theory). Purification was accomplished by recrystallization from absolute ethanol. *Anal.* Calcd. for *trans*-[Co(*active*-stien)$_2$(CNS)$_2$]CNS·1.5H$_2$O: C, 54.37; H, 5.15; N, 14.32. Found: C, 54.66; H, 5.41; N, 14.49.

***trans*-[Co(*active*-stien)$_2$(SO$_3$)$_2$]Na·C$_2$H$_5$OH.**—*trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H$_2$O (1 g., 0.00162 mole) was dissolved in 50 ml. of boiling 95% ethanol. A hot solution of 0.8 g. of sodium sulfite (0.00635 mole) in 50 ml. of water was added and the mixture was refluxed for 30 minutes. The yellow, crystalline sulfite complex was washed with water, then with 95% ethanol and dried at 100° *in vacuo* over P$_2$O$_5$. *Anal.* Calcd. for [Co(*active*-stien)$_2$(SO$_3$)$_2$]Na·C$_2$H$_5$OH: C, 50.55; H, 5.37; N, 7.86. Found: C, 50.61; H, 5.25; N, 7.74.

[Co(*active*-stien)$_2$C$_2$O$_4$]NO$_3$·1.5H$_2$O.—A mixture of *trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H$_2$O (0.7 g., 0.00114 mole), sodium oxalate (0.7 g., 0.00217 mole), water (30 ml.) and 95% ethanol (50 ml.) was refluxed for 30 minutes. During the heating, the color of the solution changed from dark green to red, and a pink precipitate formed. The hot solution was filtered and concentrated to 15 ml. on the steam-bath. After cooling to 10°, the red crystals were filtered and washed with water and then with cold absolute ethanol. After drying over calcium chloride, the product weighed 0.65 g. (86.6% of theory). The crude material was purified by two recrystallizations from 50% ethanol. *Anal.* Calcd. for [Co(*active*-stien)$_2$C$_2$O$_4$]NO$_3$·1.5H$_2$O: C, 54.54; H, 5.34; N, 10.60. Found: C, 54.28; H, 5.14; N, 10.50.

Attempted Resolution of *racemic*-Propylenediamine.—A solution of *trans*-[Co(*levo*-stien)$_2$Cl$_2$]Cl·H$_2$O (2 g., 0.0033 mole) in 100 ml. of absolute ethanol was cooled to −60° in a Dry Ice–acetone bath, and 85% *racemic*-propylenediamine (0.6 g., 0.007 mole) was added. The color of the solution changed slowly from green to red and a yellow precipitate formed. After an hour, the precipitate was filtered and an excess of 12 *N* hydrochloric acid was added to the filtrate. The amine hydrochloride which precipitated was washed with several portions of absolute ethanol. After two recrystallizations from 50% ethanol the hydrochloride showed the specific rotation $[\alpha]^{17}\mathrm{D}$ −15°. This was approximately equal to the rotation ($[\alpha]^{17}\mathrm{D}$ −18.7°) for *levo*-stilbenediamine dihydrochloride, suggesting that propylenediamine had displaced the coördinated *levo*-stilbenediamine. This was confirmed by the melting point of the amine.

Attempted Resolution of *racemic*-Tartaric Acid. Experiment I.—A mixture of *trans*-[Co(*levo*-stien)$_2$Cl$_2$]NO$_3$·1.25H$_2$O (1.232 g., 0.002 mole) and *racemic*-tartaric acid (0.6 g., 0.004 mole) was dissolved in 300 ml. of absolute ethanol. A solution of silver nitrate (1.36 g., 0.008 mole) in absolute ethanol (100 ml.) then was added and refluxing was continued for 6 hr. The filtered solution was concentrated to 10 ml., diluted with 20 ml. of water and the precipitated tartrato complex was filtered. Barium chloride 2-hydrate (0.9 g., 0.004 mole) dissolved in water (10 ml.) was added to the filtrate and, after making it slightly alkaline with dilute aqueous ammonia, the precipitated barium tartrate was isolated. The dried sample was decomposed with dilute sulfuric acid and the precipitated barium sulfate was removed. The solution showed no rotation; resolution had not been effected.

Experiment II.—Hamilton[13] effected partial resolution of *racemic*-tartaric acid by reaction of the acid with [Co(*levo*-pn)$_2$ *active*-tart]Cl$_2$. The attempted resolution of *racemic*-tartaric acid using a similar procedure but employing [Co(*levo*-stien)$_2$ *active*-tart]NO$_3$ as the resolving agent was not successful.

A solution of [Co(*levo*-stien)$_2$*active*-tart]NO$_3$·2H$_2$O (0.3926 g., 0.000539 mole) in absolute ethanol (200 ml.) showed a rotation of −0.55°. This solution was diluted to 500 ml. and 0.134 g. of *racemic*-tartaric acid was added. The rotation of this solution was −0.24°. When the solution was refluxed for three days without change in rotation, the alcohol was removed by distillation and the residue was heated in an oven at 90° for two days. The residue, again dissolved in absolute ethanol, showed a rotation of −0.28°. The solution was then concentrated to 10 ml. and the precipitated tartaric acid was removed by filtration. An aqueous solution of this acid showed no rotation.

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[13] N. H. Hamilton, Thesis, University of Illinois, 1947.

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Solvent Shifts of Absorption Bands of 8-Quinolinol and its Zinc Chelate[1]

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Positions of the long wave length absorption maxima of 8-quinolinol and its zinc chelate were investigated as a function of solvent. Both ligand and chelate exhibited similar shifts and obeyed an equation, derived by McRae, which incorporates the polarizability and dipolar character of the solvent. The chelate reacted to some extent with dimethylformamide and was decomposed completely by N-methylformamide.

Introduction

During a study of the effects of structural changes on absorption and fluorescence spectra of 8-quinolinol (oxine) and its chelates, solubility problems often necessitated the use of different solvents. As a result, spectral shifts had to be corrected for changes in solvent before they could be assigned to structural changes.

Previous knowledge of solvent effects on the spectra of oxine was limited to the qualitative observation that oxine bands experienced a red shift in the series ethanol, chloroform and isooctane.[3] Bands for oxine chelates occurred at lower frequencies in chloroform than in ethanol.

The present study shows that, in most cases, the shifts for oxine and its zinc chelate obey an equation proposed by McRae.[4]

Results

Oxine.—Ultraviolet absorption spectra of (neutral) oxine were recorded in the range between 400 mμ and the ultraviolet cut-off of the solvent in question. The study was extended over 13 solvents ranging in refractive indices from 1.329 (methanol) to 1.457 (carbon tetrachloride). In both the earlier[3] and the present study, the reported positions of the maxima and their shifts refer to the low-frequency band of oxine, because the high-frequency peak (~250 mμ) was inaccessible in many of the solvents. In the case of oxine, the low-frequency band was found to be a composite of two pi-pi bands and the n-pi band; in the chelate,

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[1] From a thesis submitted by Orest Popovych in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology, February, 1959.

[2] Allied Chemical and Dye Fellow, 1957–1958.

[3] W. E. Ohnesorge and L. B. Rogers, *Spectrochim. Acta.*, **14**, 27 (1959).

[4] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

it was a single pi-pi band.[1] Tabulated frequency shifts are "red" relative to water, whose maximum lies at the highest frequency.

Within experimental error, the shifts of oxine bands to lower frequencies in non-polar solvents obey the equation derived by Bayliss,[5] which predicts a linear relationship between the frequency shifts in absorption spectra and the expression $(n^2 - 1)/(2n^2 + 1)$, where n is the refractive index of the solvent. Thus, in the series diethyl ether, isoöctane, n-heptane, cyclohexane and carbon tetrachloride the frequency shifts vary linearly with the above expression. However, more polar solvents including alcohols, formamides and chloroform, all lie at higher frequencies than predicted from their refractive indices by the Bayliss equation, which does not take dipole effects into account.

Qualitatively the pattern is clear. While dispersion forces (polarizability of the solvent) measured by the refractive index term are shifting the maxima bathochromically, dipolar character of the solvent molecules, determined by the dielectric constant, is working in the opposite direction, producing blue shifts.

More recently McRae[4] has derived a general expression for spectral shifts in solvents, taking into account both dispersive and permanent dipole interactions. The final approximate form of McRae's equation expresses the frequency shifts of spectral bands as a function of both the refractive index and the dielectric constant of the solvent

$$\Delta\bar{\nu} = (AL_0 + B)\left(\frac{n^2 - 1}{2n^2 + 1}\right) + C\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right]$$

In the above equation A, B and C are constants characteristic of the solute, D is the dielectric constant of the solvent, and L_0 is a function of the solvent absorption spectrum, usually taken as a constant for a given class of solvents. The first term of McRae's expression takes into consideration the dispersive forces alone and is sufficient to evaluate the spectral displacements in non-polar solvents. It obviously states the same kind of relationship as the earlier Bayliss equation. The second term expresses the contributions to spectral shifts due to permanent dipoles. For polar solvents, both the first and the second terms make a significant contribution.

To evaluate the complete picture quantitatively the above equation was applied to oxine data. Since no unsaturated solvents were used, L_0 was assumed to be a constant and the whole term $(AL_0 + B)$ was replaced by a new constant A'. The constants A' and C, characteristic of the solute, were evaluated by substituting into the equation the observed frequency shifts for diethyl ether and carbon tetrachloride. These solvents were selected because, while differing considerably in their refractive indices, they should be essentially free from hydrogen bonding, a factor not included in the theoretical treatment of McRae.

Using calculated values for A' and C which were found to be 7220 and -450 cm.$^{-1}$, respectively (red shifts are taken as positive), frequency shifts for the remaining ten solvents were calculated from the known refractive indices and dielectric constants of the solvents. Observed and calculated frequency shifts are listed in Table I. Agreement between experimental and calculated values is excellent since only two solvents, N-methylformamide and chloroform deviate from the "theoretical" results by an amount greater than the experimental error (estimated standard deviation of $\mp$ 140 cm.$^{-1}$). These large deviations may be due to factors which are either not accounted for by McRae's derivation (hydrogen bonding) or have been neglected in the final simplified form of his equation (quadratic Stark effect).

TABLE I

SOLVENT SHIFTS OF THE LONG WAVE LENGTH ABSORPTION MAXIMUM OF OXINE

Solvent	n	$\frac{n^2 - 1}{2n^2 + 1}$	D	$\bar{\nu}$, cm.$^{-1}$	$\Delta\bar{\nu}$, cm.$^{-1}$ calcd.	$\Delta\bar{\nu}$, cm.$^{-1}$ obsd.
Methanol	1.329	0.1690	33.1	31,950	900	840
Water	1.332	.1702	78.54	32,790		0
Diethyl ether	1.350	.1770	4.233	31,650	[a]	1140
Ethanol	1.359	.1804	24.3	31,850	1100	940
Isopropyl alcohol	1.378	.1872	18.3	31,650	1070	1140
1-Propanol	1.384	.1898	20.1	31,750	1090	1040
n-Heptane	1.385	.1898	1.917	31,350	1370	1440
Isoöctane	1.388	.1908	1.933	31,400	1380	1390
Cyclohexane	1.423	.2030	2.015	31,350	1470	1440
Dimethylformamide	1.428	.2046	36.71	31,650	1180	1140
N-Methylformamide	1.430	.2053	182.4	31,850	1160	940
Chloroform	1.442	.2092	4.718	31,950	1380	840
Carbon tetrachloride	1.457	.2141	2.228	31,250	[a]	1540

[a] Used for calculation of constants.

The reasons for the reduced red shifts observed in polar solvents are apparent from the form of McRae's equation applied to the present data. While in non-polar solvents the second term of the equation is approximately zero, in solvents of increasing dielectric constant it becomes increasingly negative, approaching the value of C, which for oxine is -450. The contribution of the blue shift, therefore, increases with an increase in the dielectric constant of the solvent. Although the band in question is composed of both pi-pi and n-pi components, the next section reports data showing that the resolved pi-pi bands of the chelate, which has no n-pi transition, undergo blue shifts.

Zinc Oxinate.—The low-frequency absorption band of zinc oxinate has been subjected to a similar solvent study. Unfortunately, the poor solubility of the chelate limited the investigation to seven solvents. Even then, for several solvents it was necessary to prepare saturated solutions, filter off the suspended particles and determine the absorption spectrum in 5-cm. cells. Due to the small number of solvents, constants obtained for oxine were used for calculating "theoretical" shifts for the chelate.

Absorption maxima of zinc oxinate in various solvents are listed together with observed and calculated shifts (relative to water) in Table II. Considering the fact that calculations have been done with the aid of constants characteristic of the ligand, agreement for the chelate is quite good. Chloroform and carbon tetrachloride had deviations slightly outside the limit of experimental error.

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(5) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

TABLE II

SOLVENT SHIFTS OF THE LONG WAVE LENGTH ABSORPTION MAXIMUM OF ZINC OXINATE

Solvent	$\bar{\nu}$, cm.$^{-1}$	$\Delta\bar{\nu}$ red, cm.$^{-1}$ calcd.	$\Delta\bar{\nu}$ red, cm.$^{-1}$ obsd.
Water	27,550[a]	..	0
Diethyl ether	26,460	1140	1090
Ethanol	26,380	1100	1170
Tetrahydrofuran	26,250	1230	1300
Dimethylformamide	24,880	1180	2670
Chloroform	26,380	1380	1170
Carbon tetrachloride	26,180	1540	1370

[a] Zinc oxinate 5-sulfonate.

Although the shape of the chelate spectrum was retained in dimethylformamide, the observed red shift was very great (2670 cm.$^{-1}$) compared to the calculated value (1180 cm.$^{-1}$). The abnormal bathochromic displacement indicates a profound specific interaction in addition to the usual dipole and polarization effects. Preferential solvation of zinc ions by dimethylformamide could be a likely explanation.

Further light was shed on the action of formamides on zinc oxinate by extending the solvent study to N-methylformamide (NMF). It was found that when zinc oxinate was dissolved in this solvent, it lost most of its characteristic yellow color and became non-fluorescent. Furthermore, its absorption spectrum became essentially that of the ligand in the same solvent, with a flat maximum at about 315 mμ. It was clear, therefore, that NMF caused complete decomposition of the chelate, an effect which could be attributed both to its high dielectric constant (182.4 at 225°[6]) and to specific chemical action on the zinc ion.

To investigate the latter possibility the action of NMF was tested on aluminum oxinate in the expectation that this metal should have a lesser tendency to complex with nitrogen-containing compounds than zinc. This reasoning proved to be correct when the absorption spectrum of aluminum oxinate in NMF was found to exhibit two peaks: one at 371 mμ (27,000 cm.$^{-1}$) characteristic of the chelate, and one at 317 mμ (31,600 cm.$^{-1}$) due mainly to the ligand. The solution also retained some of the fluorescence due to chelate. Obviously NMF caused only partial decomposition of aluminum oxinate into the ligand. In addition to the instantaneous decomposition that occurred during dissolution, further decomposition proceeded slowly with time, the reduction of the chelate peak occurring at a rate of about 1% per hour.

Taking advantage of the fact that oxine has practically no absorption at the maximum of aluminum oxinate in NMF, and assuming that the absorbancy indices of this chelate are essentially the same in NMF as in chloroform, approximate calculations were made which indicated that 41% of the chelate had been decomposed by this solvent.

Experimental

Oxine was recrystallized twice from hot ethanol, yielding white needles melting at 73.0–74.0°. Literature melting points, ranging from 72 to 76° are listed by Hollingshead.[7]

Zinc oxinate was prepared in the usual manner[7] and its purity checked by spectrophotometry of the ligand solution following acid decomposition.

The following solvents were used in the present study: "Pure grade" ethyl alcohol, both 95% and absolute from U. S. Industrial Chemicals; "spectrograde" isoöctane from Phillips Petroleum Co.; Eastman Kodak white label tetrahydrofuran "special for spectral use"; spectral grade isopropyl alcohol from Eastman Kodak; N-methylformamide and 1-propanol, both Eastman Kodak white label materials; absolute methanol and absolute ethyl ether from Mallinckrodt Chemical Works; cyclohexane and *n*-heptane were reagent grade solvents purified by treatment with sulfuric acid and then distillation; dimethylformamide was reagent grade solvent dried with Linde molecular sieves; reagent grade chloroform and carbon tetrachloride were used without further purification.

Unless otherwise stated, all absorption spectra were recorded on a Cary spectrophotometer Model 11 MS using 1-cm. silica cells.

Refractive indices of all the above solvents were determined at 25° on an Abbe refractometer. Dielectric constants of all liquids except tetrahydrofuran were obtained from the literature.[8] The dielectric constant of the latter was determined on a Sargent Oscillometer Model V at 25°.

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(6) G. R. Leader and L. F. Gormley, THIS JOURNAL, **73**, 5731 (1951).

(7) R. G. W. Hollingshead, "Oxine and Its Derivatives," Vols. I–IV Butterworths, London, 1954–1956.

(8) N. A. Lange, "Handbook of Chemistry," 9th Edition, Handbook Pub. Inc., Sandusky, Ohio, 1956, p. 1222.