
1006. *The Optical Behaviour of Electrolyte Solutions.*

By D. A. L. Hope, R. J. Otter, and J. E. Prue.

The sensitivity of the absorption spectra of ions to the proximity of other ions is discussed. The dependence on the ionic environment of the optical rotation or absorption of several ions has been studied, and dissociation constants obtained from some of the results. The significance of such constants is discussed.

Beer's law is obeyed by many electrolyte solutions.[1] The insensitivity of the visible absorption spectrum of the ion $Cr(H_2O)_6^{3+}$ to the ionic environment [2] led Bjerrum [3] to the conclusion that many electrolytes are completely ionised, changes with concentration of thermodynamic properties and conductance being ascribed to Coulombic forces which are without effect on the optical properties of ions. Subsequently, measurements [4] of extinction coefficients of electrolytes with an accuracy of 0·02%, revealed at some wavelengths deviations from Beer's law which would not have been detectable with earlier instruments; nevertheless, the accuracy with which in certain cases, even with highly charged ions, Beer's law is obeyed up to ionic strengths of about 0·1, shows that long-range Coulombic interaction can have only a very small effect on absorption spectra. Recently, Schläfer [5] has calculated that these interactions will cause only small shifts in the absorption bands even in concentrated solutions, and has ascribed to this cause shifts of up to 60 Å he observed for four peaks in the spectrum of manganese(II) chloride as the concentration of the solution rises to saturation (4·8M). Any change in extinction coefficients in dilute solutions must therefore be due to the effects of close encounters between ions. The maximum optical effect of the close approach of two ions arises if a new electronic transition becomes possible, as with ferric and thiocyanate ions.[6] The effect on an existing transition depends on the extent to which there is a change in the immediate environment of an orbital concerned in that transition. Thus, the visible spectra, with low extinction coefficients, of transition-metal cations are due [7] to transitions of electrons between orbitals in incompletely filled *d*-shells of the cations; these spectra are in the case of stable complex ions such as $Cr(H_2O)_6^{3+}$ and $Co(NH_3)_5H_2O^{3+}$ insensitive to ionic environment.[2,8] Smithson

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[1] von Halban and Ebert, *Z. phys. Chem.*, 1924, **112**, 321.
[2] Bjerrum, *Z. anorg. Chem.*, 1909, **62**, 140.
[3] Bjerrum, 7th Internat. Congr. Applied Chem., 1909, Section X, p. 58.
[4] Kortüm, *Z. phys. Chem.*, 1936, *B*, **33**, 243.
[5] Schläfer, *Z. phys. Chem.* (*Frankfurt*), 1956, **6**, 201.
[6] Orgel, *Quart. Rev.*, 1954, **8**, 422.
[7] Dunn, "Modern Co-ordination Chemistry" (ed. J. Lewis and R. G. Wilkins), Interscience Publishers, New York and London, 1960, p. 229.
[8] Posey and Taube, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.

and Williams[9] suggest that such spectra are appreciably affected by added anions only if these enter the co-ordination sphere of the cation. On the other hand, the charge-transfer spectra of the same cations, which occur chiefly in the ultraviolet region, with high extinction coefficients, and are ascribed to electronic transitions to or from orbitals associated with attached ligands, are more sensitive to the presence of other ions even if these do not enter the co-ordination sphere of the cation.[8] If Bjerrum had been able to extend his observations[2] on the ion $Cr(H_2O)_6{}^{3+}$ into the ultraviolet region his results would have been less clear-cut, for below 3000 Å anions exert strong specific effects on the spectrum of the ion.[10,11] It is, of course, not always possible to distinguish experimentally between a new transition and an effect on an existing one.

We now consider the results of some measurements on optical rotation and absorption. We note that changes in the absorption spectrum of an ion, particularly if close to the wavelengths at which optical rotation measurements are made, will usually result in changes in its optical rotation.[12] We also examine whether dissociation constants can be obtained from our results.

RESULTS AND DISCUSSION

Optical Rotation.—*(+)-Camphor-*10*-sulphonate anion.* Measurements were made on solutions of the acid itself and on the zinc, lanthanum, and thorium salts over the concentration range 0·03—0·15M, for both the Na-D and the Hg 5461 Å lines. The results are fitted within the limits of experimental error ($\pm 0{\cdot}010°$ for α_D, $\pm 0{\cdot}015°$ for α_{5461}) by the equation $\alpha/c = a + bc$, where α is measured rotation, c the concentration, and a and b are constants. The values of the constants obtained by the method of least squares are given in Table 1. The b terms are small and specific; the values of α corresponding to the various cations are identical within the limits of experimental error up to about 0·05M. The insensitivity of the molar rotation of the ion to the concentration and nature of the cations present is also shown by earlier measurements of Drücker[13] on the acid, and of Graham[14] on a variety of salts of singly and doubly charged cations. The implication that the optical absorption of the ion is only slightly affected by added cations is reasonable, for the absorption is due to the carbonyl group which is part of a bulky organic molecule and relatively remote from the charge-carrying sulphonate group.

TABLE 1.

(a in deg. mole^{-1} l., b in deg. mole^{-2} l.^{2}.)

	a_D	b_D	a_{5461}	b_{5461}
Acid	20·20	+1·77	27·28	−0·68
Zinc salt	20·06	−0·44	26·81	−1·21
Lanthanum salt	20·10	−0·02	27·56	−5·86
Thorium salt	19·61	+2·05	26·32	+0·86

1,9-*Bis-salicylideneamino*-3,7-*dithianonanecobalt*(III) *cation.* This univalent cation formed from a sexadentate ligand has been resolved into optical isomers.[15] The ion shows optical absorption throughout the visible region (there is a maximum at 3800 Å and a sharply rising band below 3500 Å) which causes an extremely high molar rotation of the optically isomeric ions for visible light. Measurements were made on 5×10^{-5}M-solutions of the iodide with Na-D light. A molar rotation (1/10 of the so-called "molecular" rotation) of 3500° ± 170° cm.^{2} mole^{-1} for the (+)-complex was unaffected within experimental error by adding up to 1M-sodium chloride or up to 0·5M-sodium sulphate. The

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[9] Smithson and Williams, *J.*, 1958, 457.
[10] Phipps and Plane, *J. Amer. Chem. Soc.*, 1957, **79**, 2458.
[11] Gates and King, *J. Amer. Chem. Soc.*, 1958, **80**, 5011.
[12] Kuhn, *Ann. Rev. Phys. Chem.*, 1958, **9**, 417.
[13] Drücker, *Z. phys. Chem.*, 1933, *A*, **105**, 411.
[14] Graham, *J.*, 1912, **101**, 746.
[15] Dwyer, Gill, Gyarfas, and Lions, *J. Amer. Chem. Soc.*, 1952, **74**, 4188.

addition of a tervalent ion as potassium hexacyanocobaltate(III) appeared to cause a slight decrease in the molar rotation, but this was only a little greater than the experimental error at 0·13M. In the presence of potassium ferricyanide a reaction occurs in which cyanide enters the cobalt complex,[16] but it is sufficiently slow to allow extrapolation of the results back to the time of mixing the solutions. Up to 0·2M-potassium ferricyanide was added without effect on the molar rotation of the cobalt complex. It was also found that the contributions to the rotation in mixed solutions of the (+)-complex and up to 0·1M-(+)-camphor-10-sulphonate were additive. The implication that the absorption spectrum of the complex cation is unaffected by anions is again reasonable; the visible absorption is presumably due to *d–d*-transitions, and the cobalt ion is well shielded from the approach of anions by the firmly attached and bulky ligand.

(—)-*Mandelate anion.* The mandelate ion and the acid differ markedly in their molar rotations (see Table 6), so the attachment of a proton to the carboxylate group has a marked optical effect. Measurements on sodium mandelate solutions (in the presence of a small quantity of sodium hydroxide to repress hydrolysis) showed only a slight increase of molar rotation (1%) over the concentration range 0·02—0·15M, and measurements on mandelic acid (in the presence of a small quantity of hydrochloric acid and with a small correction, always less than 1%, for ionisation) likewise showed only a small increase (2%) in the molar rotation over the same concentration range. We see from the results plotted in the Figure that the rotation of sodium mandelate solutions is very sensitive to the presence of some doubly- and triply-charged cations. The marked optical effects are probably caused by the formation of chelate complexes, and the striking absence of an effect with $Co(NH_3)_6^{3+}$ shows that the carboxylate and/or hydroxyl group of the mandelate ion have to enter the first co-ordination sphere of the cation for the optical rotation to be affected.

Optical Absorption.—We made a series of measurements of moderate accuracy (a few units %) in which the absorptions of solutions 0·023M in cupric perchlorate (plus 4 × 10^{-3}M-perchloric acid to repress hydrolysis) and 0·1M in the sodium or potassium salt of various anions were measured and compared with the sums of the separate absorptions of the ions. No enhancement of absorption occurred with added chlorate, bromate, persulphate, or dithionate, but it did in the case of the five ions listed in Table 2. Nitrite and acetate ions are known to form complexes of moderate stability with the cupric ion.[17] It seems very likely that the increased ultraviolet absorption in these and the other cases is caused by transitions in which an electron is transferred from the anion to the cupric ion; two of the six water molecules of the hydrated cupric ion are probably easily displaced,[18] and univalent copper is well known. Neither condition is fulfilled by the bivalent nickel ion, and experiments with nickel(II) instead of cupric ions showed no increased absorption with added bromide ions, and only a slight increase around 2800 Å for nitrite; the effect of acetate ion is likewise known to be small.[19] Unpublished measurements by Dr. W. G. Davies show that the effect of sulphate ions on the spectrum of both nickel(II) and

TABLE 2.

Anion	Effect
IO_3^-	Edge (2900—2700 Å) IO_3^- absorption shifted 70 Å to red
NO_2^- (0·01M)	Large increase NO_2^- maximum (3550 Å); also in Cu^{2+} visible absorption
NO_3^-	New absorption band (maximum 2600 Å)
Br^-	New absorption band (maximum 2810 Å); slight increase in Cu^{2+} visible absorption
$CH_3{\cdot}CO_2^-$	Intense absorption <3000 Å; Cu^{2+} visible absorption much enhanced

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[16] Hope and Prue, *J.*, 1960, 2782.

[17] Bjerrum, Schwarzenbach, and Sillén, " Stability Constants," *Chem. Soc. Special Publ.*, 1957, **6**, 3; 1958, **7**, 53.

[18] Basolo and Pearson, " Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 59.

[19] Pestemer and Alslev-Klinker, *Z. Elektrochem.*, 1949, **53**, 387.

cobalt(II) is slight compared with their effect on the cupric ion spectrum. There is a marked shift of the edge of the ultraviolet absorption band of the cupric ion to longer wavelengths which may be due to a new charge-transfer process or an effect on an existing one (there is a smaller but detectable effect on the visible spectrum).

We selected cupric bromide solutions for precise study. The absorption band with a maximum at 2810 Å is in a region where neither the cupric ion nor the bromide ion absorbs appreciably, there are no complications due to the hydrolysis of the anion, and earlier interpretations of spectrophotometric observations are in conflict.[20-23] We shall discuss the results in the next section, together with some measurements made on cupric sulphate solutions in continuation of earlier work.[24]

Several other electrolyte mixtures were examined. The onset of intense ultraviolet absorption by the thallium(III) ion shifts from 2300 Å to 2900 Å on addition of chloride, almost certainly because of an electron-transfer process. There was no sign of new electron-transfer bands on adding Mn(II), Co(II), or Cu(II) ions to dilute potassium dichromate solutions, or on adding Mn(II) or Ag(I) ions to dilute potassium permanganate solutions.

Incomplete Dissociation.—Suppose an ion Y, which does not absorb, influences the optical behaviour of an ion X in dilute solution; such ions will ordinarily be of opposite charge. We postulate that an equilibrium $X + Y \rightleftharpoons XY$ exists, *i.e.*, X and Y ions are divided sharply into two classes, free and associated ions. We assume that all X ions whose optical behaviour is influenced by Y ions are in the latter class, but not that all X ions in this class are affected. If the fraction of X ions in the associated class is α, we can write for an experimental molar extinction coefficient

$$\varepsilon = \varepsilon_0(1 - \alpha) + \varepsilon_1\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ε_0 is the extinction coefficient of X in the absence of Y, and ε_1 is an average over the different extinction coefficients for XY pairs (the average may include a contribution from pairs with extinction coefficient ε_0). The division between free and associated ions will be given by a thermodynamic dissociation constant K defined by

$$K^{-1} = \frac{\alpha x}{(x - \alpha x)(y - \alpha x)} \cdot \frac{f_{XY}}{f_X \cdot f_Y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x and y are the stoicheiometric concentrations of X and Y respectively, and f_{XY}, f_X, and f_Y denote activity coefficients of ions with the appropriate charges. The division is only useful, however, if the values of the activity coefficients can be expressed quantitatively as some function of the solution composition or are constant. In sufficiently dilute solution we have a choice of several equations. The Debye–Hückel equation is $-\log f_i = Az_i^2 I^{\frac{1}{2}}/(1 + BdI^{\frac{1}{2}})$, where A and B are constants of the theory, z_i is the ionic charge, I is the ionic strength (corrected for ion association), and d an adjustable parameter. The Güntelberg simplification sets $Bd = 1$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$, whilst the Guggenheim equation adds to the Güntelberg equation a term linear in the concentration of oppositely charged ions (with an adjustable parameter), and the Davies equation adds to the Güntelberg equation a term $0{\cdot}2z_i^2AI$. We can attempt to keep activity coefficients constant by additions of an inert electrolyte either in sufficient quantity to keep I constant, or, better, in swamping excess.

Cupric bromide. We postulate an equilibrium $Cu^{2+} + Br^- \rightleftharpoons CuBr^+$ with $Cu^{2+} =$ X, $Br^- =$ Y, $x = y/2$. If in our experiments the absorption is due to $CuBr^+$ alone then $\varepsilon = \varepsilon_1\alpha$; this assumption is supported by the identical shapes of plots of extinction

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[20] Doehlmann and Fromherz, *Z. phys. Chem.*, 1934, *A*, **171**, 353.
[21] Näsänen, *Acta Chem. Scand.*, 1950, **4**, 816.
[22] Farrington, *J. Amer. Chem. Soc.*, 1952, **74**, 966.
[23] Kruh, *J. Amer. Chem. Soc.*, 1954, **76**, 4865.
[24] Davies, Otter, and Prue, *Discuss. Faraday Soc.*, 1957, **24**, 103.

coefficient against wavelength for the five concentrations studied. In the analysis of the results in Table 3 (2820 Å; ε in cm.$^{-1}$ l. mole^{-1}) we assume that $\alpha \ll 1$, so

$$\varepsilon = 2\varepsilon_1 f_{\mathrm{Cu}} f_{\mathrm{Br}} x / K f_{\mathrm{CuBr}}$$

Using Guggenheim's equation for the activity coefficients, we then obtain

$$\log\left(\frac{\varepsilon}{2x}\right) + \frac{4AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} = \log\left(\frac{\varepsilon_1}{K}\right) + kx \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k is a constant and $A = 0{\cdot}509$ l.$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ at 25°. From a plot of the left-hand side of equation (3) against x we obtain ε_1/K and k. The values obtained at the various wavelengths are given in Table 4, and the third row of Table 3 shows that the results can be satisfactorily fitted in this way. The fit can be slightly improved by a shift of $-0{\cdot}4$, which is just within the estimated uncertainty, in the absolute values of ε, when the value of ε_1/K obtained are $2\frac{1}{2}\%$ less. We cannot determine separate values of ε_1 and K. All one can say is that K cannot be less than about 5 mole l.$^{-1}$, for if it were the approximation $\alpha \ll 1$ would break down; the validity of the approximation was supported by the results of some experiments in which the ionic strength was kept constant by the addition of sodium perchlorate. The value of K is higher than that of 1·06 mole l.$^{-1}$ reported by Näsänen,[21] although his value of $\varepsilon_1/K = 1396$ at 2800 Å is in fair agreement with ours. A value of the dissociation quotient reported by Farrington [22] (but see Kruh [23]) corresponds to an even lower value of K than Näsänen's. Even if K is as low as 5 mole l.$^{-1}$ the value of α at 0·025M is only 0·004, a degree of association which would be scarcely detectable by measurements of thermodynamic properties or conductance.

TABLE 3.

10^3x	42·24	25·52	17·02	11·92	7·39
ε (obs.)	39·3	26·7	20·0	15·6	11·2
ε (calc.)	39·3	27·2	20·2	15·6	10·8

TABLE 4.

10^{-1} λ (Å)	275	280	282	285	290	300
ε_1/K	1250	1310	1315	1280	1190	880
k	1·94	2·02	1·98	1·98	2·04	2·02

Cupric sulphate. In the analysis [24] of measurements at 2400 Å on pure copper sulphate solutions we postulated the equilibrium $\mathrm{Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4}$, and used the Debye–Hückel equation for the mean activity coefficient of the free ions. The experimental values of ε could be fitted equally well by several sets of values of the adjustable parameters K, ε_1, and d. This is not surprising if we remember that it has been firmly established [25,26] in the interpretation of thermodynamic properties of dilute aqueous solutions of bi-bivalent sulphates that the demarcation between free and associated ions is flexible. Presumably, the smaller the value of K (*i.e.*, the smaller the fraction of ions treated as associated), the better is the approximation of treating the associated ions as single particles of zero charge, and the worse the approximation of treating the free ions as obeying the Debye–Hückel equation, so in a plot of goodness of fit against K there is a very flat maximum. An analogous statement will remain true if we endeavour to keep the activity coefficient of the free ions constant by addition of some inert electrolyte, so it is of interest to see whether under these conditions flexibility in the values of ε_1 and $K/f_{\pm}^2$ remains. Table 5 shows the results of measurements at 2400 Å on copper sulphate in the presence of

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[25] Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.

[26] Guggenheim, *Discuss. Faraday Soc.*, 1957, **24**, 53.

sufficient sodium perchlorate to keep the stoicheiometric ionic strength at 0·044 ± 0·002 throughout (0·042 ± 0·001 if we allow for ion association). Very different pairs of values of $K/f_{\pm}^2$ and ε_1 will fit the results; in the computations a small correction was made to allow for the formation of HSO_4^- and $NaSO_4^-$, but the omission of this correction does not affect the conclusions.

TABLE 5.

$10^3[Cu(ClO_4)_2]$	$10^3[Na_2SO_4]$	$10^3[NaClO_4]$	$10^4[HClO_4]$	ε (exp.)	ε′ (calc.)	ε″ (calc.)
3·991	4·247	21·09	0·745	93·0	93·5	93·5
4·311	3·330	22·31	0·821	87·9	87·8	87·6
4·664	2·554	23·00	0·886	82·6	82·5	82·6
5·033	1·789	23·52	0·989	77·5	77·3	77·2
5·411	1·023	23·88	1·031	71·8	72·0	71·8
5·587	0·513	23·86	1·064	68·3	68·3	68·6
6·044	—	—	1·150	64·7	64·5	64·6
				ε_0	64·5	64·6
				ε_1	228·5	375·8
				$10^3K/f_{\pm}^2$	15	35

It is possible that more precise measurements over a wider concentration range would narrow the range of parameters which fit. This would require measurements at a higher ionic strength, and this we believe would tend to restrict the flexibility for the additional reason that, as the swamping inert electrolyte concentration increases, the maximum permissible ionic separation in an XY pair will get less. (At a high inert electrolyte concentration, unless a pair of X and Y ions are in or close to contact, their interaction with one another will be negligible compared with their interactions with ions of the swamping electrolyte.) Therefore, the range of acceptable ε_1 values will be narrowed. It follows that if an ε_1 value obtained from an experiment with a high concentration of a swamping electrolyte is treated as a fixed parameter in analyzing results at a low ionic strength, some values of K which would fit the results if ε_1 were adjustable will be eliminated. In this way spectrophotometric measurements [27,28] may appear to lead to lower values of dissociation constants than thermodynamic measurements. However, provided values of dissociation constants obtained from optical and thermodynamic properties correspond to the same value of the association distance they should agree; [29] unfortunately, this distance is not usually known, save in the case of dilute solutions of a single electrolyte, when it can be equated [24] to d in the Debye–Hückel equation.

In conclusion, we note that it is likely that only a small fraction of the associated cupric ions is optically affected, for although the optical behaviour of the bi-bivalent sulphates is markedly different (p. 5228),[9] the thermodynamic properties are very similar.[25] Further evidence on this point has recently come from relaxation spectrometry.[30]

Metal mandelates. In this case X is the mandelate ion and Y a cation, and the extinction coefficients in equation (1) are replaced by molar rotations R_i. The results plotted in the Figure, and measurements with different sodium mandelate concentrations and on solutions of the pure acid over a concentration range, could be fitted within experimental error by dissociation equilibria using the parameters in Table 6. Other values for the molar rotations quoted in the literature are also given. We used the Güntelberg equation for the activity coefficients of ions, except that the dissociation constants for calcium and barium mandelates were used in combination with the activity coefficient equations on which their determination depended. The value for the dissociation constant of zinc mandelate cation is in fair agreement with that of $4·5 \times 10^{-3}$ obtained from kinetic measurements by Bell and Waind,[31] which they recognise is probably too high. The

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[27] Cohen, *J. Phys. Chem.*, 1957, **61**, 1670.

[28] Davies and Monk, *J. Amer. Chem. Soc.*, 1958, **80**, 5032; Richards and Sykes, *J.*, 1960, 3632.

[29] King, Espenson, and Visco, *J. Phys. Chem.*, 1959, **63**, 755.

[30] Eigen, *Z. Elektrochem.*, 1960, **64**, 115, 196.

[31] Bell and Waind, *J.*, 1951, 2357.

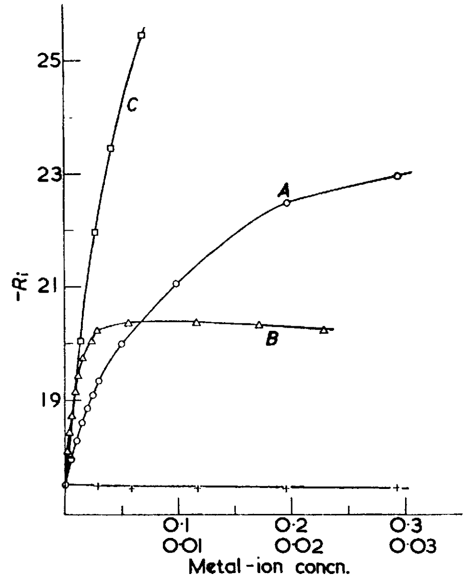
TABLE 6.

Species	K	$-R_i$(Na-D)	$-R_i$ (5461 Å)	$-R_i$ (Na-D)	$-R_i$ (5461 Å)
M^-	—	17·52 *	20·95 *	17·67 [c]	21·35 [c]
HM	3·88 [a] $\times 10^{-4}$	23·26 *	27·91 *	23·73 [c]	28·57 [c]
CaM^+	0·035 [b]	$26\cdot_2$	$31\cdot_5$	$27\cdot_6$ [b]	—
BaM^+	0·17 [a]	24	29	23 [b]	—
ZnM^+	0·003	$20\cdot_0$	$24\cdot_0$	—	—
ZnM_2	~0·2	~35	—	—	—

* Extrapolated to zero concentration (see p. 5228).

[a] Banks and Davies, *J.*, 1938, 271. [b] Davies, *J.*, 1938, 271. [c] Levene and Rothen, *J. Phys. Chem.*, 1930, **34**, 2567.

values for the dissociation constant and molar rotation of ZnM_2 are only approximate. It is to the formation of this complex and its subsequent decomposition that we ascribe the maximum in the plot for zinc perchlorate in the Figure. The effect of ZnM_2 was absent in measurements on a solution 0·0057M in sodium mandelate. The results for lanthanum perchlorate could not be satisfactorily fitted by dissociation equilibria.



Effect of added metal ions on molar rotation of sodium mandelate solution, the concentration of which is given in parentheses.

Abscissa: 0—0·3M: (*A*) $CaCl_2$ (0·026M); (*B*) $Zn(ClO_4)_2$ (0·0285M).

Abscissa: 0—0·03M: (*C*) $La(ClO_4)_3$ (0·0118M) + $Co(NH_3)_6(ClO_4)_3$ (0·0285M).

EXPERIMENTAL

Materials.—(+)-*Camphor*-10-*sulphonic acid.* This was supplied by B.D.H. Ltd., recrystallised twice from ethyl acetate, and dried ($CaCl_2$) *in vacuo.* The values of the molar rotation (+5·06° cm.^{2} mole^{-1} at 0·083M) and m. p. (193°) remained constant on further recrystallisation. A solution of the sodium salt was prepared by exact neutralisation of a solution of the acid with carbonate-free sodium hydroxide; solutions of other salts were prepared by treatment of a solution of the acid with solid oxide, excess being filtered off.

(+)- *and* (—)-*Bis*-1,9-*salicylideneamino*-3,7-*dithianonanecobalt*(III) *iodide.* This was a gift from Dr. F. P. Dwyer. The values we obtained for the molar rotations were +3500° ± 150° and —3770° ± 150° cm.^{2} mole^{-1} respectively. The value for the (+)-form depends on the presence of two molecules of water of crystallisation in the solid being taken into account. The values are some 20% lower than those reported by Dwyer *et al.*,[15] presumably because the complex slowly racemises in the solid state.

(—)-*Mandelic acid.* This was supplied by Messrs. May and Baker Ltd., and recrystallised from " AnalaR " benzene until the m. p. of 133° and the molar rotation of —22·25° cm.^{2} mole^{-1}

(0·0075M) were constant. The rotation is somewhat lower than that obtained by Levene and Rothen.[32] Following these workers a 0·15M-stock solution was kept in a refrigerator below 5°.

Sodium mandelate solutions were prepared by the exact neutralisation of the acid with a solution of carbonate-free sodium hydroxide.

Cupric bromide. This was recrystallised twice from water, dissolved in a large quantity of water (70 g. in 10 l.) in which cuprous bromide is insoluble, and filtered, and the filtrate was concentrated under a vacuum at 30° until crystals appeared; cupric bromide was then allowed to crystallise out by leaving the solution over phosphoric oxide in a vacuum. The concentration of the stock solution was determined by titration against an EDTA solution that had been standardised against a solution of cupric perchlorate analysed by electrodeposition. Other solutions were made by dilution of this stock solution; all solutions were 10^{-3}M in perchloric acid to suppress cupric ion hydrolysis.

Cupric perchlorate was made by dissolving " AnalaR " cupric oxide in " AnalaR " perchloric acid and recrystallising the product twice from water. Sodium sulphate was an " AnalaR " sample twice recrystallised from water. " AnalaR " perchloric acid was used throughout. Other reagents were of analytical reagent quality. All solutions were made up with water obtained from an ion-exchange column.[33]

Procedure.—Optical rotation. Measurements were made with a Hilger standard polarimeter with a scale graduated in 0·01° intervals. Sodium- and mercury-vapour lamps were used with suitable filters to give the Na-D line and the Hg 5461 Å line. The 20- and 40-cm. jacketed polarimeter tubes used were rinsed five times with solution before being filled, and the solution was kept at 25·00° ± 0·05° by water circulated from a thermostat tank, the temperature of which was checked against an N.P.L. calibrated thermocouple. Measurements were made in a darkened room with a shaded light source as recommended by Heller.[34] The polarimeter was checked by measurements on solutions of sucrose of organic analytical standard supplied by B.D.H. Ltd. The rotations of such solutions are accurately known,[35] and we established that the value of a rotation given by the difference of two polarimeter readings each of which was the average of at least five readings, was accurate to ±0·010° (Na-D) or ±0·015° (Hg 5461 Å).

Optical absorption. Measurements were made on solutions at 25·0° ± 0·1° with a Unicam S.P. 500 spectrophotometer, and the precise measurements on cupric bromide and sulphate were made by comparing samples of the same optical density, which we believe eliminates errors in the relative values of extinction coefficients due to stray light and multiple reflections.[24, 33] Solutions were changed without removing the cells from their holders. All stock solutions were filtered through a no. 4 glass filter to remove dust.

The cupric bromide measurements were made with cells of lengths 0·2—4·0 cm. and the nominal cell lengths were used in calculating the extinction coefficients. At 2750 and 2890 Å a small correction was made for the separate absorption of cupric and bromide ions; this never exceeded 0·35%, and was calculated from the results of measurements on concentrated aqueous solutions of cupric perchlorate and sodium bromide.

The cupric sulphate measurements were all made with a 1 cm. cell. Each value of ε is the mean of two determinations and has been corrected for the slight absorption due to the perchlorate ion. The relative values should be accurate to 0·5%, but the absolute values may be in error by several units %; they depend on a measurement against water in which stray light errors may be large, and if the setting or reading of the wavelength scale (which was untouched during the measurements) was wrong, a large error would arise owing to the steepness of the absorption band at 2400 Å.

We thank Dr. F. P. Dwyer for the gift of the cobalt complex, the British Rayon Research Association for a scholarship (D. A. L. H.), and the Department of Scientific and Industrial Research for a maintenance award (R. J. O.).

THE UNIVERSITY, READING. [*Received, July 12th,* 1960.]

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[33] Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

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