt of α,α'-bis(dithiocarboxyoxy)-*p*-xylene, (K_2-XDX), was prepared from *p*-xylene-α,α'-diol. This derivative reacted with many ions and produced light-scattering colloidal solutions. Among these, the mercury(II)–XDX solution scattered very remarkable pearl-blue light. This colloidal solution was very stable for a long time. The substance could be extracted into 1-octanol and 3-heptanone, which were good solvents for some organic polymers. The solution was colloidal and scattered light as well as in the case of an aqueous solution. This colloidal solution was also very stable for a long time.

This solution could be used in the determination of mercury(II) by the nephelometric method, and the amount of the mercury(II) ion (from 0.03—25.00 $\mu g\ cm^{-3}$) was detectable. The molecular weight of the mercury(II)–XDX chelate was measured by the light-scattering method and found to be about 2×10^7. Therefore, a polynuclear chelate compound might be produced.

Although there have been reported several nephelometric methods for the determination of such metals as Ag, Ba, and Zn, nephelometry with a colloidal solution of polymeric polynuclear chelate has not yet been reported.[8] It should be emphasized that this analytical method may be a new tool for trace analysis.

Experimental

Reagents. Dust-free water was obtained by distilling deionized water with an all-quartz distillation apparatus and by then filtering it through a G-5 glass filter, it has been used throughout all the processes. Mercury(II) chloride was purified by sublimation. All the other reagents were of a chemically pure grade and were used without further purification. Each of the reagents was dissolved with the dust-free water until it became the desired concentration and then filtered through the G-5 glass filter.

Buffer Solution. Among many kinds of buffer solutions, the most rapid clearance of the reaction mixture was observed in the case of Walpole's buffer solution. At pH values of 3.8 or below, XDX^{2-} was decomposed rapidly, while above this pH, even in an alkaline solution, it was stable. This buffer solution was prepared by mixing hydrochloric acid and a sodium acetate solution. The maximum intensity of the scattering light from the chelate complex suspension was obtained at about pH 4.0.

Synthesis of K_2-XDX. This was synthesized according to the method given by Price.[9] The procedure was as follows: one gram of *p*-xylene-α,α'-diol (α,α'-dihydroxy-*p*-xylene) was dissolved in 6 cm^3 of a 15% potassium hydroxide solution, and then the mixture was added to 5 cm^3 of carbon disulfide. The mixture was stirred for 16 h, with the temperature kept at 5 °C. After the surplus carbon disulfide had been removed by filtration, ethanol was added to the solution until a slightly yellow crystalline was produced. The precipitate was filtered out, washed by ethanol, and recrystallized by dissolving them in a minimum amount of water and adding ethanol. The resulting product was filtered, washed with ethanol, and dried at room temperature under reduced pressure.

Properties of K_2-XDX. The K_2-XDX synthesized was not changed when kept for at least 50 days in a brown desiccator at reduced pressure. It is very soluble in water and acetone, and insoluble in carbon tetrachloride, ethanol, and benzene.

Some of its physicochemical properties were as follows.

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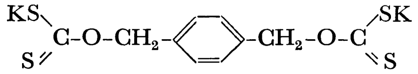
The ultraviolet spectrum of an aqueous solution of this compound in a neutral medium showed an absorption maximum at 303 nm. This is due to the replacement of a hydrogen atom by a carbodithioic group.[10]

The infrared spectra of the compound was measured in a KBr disc, and the bands were assigned (cm^{-1}) to the stretching vibrations of C=S (1150), and C–S (915, 870, and 650).[11,12] The ^1H NMR spectrum of a deuterium oxide solution of *p*-xylene-α,α′-diol (the starting material) showed a peak at 4.55 ppm by the existence of two protons of $-R-CH_2-O-$. In the case of this derivative, however, the identical peak was shifted to 5.48 ppm by substitution with the dithiocarboxyoxy group.

According to the data presented above, the structural formula was determined to be as follows:



The purity of this compound was determined to be over 99.7% by the method of JIS-K8269.

Stability of the Reagent Solution. The absorbance of the aqueous solution adjusted at pH 6.8 was measured at the wavelength of 303 nm. It showed little change for at least 120 min. After 24 h, however, it decreased 30%. On the basis of the results, all the measurements were designed to be completed within 30 min.

Apparatus. For the measurement of the intensity of the scattering light, a Hitachi EPS-3T recording spectrophotometer with an L-3 model fluorometer was used. As a light source, an ultra-high pressure lamp was used. Two monochromatic rays of 365 nm, through a ultraviolet filter, and 546 nm, through a green interference filter, were used in order to excite the sample. The intensity of the scattering light from the sample was measured perpendicular to the incident light. A greater intensity was always obtained in the case of 365 nm than in that of 546 nm.

For the estimation of the molecular weight, a Fica 4200 model light-scattering spectrophotometer was used.

Procedure for the Determination of Mercury(II). All the measurements were carried out at room temperature. The general procedure for the determination of mercury was as follows: 10-cm^3 portions of the sample solutions containing 0.06—50.00 $\mu g\ cm^{-3}$ of the mercury(II) ion, which had been prepared from 100 $\mu g\ cm^{-3}$ of the mercury(II) ion stock solution, were placed in a 30 cm^3-test tube fitted with a ground-glass stopper. 5 cm^3 of an acetate buffer solution (pH 4.0) and 5 cm^3 of an XDX^{2-} solution (150 mg dm^{-3} of K_2-XDX) were added. The XDX^{2-} solution was prepared afresh each time. The test tube was vigorously shaken and then allowed to stand for 10 min. The intensities of the scattering light were measured at 365 nm. The constant regulation of the slit width and the photomultiplier sensitivity was necessary in order to choose the best conditions between the concentration range of the mercury(II) ion and the intensity of the scattering light.

Results and Discussion

Reactions of XDX^{2-}. As is shown in Table 1, in the reactions between XDX^{2-} and various kinds of metal ions, the coloration was often similar to those which were observed in a reaction with the ethylxanthate ion. In an aqueous solution, however, XDX^{2-} differed from the ethylxanthate ion, in which turbidity or a precipitate more often appears when a kind of metal ion is mixed with it. The apparent values of the molar absorption coefficients, (ε), shown in the table might be slightly higher because of the influence of light scattering. They are, however, lower than those obtained by the use of ethylxanthate.[13] From the graph of the calibration curve prepared for each metal ion except Mo^{5+}, we obtained a straight line passing a point near to zero.

Calibration Curve. The two linear calibration curves were obtained for the concentration ranges of 0.03—1.00 $\mu g\ cm^{-3}$ and of 0.50—25.00 $\mu g\ cm^{-3}$.

Solvent Extraction. Twenty-one kinds of generally available polar and nonpolar organic extractants were examined for the selective extraction of the mercury(II)–XDX chelate polymer. The polymer could be extracted into only 1-octanol and 3-heptanone, as is shown in Table 1. The light scattering was observed by this extracted sample, and the intensity of the scattered light was the same as in the aqueous solution. Other kinds of metal chelates, such as Co(II)–, Ni(II)–, Cu(II)–, and Cd(II)–XDX, were also extracted into both solvents.

Effect of Diverse Ions. For the study of the tolerance limits for diverse ions, 1 cm^3 of a 5.00 $\mu g\ cm^{-3}$ mercury(II) ion solution was mixed with 1 cm^3

Table 1. Reactions of metal ions with XDX^{2-}

Ion	Color	λ_{max} / nm	ε / $dm^{-3}\ mol^{-1}\ cm^{-1}$	Extractant[a]
Fe^{2+}	Brown (unstable)	—	—	None
Co^{2+}	Pale-blue	360	1.5×10^4	3-Hept., 1-Oct.
Ni^{2+}	Brown-yellow	430	2.6×10^3	3-Hept., 1-Oct.
Cu^{2+}	Yellow	408[b]	3.5×10^3	3-Hept., 1-Oct.
As^{3+}	Colorless (precipitate)	—	—	None
Bi^{2+}	Yellow (precipitate)	—	—	None
Cd^{2+}	Pearl-blue	305	2.8×10^3	3-Hept., 1-Oct.
Hg^{2+}	Pearl-blue	295	2.8×10^3	3-Hept., 1-Oct.
Mo^{5+} [c]	Reddish-orange	521	5.8×10^3	None
V^{5+}	Yellow (precipitate)	—	—	None
UO_2^{2+}	Reddish-orange (precipitate)	—	—	None

a) 3-Hept. is 3-heptanone. 1-Oct. is 1-octanol. b) In the case of Cu^{2+}, undistinct peak of absorption was found.
c) Reduced MoO_4^{2-} with hydrazine sulfate.

of another ion solution in different concentrations. To each of these solutions 3 cm^3 of the buffer solution (pH 4.0), 2 cm^3 of the EDTA solution (3.7% of Na_2 edta) as a masking agent, and 3 cm^3 of the XDX^{2-} solution (150 mg dm^{-3} of K_2–XDX) were added. Then, in order to extract the mercury(II)–XDX chelate polymer, these were vigorously shaken with 10 cm^3 of 1-octanol.

According to the result, a large excess (300 $\mu g\ cm^{-3}$ each) of the following ions—Ag^+, Al^{3+}, Ba^{2+}, Be^{2+}, Ca^{2+}, Cr^{3+}, Mg^{2+}, Mn^{2+}, MoO_4^{2-}, and Sr^{2+}—had no effect on the intensity of the scattering light. Co^{2+}, Fe^{2+}, Fe^{3+}, Mo^{5+}, UO_2^{2+}, and Zn^{2+} did not interfere in concentrations 30 times or less that of the Hg^{2+}. Even if, in the same concentration as that of the Hg^{2+}, Cd^{2+} caused a positive interference, As^{3+}, Bi^{2+}, $Cr_2O_7^{2-}$, Cu^{2+}, Pb^{2+}, and V^{5+} showed a negative interference. The reason for the negative interference is probably that, in the case of Cu^{2+}, the solution formed with XDX^{2-} has a broad absorption band in the near-ultraviolet region, and the exciting and scattering lights are absorbed by the solution. In the cases of As^{3+}, Bi^{2+}, $Cr_2O_7^{2-}$, Pb^{2+}, and V^{5+}, they co-precipitate the Hg–XDX polymer. The addition of Na_2edta as a masking agent for these ions was not effective.

Composition of the Chelate. A continuous-variation method by means of nephelometry was carried out. Both mercury(II) and XDX ion solutions were adjusted to 5×10^{-3} mol dm^{-3} in concentration, (Hg:10 $\mu g\ cm^{-3}$), they were mixed in proper proportions, and a 4-cm^3 portion of a buffer solution (pH 4.0) was added. The total volume of this solution was finally made up to 14 cm^3, and then we measured the intensity of the scattering light. The results are shown in Fig. 1.

Since the maximum intensity was obtained with a concentration ratio of 0.5, the ratio of mercury(II) to XDX in this polymer was confirmed to be 1 to 1.

Estimation of the Molecular Weight of the Polymer. The molecular weight of the colloidal polymer can be determined by light-scattering spectrophotometry at the wavelength of 546 nm. The variation in the refractive index at various concentrations, (d*n*/d*c*), was obtained by using a differential refractometer (Narumi Co., Ltd.). To obtain a dust-free sample, pretreatment by centrifuging (10000 rpm) was necessary. Because the aqueous solution, however, had too low a viscosity to maintain the suspension, the sample extracted by high viscous 1-octanol was used.

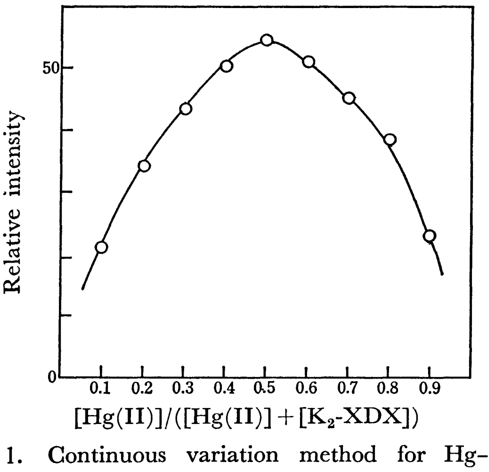


Fig. 1. Continuous variation method for Hg–XDX complex. This was obtained by means of nephelometry using the excitation at 365 nm. [Hg(II)]+[K_2-XDX]: 3.6×10^{-5} mol dm^{-3}.

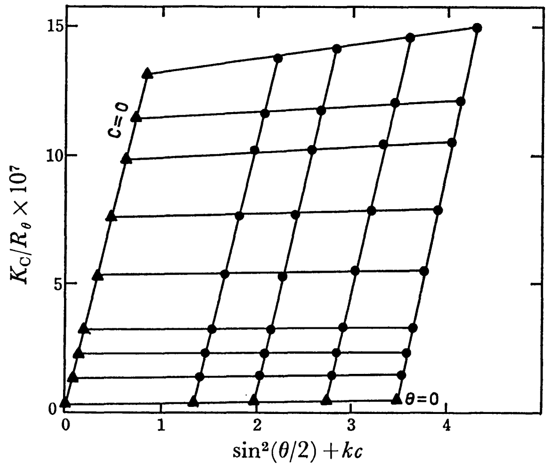


Fig. 2. Zimm plot for 1-octanol suspension of Hg–XDX complex.

From the measurements carried out on solutions ranging in concentration from 1.3×10^{-2} to 6.6×10^{-2} mg cm^{-3}, the d*n*/d*c* was calculated to be 1.65 $cm^3\ g^{-1}$. As is shown in Fig. 2, the molecular weight estimated by extrapolating into the Zimm plot was about 2×10^7. It is thus proved that the intense light scattering is due to the formation of a large molecule which can be considered to be a kind of colloid.

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