

Aquo Ion Formation

II. The First Transition Group in Ethanol

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J. Bjerrum and Klixbüll Jørgensen¹ recently studied the consecutive formation of aquo neodymium ions in alcoholic solution *. Investigations of this kind have been continued, and the present paper reports results for some of the first transition group metal ions, enabling conclusions to be drawn on the relative affinity of water and ethanol molecules to the different metal ions. After some remarks on the experimental methods in general, there follow sections on each of the divalent ions of cobalt, nickel and copper together with the relevant experimental details. Most of the theoretical discussion and the analytical applications are given in the section on cobalt(II) nitrate. A preliminary study of the hydration of bis(ethylenediamine)copper(II) ion and of the slow reactions of chromium(III) salts in aqueous ethanol is also given.

EXPERIMENTAL

A Beckman DU spectrophotometer was used for the measurements. The absorption cell chamber was thermostated at $25^{\circ} \pm 2^{\circ}$ C. With the exception of a few measurements at low concentrations, the 1 cm rectangular cells were used in the short chamber. This has the advantage that three measurements, on different solutions, can be carried out with the same adjustment instead of one as in the cylindrical cells. This is valuable for the demonstration of small relative differences in optical density at a given wavelength which is not exactly reproducible.

No special technique was used for excluding moisture from the air; the solutions were pipetted from glass-stoppered bottles, covered with latex foil, and water added from a microburette. Experiments showed that high humidities do not have significant effects. In the covered cells, the ethanol solutions concentrated by evaporation by about 2 % per hour. Effects of water have only been observed when one of the cells was filled with an aqueous solution. The comparison cell was filled with the absolute ethanol from De Danske Spritfabrikker. This ethanol was used for nearly all the solutions, and its water content determined by comparison with magnesiumdehydrated ethanol², using the optical densities of dilute $\text{Co}(\text{NO}_3)_2$ solutions in the 10 cm cells. It was found to contain 0.11 wt. % of water, *i. e.*, $0.05 M \text{H}_2\text{O}$. Dust errors were computed by comparison with some accurate values (see p. 180) for the absorption of cobalt ions in water and found to be of the order of magnitude of 0.005 in optical density, and proportional to λ^{-2} , where λ is the wavelength.

* In the following this paper is referred to as *Aquo Ion Formation I.*

Extinction coefficients were not measured in the ultraviolet because nitrate ions absorb in this region. In the near infrared, the solvents showed characteristic absorption, which is given in the section on copper(II) nitrate. This also explained an early observation that strong solutions of praseodymium nitrate in water had a regular negative molar extinction coefficient in a double band near 1 200 $m\mu$ when the comparison cell was filled with pure water. The spectrophotometer gives reproducible results out to the end of scale, 2 000 $m\mu$, but their physical significance is perhaps dubious. The narrowest possible slit-width was always used. This corresponds, according to information from the Beckman company, to an effective band-width of 5 $m\mu$ at 1 100 $m\mu$, 20 $m\mu$ at 1 200 $m\mu$ and 60 $m\mu$ at 1 300 $m\mu$, while in the visible range the band-width is about 0.5 $m\mu$.

The cobaltous nitrate used was B.D.H. Analar $\text{Co}(\text{NO}_3)_2$ with 5.5 H_2O . This partly dehydrated, rose-red powder did not resemble the usual transparent deep red crystals with 6 H_2O or more. After standing over concentrated sulphuric acid in a desiccator at 100° C for 20 hours, it contained 3.7 H_2O . The solidified mass was dissolved in ethanol, and weighed portions of the approximately 1 *M* solution diluted in graduated flasks.

Some of the copper solutions were made by dissolving known amounts of pure copper in nitric acid, evaporation nearly to dryness at 120° C and diluting with ethanol after cooling. The bis(ethylenediamine) complex was made from Merck's cupric chloride dihydrate. All concentrations in this paper are given in moles per liter.

COBALT(II) NITRATE

The much greater absorption, and correspondingly deeper red colour, of this salt in ethanol than in ethanol containing a few percent of water has been observed by Katzin and Gebert³. They explained it by nitrate complex formation, but as pointed out in *Aquo Ion Formation I*¹, it is more likely caused by the exchange of alcohol with water in the solvated cobalt(II) ions.

The total water concentration, $C_{\text{H}_2\text{O}}$, of one of the solutions, which were used for these measurements can be found from

$$C_{\text{H}_2\text{O}} = \frac{0.05 + 3.7 C_{\text{Co}} + \frac{V_w}{0.018 V_0}}{\frac{V_0 + V_w}{V_0}}, \quad (1)$$

where C_{Co} is the cobalt concentration, V_0 the original volume of the solution, V_w the volume of the added water, 0.018 the molar volume of H_2O , and 0.05 and 3.7 the quantities stated in the general experimental part. Corrections for the contraction of the ethanol by admixture of water are not, in general, necessary, since they are not more than 1 % for 10 wt. % of water, and 2 % for 40 % water, for salt free mixtures⁴. The free water concentration $[\text{H}_2\text{O}]$ is given as the difference between the total water concentration and the water bound to cobalt

$$[\text{H}_2\text{O}] = C_{\text{H}_2\text{O}} - \bar{n}C_{\text{Co}}, \quad (2)$$

where \bar{n} is the average number of water molecules bound per cobalt ion. It is assumed here, as in the previous paper¹ that the ratio $\frac{f_{\text{H}_2\text{O}}}{a_{\text{alc}}}$ between the activity coefficient of water ($f_{\text{H}_2\text{O}} = \frac{a_{\text{H}_2\text{O}}}{[\text{H}_2\text{O}]}$) and the activity of alcohol (both of which are defined as 1 in pure ethanol) remains nearly constant, even at high water concentrations. This is quite justified for salt-free solutions where

$C_{\text{H}_2\text{O}} < 20$ for methanol and ethanol, as shown by the vapour-pressure measurements of Wrewsky⁵. Therefore it is permissible to substitute in the activity expression for the uptake of the n 'th water molecule

$$K_n = \frac{a_{\text{Co}(\text{H}_2\text{O})_n^{++}} \cdot a_{\text{alc}}}{a_{\text{Co}(\text{H}_2\text{O})_{n-1}^{++}} \cdot f_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]} \quad (3)$$

concentrations for activities, since the relative ionic activities probably remain constant:

$$K_n \sim \frac{[\text{Co}(\text{H}_2\text{O})_n^{++}]}{[\text{Co}(\text{H}_2\text{O})_{n-1}^{++}][\text{H}_2\text{O}]} \quad (4)$$

In the formulae, $\text{Co}(\text{H}_2\text{O})_n^{++}$ represents $\text{Co}(\text{H}_2\text{O})_n(\text{C}_2\text{H}_5\text{OH})_{N-n}^{++}$, where N is the coordination number.

From the N consecutive formation constants, K_n , we define an average formation constant

$$K_{\text{av}} = (K_1 \cdot K_2 \cdot \dots \cdot K_N)^{\frac{1}{N}} \quad (5)$$

In systems where related ligands are exchanged, the average ligand number often corresponds closely to the statistical formula:

$$\bar{n} = \frac{N \cdot K_{\text{av}} \cdot [\text{H}_2\text{O}]}{1 + K_{\text{av}} \cdot [\text{H}_2\text{O}]}, \quad (6)$$

where $K_n = \frac{N-n+1}{n} K_{\text{av}}$. It should be noted that the average formation constant is the reciprocal water concentration when the system has reached its midpoint of formation (*viz.*, $\bar{n} = \frac{N}{2}$)

$$K_{\text{av}} = \left(\frac{1}{[\text{H}_2\text{O}]} \right)_{\bar{n} = \frac{N}{2}} \quad (7)$$

This relation is often a valid approximation, even when the assumption of statistical exchange is not correct.

In our special case, the correction $\bar{n}C_{\text{Co}}$ is quite small compared with $C_{\text{H}_2\text{O}}$. At small concentrations, for $\bar{n} < 1$,

$$\bar{n} \sim K_1 [\text{H}_2\text{O}],$$

and thus

$$[\text{H}_2\text{O}] \sim \frac{C_{\text{H}_2\text{O}}}{1 + K_1 C_{\text{Co}}}. \quad (8)$$

K_1 is about 6 liter/mole, and, therefore, at very small water concentrations, $[\text{H}_2\text{O}]$ is about 20 % lower than $C_{\text{H}_2\text{O}}$ in a 0.05 M cobalt solution, and only 2% lower than $C_{\text{H}_2\text{O}}$ in a 0.004 M $\text{Co}(\text{NO}_3)_2$. The optical estimate of \bar{n} as function of $[\text{H}_2\text{O}]$ (see Fig. 2) was used for the correction at greater water concentrations. In Fig. 1, several spectra of cobalt(II) nitrate in aqueous ethanol are shown. In the text to the figure, $C_{\text{H}_2\text{O}}$, C_{Co} and the calculated \bar{n} and $[\text{H}_2\text{O}]$ are given for each solution.

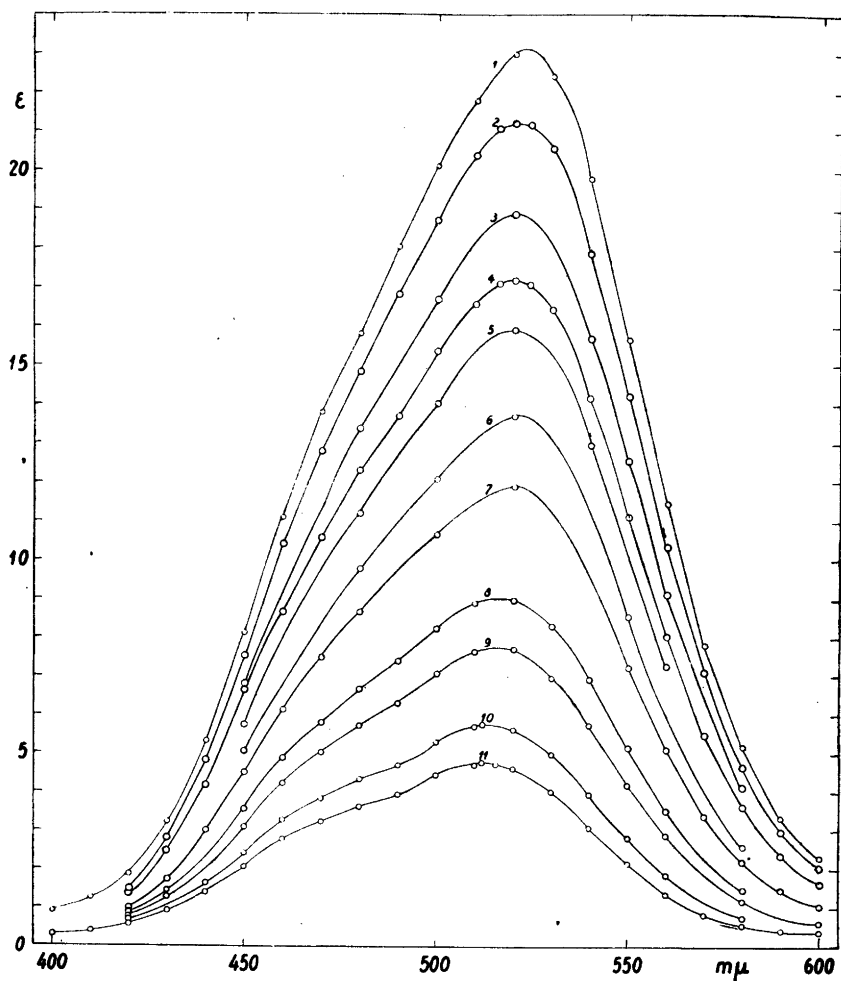


Fig. 1. Absorption spectra of cobalt (II) nitrate in aqueous ethanol at 25° C. \bar{n} and $[H_2O]$ calculated from the statistical case for $N = 6$ and $K_{av} = 1.08$.

Curve	C_{H_2O}	C_{Co}	\bar{n}	$[H_2O]$
1	0.06	0.004	0.4	0.06
2	0.20	0.040	0.9	0.16
3	0.47	0.040	1.8	0.40
4	0.63	0.040	2.2	0.54
5	0.81	0.039	2.6	0.71
6	1.13	0.039	3.1	0.99
7	1.63	0.125	3.4	1.21
8	2.66	0.123	4.2	2.15
9	3.66	0.121	4.6	3.11
10	9.2	0.108	5.4	8.6
11	55.		6.0	

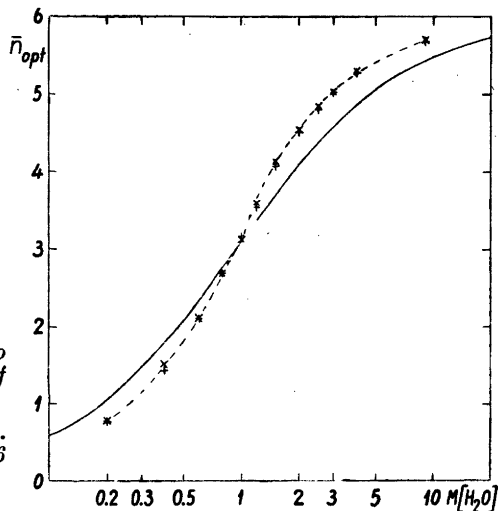


Fig. 2. Optical formation curve of aquo cobalt ions in ethanol. Logarithmic scale of free water concentration.

+ from wavelength 500 $m\mu$, \times from 520 $m\mu$. Full drawn the statistical case for $N = 6$ and $K_{av} = 1.08$.

From these spectra, and especially from the interpolated data in Table 1 (see p. 180) the average ligand number \bar{n} , which is only a second order correction for the calculation of $[H_2O]$, can be found by a method similar to that used for the hypothetical points of Fig. 2 in *Aquo Ion Formation I*, assuming that the extinction coefficients at a given wavelength are a linear function of \bar{n} . This is quite reasonable, since the spectra, as seen from Fig. 1 and Table 1, are nearly geometrical transformations of each other. Thus, a quantity \bar{n}_{opt} can be defined

$$\bar{n}_{opt} = \frac{\varepsilon_0 - \varepsilon}{\varepsilon_0 - \varepsilon_w} N, \quad (9)$$

where, for the same wavelength, ε_0 is the molar extinction coefficient in pure ethanol, ε_w in pure water and ε in the given solution. For cobalt(II) ions N is assumed to be 6 (ref. 6, p. 80, as also discussed in *Aquo Ion Formation I*). Fig. 2 is the formation curve, *i. e.* \bar{n}_{opt} as function of $\log [H_2O]$, determined at two wavelengths in order to demonstrate that the assumption was reasonable. It follows quite closely the statistical curve with $K_{av} = 1.08$ liter/mole. The deviations may be due to activity effects or non-linear variation of ε . If ε varies, *e. g.*, in an exponential way, \bar{n}_{opt} will be greater than the real \bar{n} , and the optical formation curve will be distorted. For the possible relation $\log \varepsilon = \log \varepsilon_0 - \frac{\bar{n}}{6} \log \frac{\varepsilon_0}{\varepsilon_w}$, $\bar{n} = 3$ would occur at $[H_2O] = 1.55$, corresponding to $K_{av} = \frac{1}{[H_2O]} = 0.64$ liter/mole.

Yates *et al.* have shown ⁷ by extraction experiments in octanol that perchlorates of divalent metals hydrate with over 20 moles H_2O per metal ion. This may suggest that \bar{n} would have values well beyond 6, when a water activity comparable to that of pure H_2O is reached. It is interesting in this

connection to note that the spectra of cobalt and nickel salts in octanol are not changed by increasing water concentration above 6 times that of the metal concentration. This seems to show that only very small free water concentrations are necessary to stabilize the hexaquo ions. The excess water is very likely second-sphere-water without much influence on the spectra.

Table 1. Molar extinction coefficients of cobalt(II) nitrate in aqueous ethanol.

by given [H ₂ O]	450 m μ	480 m μ	500 m μ	520 m μ	540 m μ	560 m μ
0.00	8.3	16.1	20.7	23.7	20.4	11.8
0.20	7.5	14.7	18.6	21.1	17.7	10.3
0.40	6.7	13.4	16.8	18.9	15.7	9.1
0.60	6.1	12.1	15.0	17.0	13.9	7.9
0.80	5.5	10.9	13.4	15.2	12.4	6.7
1.00	5.0	9.8	12.1	13.7	10.9	5.8
1.20	4.6	8.9	11.1	12.3	9.7	5.2
1.50	4.1	7.8	9.7	10.6	8.3	4.5
2.00	3.7	6.9	8.5	9.3	7.2	3.7
2.50	3.3	6.2	7.7	8.3	6.4	3.2
3.00	3.1	5.8	7.1	7.7	5.8	2.9
4.00	2.8	5.2	6.4	6.8	5.1	2.5
55.	2.05	3.63	4.45	4.60	3.09	1.35

Table 1 contains the molar extinction coefficients for some free water concentrations at six selected wavelengths, obtained by interpolation of several spectra of the type in Fig. 1. The data given in Table 1 are useful for analytical purposes, since the free water concentration of a given solution can be found by addition of a known amount of a nearly anhydrous standard solution of cobalt(II) nitrate, and measuring the resulting extinction. If ϵ can be determined with accuracy to 1 %, the water concentration can be found, with a mean error of 0.02 *M*, provided [H₂O] < 1. If colourless constituents in solution (*e. g.* other metal ions) also hydrate, the decrease in [H₂O] can be found from Table 1. This is the method of J. Bjerrum⁸ for optical use of a coloured complex system. The temperature-sensitive chloro-complex system of cobalt(II) has recently been used by Ayres and Glanville⁹ for determination of water in ethanol.

The last row of extinction coefficients in pure water (Table 1) was determined in this laboratory by Miss Lene Rasmussen, M. Sc., who took great care to exclude dust-errors. Her data also have analytical application, since by dilution to a large known volume with water, the cobalt content of an alcoholic solution can be spectrophotometrically determined. The agreement at different wavelengths is very good.

Media effects in solutions of low dielectric constant. To examine whether a given change in spectra by addition of water is due to the change of medium or to specific effects of water and ethanol the optical effects of addition of small quantities of water can be compared with a similar system with large amounts of an inert solvent which can be assumed not to solvate with metal ions, *e. g.* carbon tetrachloride. Since dielectric constants vary surprisingly linearly with the composition of mixtures¹⁰, it cannot reasonably be maintained that the

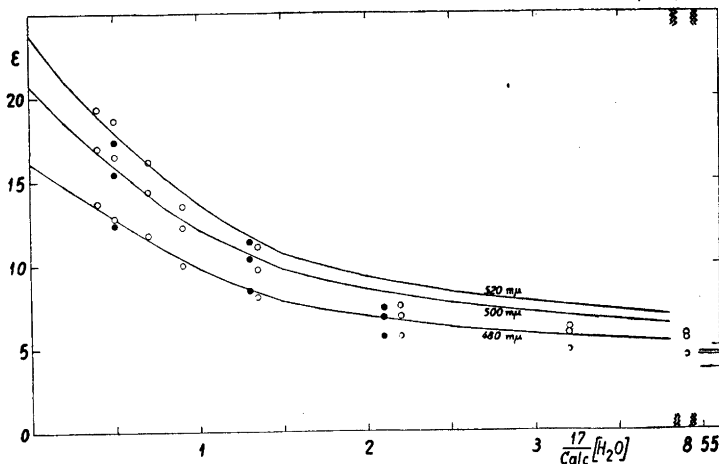


Fig. 3. Media effect of CCl_4 on ethanol-water cobalt (II) solutions. Extinction coefficients for three different wavelengths as function of $\frac{17}{C_{\text{alc}}} [\text{H}_2\text{O}]$. Full drawn curve gives the results from Table 1 without inert solvent added. Open circles for 50 volume percent CCl_4 and full circles for 75 vol. percent. At the right hand side of the figure are given the three extinction coefficients in 50 vol. percent CCl_4 , 4 M in H_2O ($\frac{17}{C_{\text{alc}}} [\text{H}_2\text{O}] = 8$) as circles, and in pure water as levels.

medium effects of a few vol. % of water can prevail at fifty or more vol. % carbon tetrachloride.

It was suggested by Professor J. Bjerrum that the relative affinity of water and ethanol to the metal ion is little changed by addition of an inert solvent. This means that the mass-action-determining factor $\frac{f_{\text{H}_2\text{O}}}{a_{\text{alc}}} [\text{H}_2\text{O}]$ in (3) can be represented by $\frac{17}{C_{\text{alc}}} [\text{H}_2\text{O}]$, where 17 is the molar concentration of pure ethanol.

In Fig. 3, ϵ is given for different wavelengths as a function of $\frac{17}{C_{\text{alc}}} [\text{H}_2\text{O}]$ in ethanol alone (full curve) and in 50 (circles) and 75 (filled circles) vol. % CCl_4 . It is seen that at higher water concentrations, the activity of water seems to be slightly greater than calculated. See especially the extinction coefficients in 4 M H_2O , 50 % CCl_4 , which is near to separating in two phases.

Salt-effects. In order to use Table 1 for determining free water concentrations, and thus for instance the uptake of water by colourless constituents of the solution, it is important to consider possible salt-effects on the cobalt spectrum which are not caused by solvate-exchange. As shown for instance by Scheffer and Hammaker¹¹ in a paper on cobalt(II) tetrafluoroborate in water, there is often an increased absorption by approximately the same percentages throughout the whole spectrum, analogous to the solvation spectra in organic

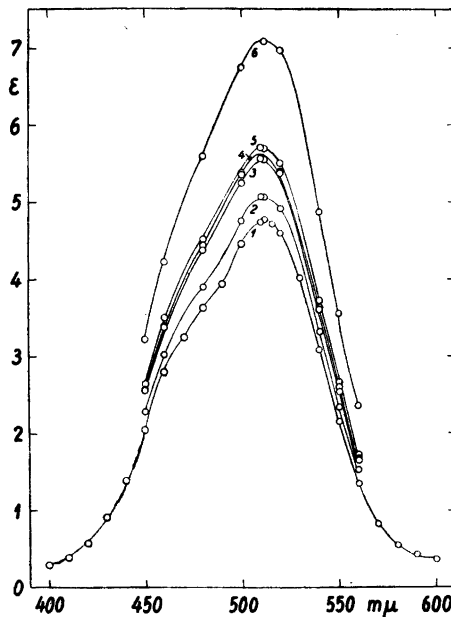


Fig. 4. Salt effects on spectrum of 0.2 M cobalt (II) nitrate in water.

Curve	Added Substances
1	none
2	8 M HClO_4
3	3.5 M $\text{Ca}(\text{NO}_3)_2$
4	6 M HNO_3
5	8 M NH_4NO_3
6	12 M HNO_3

solvents. Some spectra of solutions, 0.2 M in $\text{Co}(\text{NO}_3)_2$, are given in Fig. 4. It is seen that 6 M HNO_3 , 8 M NH_4NO_3 and 3.5 M $\text{Ca}(\text{NO}_3)_2$ each increase the absorption about 20 %, and 12 M HNO_3 about 50 % against pure water. Perchloric acid has only about a third the effect of nitric acid per mole.

It is very difficult by optical means alone to distinguish between a salt-effect and a complex formation, which is far from being complete in the strongest possible solutions of the complexing agent. The salt-effect is usually linear in the salt concentration, to a first approximation, thus:

$$\epsilon = \epsilon_0 + \epsilon_s C_s, \quad (10)$$

where ϵ_0 is the extinction coefficient in pure water, ϵ_s a constant and C_s the salt concentration. For a true complex formation:

$$\bar{n} = K_1 \cdot C_s \quad (11)$$

There may thus be postulated in complex whose extinction coefficient is

$$\epsilon_c = \epsilon_0 + \frac{\epsilon_s}{K_1}. \quad (12)$$

Such dubious complexes are the result of many unfortunate applications of Job's principle and similar methods on systems where the activities were not constant.

In our particular case, the decision between formation of nitrate-complexes or a general salt effect, greater for nitrates than perchlorates, is not easily made. But it is interesting to note that media with low dielectric constants do

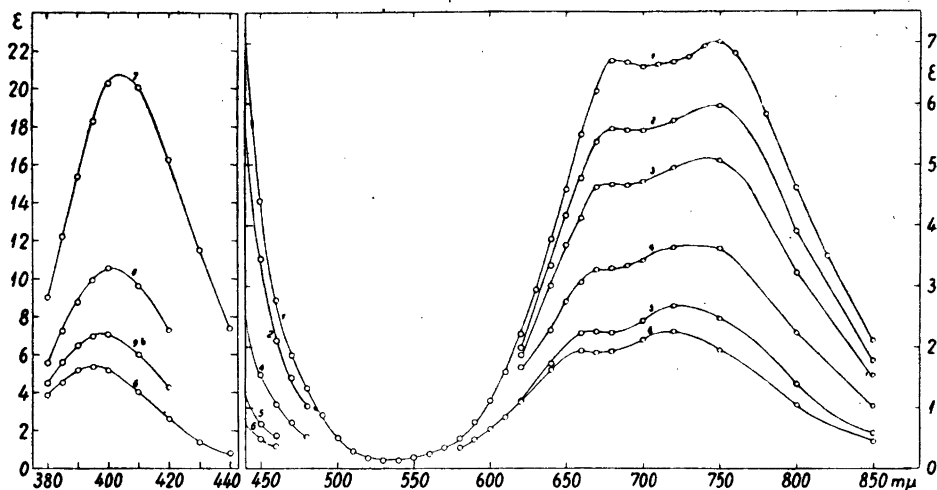


Fig. 5. Absorption spectra of nickel(II) nitrate in aqueous ethanol at 25°. \bar{n} and $[H_2O]$ calculated from the statistical case for $N = 6$ and $K_{av} = 0.82$.

Curve	CH_2O	C_{Ni}	\bar{n}	$[H_2O]$
1	0.1	0.01	0.5	0.1
2	0.5	0.11	1.3	0.35
3	1.0	0.11	2.3	0.7
4	2.1	0.11	3.5	1.7
5	10.6	0.40	5.3	8.5
6	55.	0.40	6	—
7	0.2	0.04	0.7	0.17
8	1.8	0.04	3.4	1.6
9	5.2	0.04	4.9	5.0

not alone produce optical effects (see Fig. 3) which resemble the salt effect, but that ionized salts in such media have even greater salt effects^{1,12} on the spectra than in aqueous solutions. This makes it probable that the salt effect is not due to complex formation but rather to the Stark effect from the strong electric fields from ions, since the effect $\frac{\epsilon_s}{\epsilon_0}$ per mole is roughly proportional to the reciprocal dielectric constant.

NICKEL(II) NITRATE

In absolute ethanol, nickel nitrate dissolves with a distinctly more intense yellow-green colour than in water or in 90 % ethanol. This behaviour closely resembles that of cobalt(II) nitrate, but the intensity differences are not so great. Fig. 5 shows some of the spectra. It is divided into two parts, because the band at 400 $m\mu$ is essentially higher than the bands in the red. The flat minimum in the red is preserved in the spectra of ethanol-solvates in contradistinction to the ammine complexes⁶. From the spectra a reasonable mid-

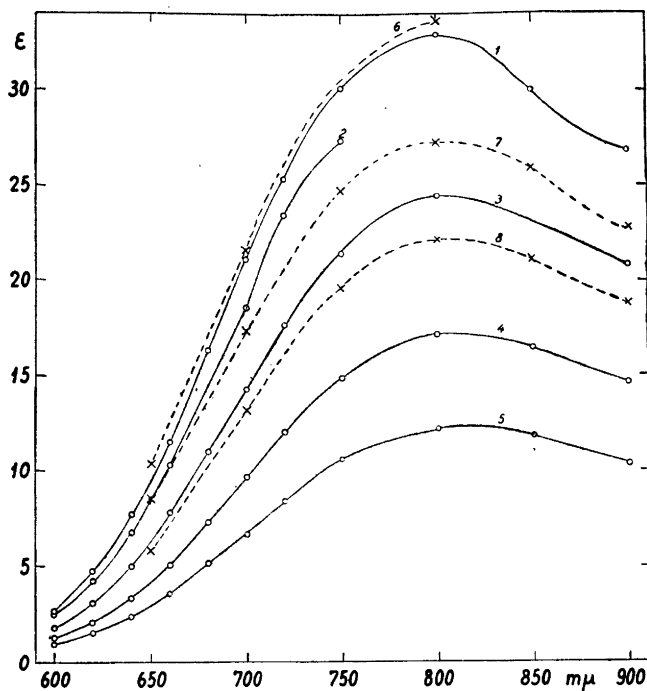


Fig. 6. Absorption spectra of copper(II) nitrate in aqueous ethanol at 25° C.

Curve	[H ₂ O]	C _{Cu}	Volume % CCl ₄
1	0.5	0.02	0
2	2.0	0.07	0
3	5.4	0.07	0
4	16.	0.06	0
5	55.	0.05	0
6	0.3	0.04	50
7	1.3	0.04	50
8	2.9	0.04	50

point of change (*i. e.* $\bar{n}_{\text{opt}} = \frac{N}{2}$) can be found at [H₂O] = 1.2, *i. e.* $K_{\text{av}} = 0.82$

liter/mole, a slightly lower formation constant than found for cobalt ions. In 62.5 vol. % CCl₄, the variations of spectra due to water addition are similar, and the relative complexity constants seem to be slightly lower than in pure ethanol. Nitrato-complex formation, which would be promoted by low dielectric constant, is thus not the cause of the change in spectra.

COPPER(II) NITRATE

This salt dissolves in ethanol with a distinctly deeper blue colour, but the changes from water addition continue even at great water concentrations. Since the CCl₄-mixtures show similar behaviour, it can be concluded that there

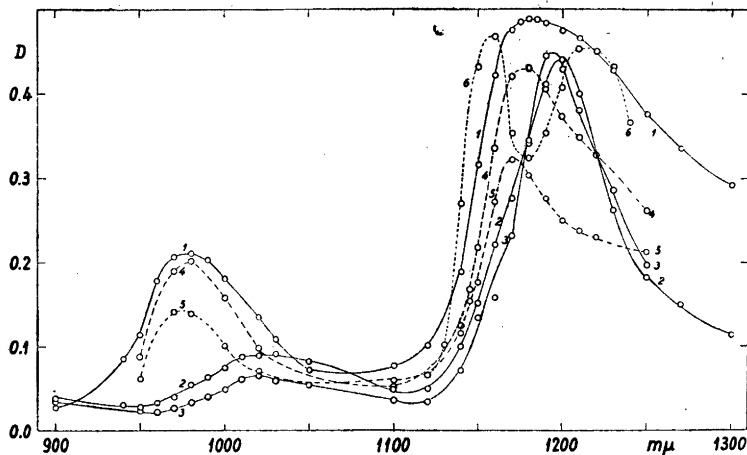


Fig. 7. Absorption spectra of solvents in the near infra-red.

Curve

- | | |
|---|--|
| 1 | Water (55 M) |
| 2 | Methanol (25 M) |
| 3 | Ethanol (17 M) |
| 4 | 4.2 M calcium nitrate (42 M H ₂ O) |
| 5 | 14 M nitric acid (22 M H ₂ O) |
| 6 | Numerical value of negative absorption of praseodymium nitrate, compared with pure H ₂ O, calculated for a 10 M solution. |

is really aquo ion formation analogous to that of Co⁺⁺ and Ni⁺⁺, but of lesser complexity.

The ethanolic solutions are unstable and on ageing deposit green-blue basic nitrates, while the free nitric acid esterifies to ethyl nitrate. Dilute copper solutions may, however, be stored for weeks without decomposition. The mixtures with CCl₄ turn bright yellow green in a few days, because the hydrolysis of CCl₄ involves chloro-complex formation.

Fig. 6 shows some spectra at different water concentrations. It is seen that the midpoint of change in spectra lies at [H₂O] = 5.3, or $K_{av} = \frac{1}{[H_2O]} = 0.19$. The extrapolated spectrum of anhydrous solution is similar to a 50 vol. % CCl₄ solution, and the cross-points in the figure show that the relative complexity is increased a little in the CCl₄-mixture.

The spectra of the solvents. It was found that Beer's law was not obeyed in the infrared by the copper solutions. This was explained as being due to absorption by the solvents themselves. Fig. 7 shows the spectra in the range 900—1 300 mμ of water, methanol, ethanol and 4.2 M calcium nitrate and 14 M nitric acid in water, all with carbon tetrachloride in the comparison cell. The bands are those which Mecke *et al.* have used¹³ for the investigation of association of water, alcohols and other hydroxy-compounds in inert solvents.

It may be seen that the double band of water is distorted by salts, and the lowered water concentration has decreased the optical density in general. Salt effects on the absorption bands of water have been studied by Suhrmann, Breyer and Ganz¹⁴. The negative extinction coefficient of $\text{Pr}(\text{NO}_3)_3$, compared with water, as mentioned p. 176, is shown on the figure for a 10 *M* solution, which according to the molar volume would nearly correspond to pure salt. When benzene was compared with CCl_4 , no difference in optical density was observed, except a very narrow band at 1 148 $\text{m}\mu$, which had an optical density of 0.680 in the 1 cm cells.

BIS(ETHYLENEDIAMINE)COPPER(II) CHLORIDE

The complex ion $[\text{Cuen}_2]^{++}$ is soluble with bluish violet colour in ethanol and reddish lilac in water, and it shows the usual effects upon addition of small quantities of water. Fig. 8 shows some spectra at different water concentrations. The cross-points refer to measurements in 50 % CCl_4 .

Bjerrum and Juhl Nielsen¹⁵ investigated the copper(II) complexes with ethylenediamine in water, and found that the third amine molecule is much more weakly bound than the first two. Since the stability of ammine complexes is not increased greatly in ethanol (compare the measurements by Rosenblatt¹⁶, which J. Bjerrum¹⁷ used for calculation of the binding of the fifth ammonia to copper in methyl glycol) the colour change cannot be caused by formation of tris(ethylenediamine)copper(II) ions, the characteristics of which would otherwise resemble the observed spectra. Experiments also show that addition of a considerable excess of ethylenediamine has no influence on the spectrum of the solution in ethanol, which was about 0.008 *M* CuCl_2 and 0.02 *M* in ethylenediamine. It was necessary to use the chloride, since the nitrate was only slightly soluble in ethanol. The change in spectra cannot be due to chloro-complex formation, since anhydrous lithium chloride does not have a very great influence on the aqueous-ethanolic solutions.

Hantsch and Robertson¹⁸ considered that $[\text{Cu}(\text{NH}_3)_4]^{++}$ contained no water of constitution, since the colour was similar in ethanol and water. This argument was partially reversed by Rosenblatt's measurements¹⁶, where the tetrammine, but not the pentammine, complex showed changes similar to those in this paper for $[\text{Cuen}_2]^{++}$ in ethanol. This ion thus exchanges at least one molecule H_2O .

According to the theory of J. Bjerrum^{12,15,17}, the maximum coordination number of divalent copper is 5, so only one H_2O molecule should exchange with one $\text{C}_2\text{H}_5\text{OH}$ molecule in the bis(ethylenediamine) complex. Because of the large extinction coefficients, it has not been possible to measure at a copper concentration high enough to utilize J. Bjerrum's principle of corresponding solutions⁸. However, the spectra in Fig. 8 are treated by the method used by J. Bjerrum¹⁹ to prove the existence of penta- and tetra-ammine copper complexes only in strong ammonia solutions. If only two copper complexes, $[\text{Cuen}_2(\text{C}_2\text{H}_5\text{OH})]^{++}$ and $[\text{Cuen}_2(\text{H}_2\text{O})]^{++}$, are present in our case, the observed spectra should be linear combinations of the two pure spectra, *i. e.* \bar{n}_{opt} (see eq. 9) should be the same for each wavelength of the spectrum, and equal to the real \bar{n} . When the three spectra of solutions 2, 3 and 4 in Fig. 8 are conside-

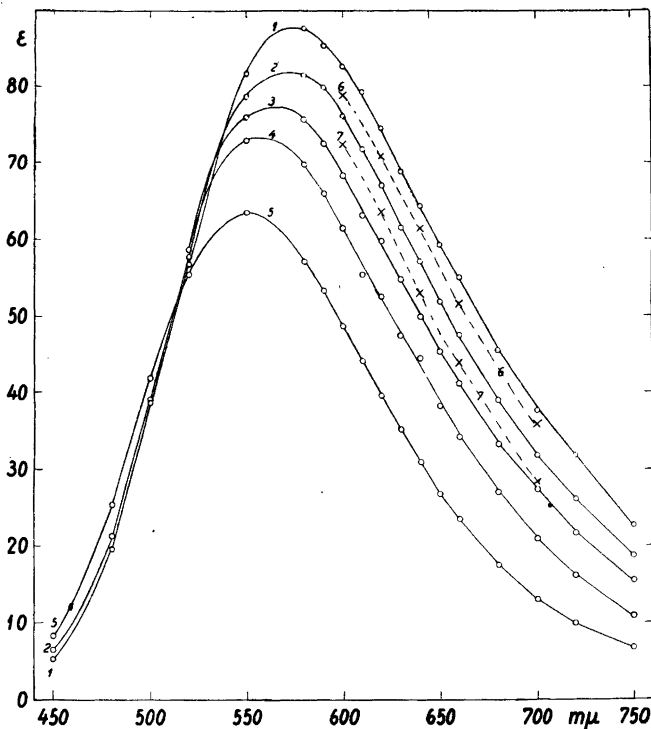


Fig. 8. Absorption spectra of bis(ethylenediamine)copper(II) chloride in aqueous ethanol at 25°C. In all cases $C_{Cu} = 0.008$ and $C_{en} = 0.02$.

Curve	$[H_2O]$	Volume % CCl_4
1	0.1	0
2	1.7	0
3	4.2	0
4	9.2	0
5	55.	0
6	0.1	50
7	1.7	50

red, we obtain $\bar{n} = 0.23, 0.43$ and 0.65 , respectively, for $[H_2O] = 1.7, 4.2$ and 9.2 . The numbers are nearly independent of wavelength when small media effects and experimental uncertainty are disregarded. It is remarkable that the formation constants K in the three cases are nearly equal, being $0.18, 0.18$ and 0.20 liter/mole. This is strong evidence for the theory of pentacovalency, since an ion with coordination number of, *e. g.*, 6 , must take the two water molecules up nearly statistically in order to explain the constant K , which then would be the real K_{av} for the two formation constants of aquo ions. In the ammonia system^{17,19}, if $[Cu(NH_3)_6]^{++}$ exists at all, it is formed at much higher concentrations of ammonia than necessary for the pentammine com-

plex, and there is no evidence for statistical behaviour after the fourth complex is formed in any ammine system of copper.

In 50 vol. % carbon tetrachloride, the anhydrous solutions seem to have a slightly lower extinction than in ethanol alone, and the relative complexity of aquo ions is slightly lower, *i. e.* $\frac{f_{\text{H}_2\text{O}}}{a_{\text{alc}}} < \frac{17}{c_{\text{alc}}}$. These solutions are unstable, since the HCl from hydrolyzed CCl_4 neutralizes the ethylenediamine.

CHROMIUM(III) SALTS

At ordinary temperatures, chromium(III) nitrate displays remarkable behaviour in ethanol, for the violet colour of the hexaaquo ions transforms to a deep green. If equal amounts of water are added to such green solutions, they turn violet again. Both processes take place over the course of several days.

Recently, Taube *et al.*²⁰ discovered that the water in $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ exchanges with oxygen-18-water, with half-times nearly proportional to the anion concentration and of a magnitude of two days at ordinary temperatures. Some preliminary experiments on the change in ethanol of hexaaquo ions to the green form show that a small spectrum change corresponding to $\bar{n}_{\text{opt}} = 5.6$ (see eq. 9) occurs 7 minutes after mixing of the strong chromium nitrate solution with ethanol at 27° C, while at 0° C it takes 360 minutes. Assuming ethanol to be the reacting agent, these data corresponds to an activation energy ~ 22 kcal/mole and a frequency factor $\sim 10^{12} \text{ sec}^{-1}$ ($C_{\text{C}_2\text{H}_5\text{OH}} = 17 M$). The activation energy is thus similar to that found by Taube *et al.*²⁰: many chromium(III) complexes²¹ have activation energies ~ 25 kcal/mole. The latter processes, leading to the green form, proceed more slowly; this is even more pronounced at low temperatures, corresponding to increasing activation energies for these processes. The curves of Fig. 9, Nos. 5—8, correspond to solutions of chromium(III) nitrate enneahydrate in ethanol with different water content, which have remained at 25° C for four days. Storage for six months does not change the spectra much. * * *

According to the measurements of N. Bjerrum²² and Brønsted and King²³, the first acid dissociation constant of $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ is about $10^{-4.0}$. The small difference in spectrum, which develops instantaneously (see curves 2 and 1) is due to the formation of monohydroxo-complexes, about 6 % and 0.07 %, respectively.

The green solutions in ethanol do not change their spectra much by addition of acids, as shown by curve 9 compared with curve 6. In ethanol, where nitric acid is a weak acid and an active oxidant, *p*-toluenesulphonic acid was used. This acid does not easily esterify with alcohols. The monohydrate of this acid was delivered chloride- and sulphate-free from L. Light & Co.

When chromium(III) salts are acidified before the reaction with ethanol, the change to the green form goes very slowly, and the problem is whether the same equilibrium solution is obtained as without acid. Such "negative hydrogen ion catalysis", *i. e.* a reaction mechanism with hydroxo-complexes, was described in the chloro-chromium(III) system by N. Bjerrum²⁴. Curves 3 and 4 show spectra at high water concentrations and containing nitric acid,

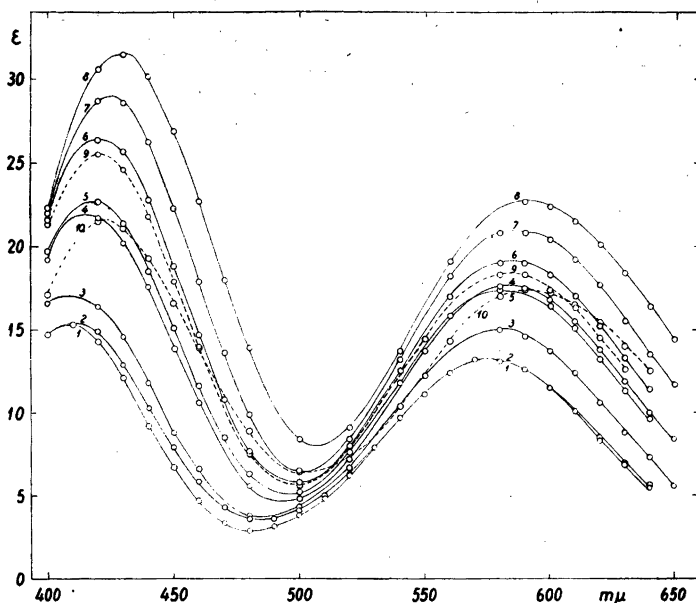


Fig. 9. Absorption spectra of chromium(III) salts in aqueous ethanol.

Curve	C_{H_2O}	C_{Cr}	Remarks
1	55	0.025	0.15 M HNO_3 , stable.
2	55	0.025	two hours after preparation, no acid added.
3	9.2	0.050	0.06 M HNO_3 , remained 17 days.
4	2.7	0.050	0.06 M HNO_3 , remained 17 days.
5	9.4	0.021	after 4 days.
6	4.2	0.023	after 4 days.
7	1.4	0.025	after 4 days.
8	0.3	0.025	after 4 days.
9	4.2	0.023	after 17 days added 0.1 M <i>p</i> -toluene sulphonic acid.
10	0.4	0.022	0.1 M <i>p</i> -toluenesulphonic acid, then reaction for 4 days.

which after 17 days are in reasonable agreement with the solvation hypothesis. But curve 10, with *p*-toluenesulphonic acid, shows that after four days the spectra resemble ethanol solutions containing no acid, but with some water. Later, however, it shifts to higher wavelengths, as the spectrum of the acidified green forms also does after some days. Nevertheless, the formation of polynuclear hydroxo chromium complexes, which react slowly with acids (*i. e.* N. Bjerrum's "latently basic chromium") is not very probable as an explanation of the optical change. The green solutions react only three times faster with four parts of 4 M HNO_3 than with four parts of pure H_2O , and even slower with 0.1 M acid than with pure water. The formation of nitrate-complexes in our case seems to be excluded, since after several days 0.15 M NH_4NO_3 has no influence on the partially green solution with 3 M H_2O .

If the various spectra between the hexaquo spectrum (curve 2) and the nearly pure green form (curve 8) are interpreted as solvate spectra, a K_{av} can be calculated, similarly to the other metal ions, to be 0.25 liter/mole, since $\bar{n}_{opt} = \frac{N}{2}$ at $C_{H_2O} \sim 4$.

Discussion of the average formation constants. In Table 2, the different K_{av} are given directly and multiplied by the ethanol concentration C_{alc} , when the aquo ion formation is half completed ($\bar{n}_{opt} = \frac{N}{2}$). The quantity $K_{av} \cdot C_{alc}$ is the numerical expression for the relative tendency of the metal ion to be bound to a water molecule rather than to an ethanol molecule. It is, therefore, independent of the concentration scale, and is used in the fifth column of the table for calculation of the standard free energy change — $\Delta G = RT \ln (K_{av} \cdot C_{alc})$ per mole H_2O .

Table 2. Average formation constants in ethanol at 25° C.

	$[H_2O]_{\bar{n}} = \frac{N}{2}$ mole/liter	K_{av} liter/mole	$K_{av} \cdot C_{alc}$	— ΔG kcal/mole H_2O
Co ⁺⁺	0.93	1.08	18	1.7
Ni ⁺⁺	1.2	0.82	13	1.5
Nd ⁺⁺⁺	3 *	0.33	5	0.9
Cr ⁺⁺⁺	4	0.25	4	0.8
Cu ⁺⁺	5.3	0.19	2.9	0.65
Cu _{en} ⁺⁺	5.5	0.18	2.7	0.6

According to Irving and Williams²⁵, the stability of complexes of the divalent transition metal ions in general increases in the direction



The results from the aquo ion formation in ethanol seem distinctly to indicate the opposite order.

SUMMARY

The spectra of divalent cobalt, nickel and copper ions in mixed solutions of ethanol and water are studied, and they are interpreted analogously to the neodymium ion spectra as being caused by solvation with ethanol and water molecules. From the spectra, estimates can be made of the water concentration, when the aquo ion formation is half complete (*i. e.* $\bar{n} = \frac{N}{2}$). The average consecutive formation constants K_{av} are given in Table 2. Salt and medium effects are discussed, and the addition of inert solvents as carbon tetrachloride shown not to disturb the specific chemical effects of water and ethanol. For the bis(ethylenediamine)copper(II) ion, a similar uptake of water is found, and it may be assumed to take place on the fifth and last coordination place of

* in CH_3OH . According to H. C. Jones the influence on the spectrum in methanol and ethanol is equal at the same water concentration.

divalent copper. For hydrated chromium(III) salts, reactions take place in ethanol, which seem to be reversible and reach equilibrium at room temperature only after some days.

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