Consecutive Formation of Aquo Metallic Ions in Alcoholic Solution

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In some cases the absorption spectra of metallic ions are distinctly different, according to the solvation. Thus, as early as 1909, Jones et al.[1] discovered that many rare earth salts in solutions of alcohol containing relatively small amounts of water showed features of the spectra in pure water as well as in pure alcohol. The phenomenon is largely independent of the anion concentration and, therefore, can be caused only by the changes in the solvation. The most remarkable case of this kind is neodymium chloride in methanol and water. Neodymium chloride in aqueous solution among many other bands has one at 427.5 mμ corresponding to a band at 429.5 mμ in alcoholic solution. We have examined this case thoroughly with a Beckman DU spectrophotometer and found, in contradistinction to the conclusion which Jones et al. draw from their measurements, that the spectra cannot be described by two juxtaposed bands with gradually changing intensity alone. This agrees well with the modern views of consecutive complex formation [2], and in this paper attention is drawn to the manner in which measurements of this kind can be used for determining formation curves of aquo ions in alcoholic solution by use of J. Bjerrum's [3] principle of corresponding solutions.

In the experiments, a preparation of anhydrous didymium chloride [4] (about 58 per cent of the total rare earth being neodymium) was dissolved in anhydrous methanol [5], and the optical density was measured at 25° C. (Curve 1 in Fig. 1). The solution was subsequently diluted with small quantities of water and measured after each addition. One part of the anhydrous solution was diluted with four parts of CH_3OH and treated analogously (Curves 2 and 4). The observed optical densities were reduced to a quantity D_{corr} by referring to a 2 cm thick layer of 0.600 molar $DiCl_3$ (or in case of the diluted solutions 10 cm of 0.120). Fig. 1 shows some of the spectra. The influence of the Di-concentration on solutions with nearly the same water concentration may be seen from curves 3 and 4.

By the principle of corresponding solutions two solutions with the same absorption spectrum have the same percentage distributions of the solvated ions and the same ligand number $\bar{n}$, i.e., average number of water molecules bound
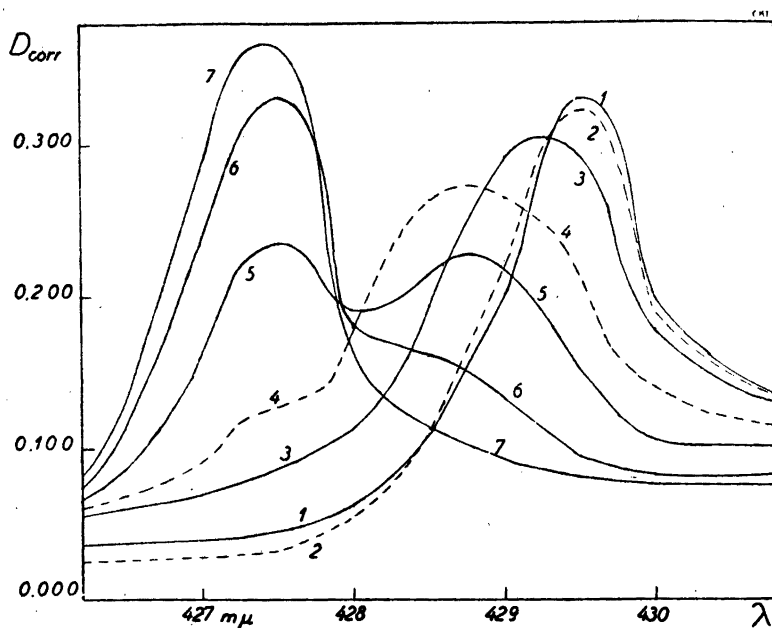
Fig. 1. The corrected optical density as function of wavelength in the interesting interval.

Curve	C_{Di}	C_{H_2O}	$\bar{n}$ (calc. from $N = 6$, $K = 0.333$)	$[H_2O]$
1	0.600	0	0	0
2	0.120	0	0	0
3	0.580	1.81	1.5	0.96
4	0.116	1.92	2.2	1.68
5	0.533	6.20	3.5	4.25
6	0.477	11.20	4.5	9.05
7	0.82	55	6	—

per metal ion, and, consequently, according to the mass action law, also the same concentration of free water, $[H_2O]$. If the total concentrations, C'_{H_2O}, C'_{Di} and C''_{H_2O}, C''_{Di}, respectively, in two corresponding solutions are known, the ligand number and the concentration of free water can be determined by the formulae:

$$\bar{n} = \frac{C'_{H_2O} - C''_{H_2O}}{C'_{Di} - C''_{Di}}, \qquad [H_2O] = C_{H_2O} - \bar{n} \cdot C_{Di}$$

Total concentrations of corresponding solutions were obtained by interpolation as previously described [3], and the data obtained by this principle plotted in Fig. 2. From the experimental points at the lowest water concentrations the first complexity constant

$$K_1 = \frac{a_{Di(H_2O)(alc.)_{N-1}} \cdot a_{alc.}}{a_{Di(alc.)_N} \cdot f_{H_2O}[H_2O]} \sim \frac{[Di(H_2O)^{+++}]}{[Di^{+++}] \cdot [H_2O]}$$
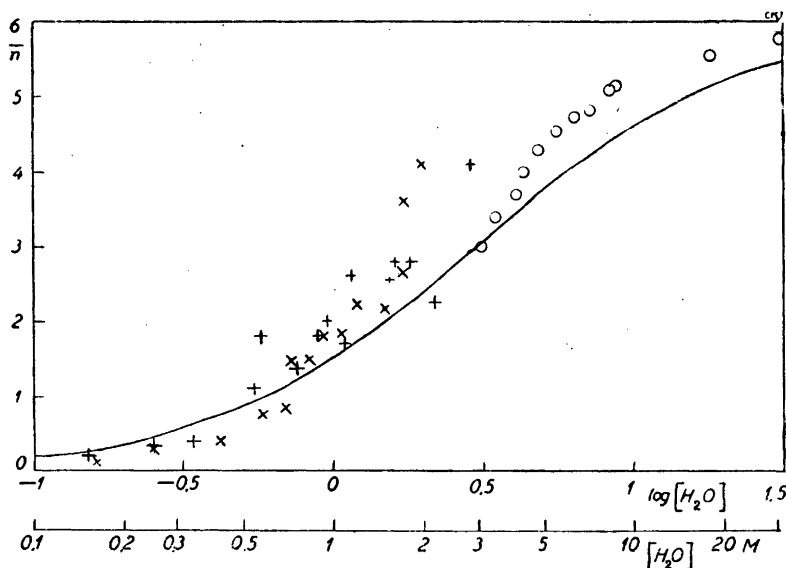
Fig. 2. Formation curve of aquo-didymium ions in methanol at 25° C. Points determined by the principle of corresponding solutions: × from the wavelength 427.5 mμ alone, + average of values for several wavelengths. Full-drawn the statistical case for N = 6 and K = 0.333. O-points from the hypothesis of relative band intensity.

is estimated to be of the order of magnitude of 1.7. For $[H_2O] \gtrsim 1$, $a_{alc.}$, the activity of alcohol, and f_{H_2O}, the water activity coefficient in alcohol, deviate measurably from 1, but vapour pressure measurements [6] show that the ratio $f_{H_2O}/a_{alc.}$ in salt-free solutions of methanol and also fairly well in ethanol is close to 1, until $[H_2O] \sim 30$ molar. For related ligands, as here, the formation curve for $\bar{n}$ as function of $\log \dfrac{f_{H_2O}[H_2O]}{a_{alc.}} \sim \log [H_2O]$, often follows the statistical formula

$$\bar{n} = \frac{NK[H_2O]}{1 + K[H_2O]},$$

where N is the coordination number, and K is the average consecutive constant. The full-drawn curve in Fig. 2 shows that $N = 6$ and $\bar{K} = \frac{1}{3}$ agrees reasonably with the data. The coordination number is possibly higher, *e.g.* 9 as in $Nd(BrO_3)_3$, $9 H_2O$,[7] but the estimated value for the 1st complexity constant $(K_1 \cong 1.7)$, which in the statistical case is equal to NK, makes $N = 6$ plausible. The o-points on the upper part of the formation curve are roughly estimated under the assumption that the integrated intensities of the water and alcohol bands in the mixed solutions are in the ratio $\bar{n}$ to $6-\bar{n}$. As a whole the experimental points correspond to a formation curve slightly steeper than the statistical curve. This may be explained by assuming that the metal ion to

some extent prefers to solvate with alcohol alone or water alone in preference
to forming mixed solvates, but the deviations may also be caused by the great
experimental uncertainty and systematic errors. Among the experimental
difficulties with the very narrow bands (which necessitate a constant slit-
width for all measurements, here 0.0125 mm) is the bad reproduction of the
wavelengths in the Beckman DU spectrophotometer. A piece of didymium
glass was placed in the third filter-place of the instrument, and the extinction
of this used as internal wavelength standard. The background in the spectra
is partly due to a trace of ferric ion, which in these strong chloride solutions
has a rather strong absorption, and also caused Jones' description of his
chloride as yellow-brown.

Cobaltous nitrate gives another example of greatly varied absorption
according to the solvation. The extinction coefficient of this salt in various
organic solvents is often many times (in ethanol 5 times) higher than in aqueous
solution, with only a slight shift of the broad band near 512 mμ towards
longer wavelengths. This was discovered by Katzin and Gebert [8], who explain
the great colour change by addition of small amounts of water as an exchange
of complex-bound nitrate ions with solvent molecules. In our opinion the main
effect consists in an exchange of solvated alcohol molecules with water, and
this view is supported by the fact that the extinction coefficients of 0.005
molar $Co(NO_3)_2$ in pure ethanol as well as in alcohol containing a few per cent
of water increase only about 10 per cent upon addition of 0.5 mole ammonium
nitrate per liter. This is not more than corresponds to a normal salt effect [9]
and excludes the possibility of nitrato complex formation. On the other hand,
some preliminary conductivity measurements show that $Co(NO_3)_2$ in ethanol
behaves as a medium dissociated electrolyte, and that the conductivity increa-
ses twice in the interesting range from 100 to 92 per cent alcohol, and totally
8 times until pure water is reached. This is a quite normal behaviour for many
strong electrolytes in ethanol, and it is to be explained mainly by ion-pair
formation. In media with lower dielectric constant this effect is more pro-
nounced. *E.g.* in 75 volume per cent carbon tetrachloride the conductivity
is about 50 times smaller than in pure alcohol. Addition of one per cent water
increases the conductivity only 2—3 times, but the colour is nearly totally
changed to the pink of the aquo ions *.

The independent behaviour of the conductivity and the absorption spectra
seems to show that the association with nitrate ions occurs outside the solvation
shell, and for this reason does not interfere much with the exchange of alcohol
with water, which determines the change in colour. It is also of interest in
this connection that Katzin and Ferraro [10] have prepared the following mixed
solvates as solid salts: $[Co(alc.)_n(H_2O)_{6-n}](NO_3)_2$ with $n = 2$, 3, 4, and 6
(alc. = t-butanol).

The formation curve of the aquo-cobaltous ions themselves is not easily
determined due to the great optical density of the more concentrated cobaltous
solutions, but the cobaltous ion, *e.g.* in ethanol, is a good indicator [3] for the
determination of the hydration of colourless ions. Using the cobaltous system

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* The solutions are becoming blue by standing, but this is due to chloro-complex formation
caused by HCl from the hydrolysis of CCl_4, which proceeds quite fast in this mixture.

as an indicator, we have found that $Th(NO_3)_4$ hydrates with $K_1 \sim NK \sim 1.5$, and perhaps $N = 8$. For $LiNO_3$ in ethanol was found $K_1 \sim 0.5$. The didymium chloride system in methanol has in a similar way been used as indicator for LiCl, which was found to bind 3 or 4 molecules of water with $K_1 \sim 1.5$. As also indicated by other methods [11], the metal ions seem to bind water molecules about 10 times $(= K \cdot C_{alc.})$ more strongly than methanol and ethanol, and only the exceptional hydrogen ion binds one water molecule much more strongly [12] $(K_1 \cdot C_{alc.} \sim 200)$.

The experiments on this subject are being continued.

SUMMARY

It is known that addition of small amounts of water to alcoholic solutions of metal salts cause characteristic changes in the absorption spectra. In some cases these changes seem independent of the anion concentration. In this paper is shown that these changes are caused by consecutive formation of aquo ions. It is also shown how spectrophotometrical measurements can be used for estimation of the relative affinity of water and alcohol molecules to the metal ions.

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