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Solvent Effects on the Formation Equilibria of Cobalt(II)-Chloride System in Acetone-Water Mixture*

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The data about cobalt(II) - chloride complexes in acetone solution have been completed by recent spectrophotometric methods ($K_3=4.5\ 10^7$; $K_4=6.1\ 10^2$). Furthermore, the influence of water addition on the system has been pointed out by considering the dielectric and donor properties of the solvent mixture. The results show a linear correlation of the complex species distribution with the reciprocal dielectric constant of the simple binary system, so that a possible explanation of the present data and of those of some oher authors has been discussed in terms of DEC influence on dissociation reactions. Donor number equality for water and acetone has made it possible to minimize the solvent influence on the ionization processes when varying water-acetone ratio.

Introduction

The complexes of the cobalt(II)-chloride system have been investigated in various molecular liquids to get information about solvent effect on formation equilibria and eventual configuration transformations.[1-9]

Since solvent influence may be due both to dielectric and electron-donor properties, we have investigated the system in mixtures of water and acetone at variable ratios. The dielectric constant values of the latter two solvents are very different from each other,[10] whereas those of DN_{SbCl_5} are about the same.[11] The fact that the two DN_{SbCl_5} values are almost equal, gives only a qualitative estimation of the coordinating affinity of the solvent both because of he donor number definiion itself and the uncertainty of the limits within which such equality can be evaluated.

The choice of such a mixture has been made on the basis of some properties of the components. First of all, it was considered that the dielectric constant of the binary system taken into examination is a linear function of the compositions, at any given ratio,[10] from which it can be deduced that the effects caused by the interactions between the mixture components are scarcely relevant. It follows that a linear correlation between the species distribution and the dielectric constant[12,13] is as more valid as smaller are the variations of other properties of the medium, mainly the donor properties. The presence in the mixture of variable quantities of water, whose donicity may vary because of the formation of hydrogen bonds, should bring to an estimate of the actual coordinating power different from that expected on the basis of DN_{SbCl_5} value. On the other hand, some observations on the cobalt(II)-chloride system behaviour in mixed solvents allow the assumption that such a difference be negligible. Even if some authors[14] assert that for cobalt(II) the affinity of some solvents follows the order

$$H_2O > MeOH > Me_2CO$$

on the basis of the analysis of the absorption bands, yet, if it is considered that in configurational equilibrium

$$^{tet}CoCl_2D_2 + 2D \rightleftharpoons {}^{oct}CoCl_2D_4\ (*)$$

the shift towards the octahedral form can be an indication of the coordinating power, from data reported in the literature the following donicity order is obtained

$$MeOH > H_2O \simeq Me_2CO$$

since in acetone-lithium chloride[2,15] and in water-hydrochloric acid[16] Cl/Co = 2 species has a tetrahedral form, whereas in methanol-lithium chloride[2] has an octahedral one. So, at least when water does not exceed a given amount (HCl 6m is necessary to obtain the cited Cl/Co = 2 species), water donicity does not seem enhanced by the hydrogen bond effect. This

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(*) CoD_6^{2+} and $CoClD_5^+$ species are octahedral, $CoCl_3D^-$ and $CoCl_4^{2-}$ are tetrahedral, undependently from the solvent.

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behaviour allows the assumption that the actual water donicity is not very different from that of acetone.

With these reservations, since the system under investigation is actually the cobalt(II)-chloride one and water concentration in water-acetone mixtures does not exceed 18% in weight, in our experimental conditions, it seems reasonable to accept DN_{SbCl_5} as an indication of the cordination power for H_2O too, as well as Me_2CO. The equality of the two values, within the above limitations, allows us not to take into consideration, at least in first approximation, the variation on the metal coordinating properties in the solvents under investigation.

The present work was carried out by absorption spectrophotometry in the visible region. Beforehand, an analysis of the species present in pure acetone was made, aiming at completing the data previously obtained by Fine,[15] by more recent methods: the straight line method[17] and Siefker mathematic method.[18]

Results

100% Acetone. Solutions with initial molar ratio (C_L/C_M) in the range from 2.0 to 3.5 were used. Such ratio represents the interval within which the equilibrium of the species characterized by complexation ratios M/L = 1:2 and 1:3, respectively,[15] can be experimentally approached. The mathematic method has allowed the determination of the concentration quotient value at the equilibrium

$$K_3 = \frac{[CoCl_3^-]}{[CoCl_2][Cl^-]} \tag{1}$$

from the absorbance values at different wavelengths reported in Table I. Such quotient, obtained from the mean of 50 values, is $(4.5 \pm 0.5)10^7$, which lies in the range previously estimated ($K_3 > 10^5$).[15]

Table I. Absorbance Values at Certain Wavelengths (A_{nm}) of the Cobalt(II) - Chloride System in Acetone for the C_M/C_L Range = $2.0 \div 3.5$ (Constant Metal Concentration, $C_M = 1.49 \times 10^{-4}$ *M*, Blank: Solvent, b = 10.00 cm, t = 25°C).

$C_L \times 10^4$ *M*	$\frac{C_L}{C_M} - 2$	A_{670}	A_{610}	A_{590}	A_{550}
2.98	0	0.360	0.320	0.200	0.102
3.74	0.756	0.425	0.265	0.280	0.070
3.96	0.983	0.440	0.250	0.305	0.065
4.26	1.285	0.465	0.240	0.335	0.035
4.49	1.512	0.490	0.243	0.345	0.037
4.87	1.890	0.490	0.245	0.343	0.035
5.25	2.268	0.500	0.255	0.337	0.032

By employing the mathematic method to the reaction

$$ML_2 + xL \rightleftharpoons ML_{2+x} \tag{2}$$

it was found x = 1. Since by the mole ratio method it was found that in the interval taken into consideration the minimum complexation ratio[15] is M/L = 1:3, it can be deduced that the metal index is 1 and, therefore, the species are mononuclear. In the calculations the quantity of L bound in ML_3 and the absorbance of such species were taken into account. It was also postulated that the side reactions are negligible in the examined concentration interval.

In 100% acetone 1:4 species could also be evidenced. Since in the all visible region the absorbance variation, as a function of the ligand concentration, is little (Table II), it was impossible to follow Asmus' method with satisfactory accuracy. The difficulty was overcome by reading the absorbance variations at two different wavelengths chosen so that one diminuishes and the other one increases by varying C_L/C_M. In this way the variations in the absorbance difference, which are clearly higher than the single variations at each wavelength, can be better appreciated.

Asmus' straightline method has been therefore applied with convenient modifications.

If the prevailing reaction is $ML_3 + L \leftrightarrows ML_4$,

$$A_1 = \varepsilon_{1M}[ML_3] + \varepsilon_{1C}[ML_4]$$

and

$$A_2 = \varepsilon_{2M}[ML_3] + \varepsilon_{2C}[ML_4]$$

are obtained per unit path length, where A_1 and A_2 are the absorbances at wavelengths λ_1 and λ_2, ε_{1M} and ε_{2M} are the molar absorptivities of reagent ML_3 at wavelengths λ_1 and λ_2, ε_{1C} and ε_{2C} are the molar absorptivities of product ML_4 at wavelengths λ_1 and λ_2. Hence, ML_1 can be expressed as follows:

$$[ML_4] = \frac{\varepsilon_{1M}A_2 - \varepsilon_{2M}A_1}{\varepsilon_{1M}\varepsilon_{2C} - \varepsilon_{2M}\varepsilon_{1C}} \tag{3}$$

if wavelengths are chosen so as $\varepsilon_{1M} \simeq \varepsilon_{2M} = \varepsilon_M$

$$[ML_4] = \frac{1}{\varepsilon_{2C} - \varepsilon_{1C}}(A_2 - A_1) \tag{4}$$

is obtained, *i.e.*,

$$\Delta A_{2\,1} = A_2 - A_1 = [ML_4](\varepsilon_{2C} - \varepsilon_{1C}) = [ML_4]\Delta\varepsilon_{2\,1C} \tag{5}$$

a relation which can be employed in the Asmus' method instead of the Lambert-Beer's relation for one absorbent species, $A = \varepsilon_i[ML_i]$, which is formally identical.

In the system under examination condition $\varepsilon_{1M} \cong \varepsilon_{2M}$ was obtained by choosing wavelengths at 575 and 605 nm, which are symmetrical to a maximum of the absorption spectrum when species ML_3 is prevailing. The molar absorptivity values, which correspond to the latter wavelengths, are similar to each other with good approximation when considering the spectrum recorded at $Cl/C_o = 6$ initial ratio, where $CoCl_3^-$ species is prevailing (Figure 1).

For the examined reaction, the function at variable ligand concentration, where the correction for the ligand bound to the metal in $CoCl_3^-$ species is applied (Figure 2), has made it possible to calculate the ligand index and the concentration quotient at the equilibrium

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Table II. Absorbance Values at Certain Wavelengths (A_{nm}) of the Cobalt(II) - Chloride System in Acetone for the C_L/C_M Range = 22.1÷82.1 (Constant Metal Concentration, $C_M = 1.20 \times 10^{-4}$ *M*, Blank: Solvent, b = 10.00 cm, t = 25°C).

$\frac{C_L}{C_M}$	$\frac{C_L}{C_M}-3$	A_{695}	A_{680}	A_{670}	A_{660}	A_{620}	A_{610}	A_{605}	A_{590}	A_{575}
12	9	0.520	0.500	0.460	0.430	0.165	0.180	0.212	0.235	0.140
22	19	0.540	0.520	0.500	0.425	0.207	0.215	0.228	0.205	0.115
32	29	0.550	0.525	0.520	0.420	0.238	0.235	0.245	0.185	0.085
42	39	0.555	0.530	0.525	0.412	0.255	0.250	0.249	0.165	0.085
52	49	0.555	0.530	0.535	0.400	0.275	0.260	0.250	0.155	0.075
62	59	0.560	0.540	0.550	0.390	0.290	0.268	0.255	0.150	0.072
82	79	0.570	0.545	0.550	0.380	0.300	0.278	0.265	0.135	0.060
102	99	0.575	0.550	0.565	0.355	0.310	0.285	0.265	0.135	0.060

$$K_4 = \frac{[CoCl_4^{2-}]}{[CoCl_3^-][Cl^-]} \quad (6)$$

which resulted to be $6.1 \cdot 10^2$ (log $K_4 = 2.78$). Such a value is in good agreement with that determined by Fine for the concentration quotient at the equilibrium in solutions in which initial molar ratios are Cl/Co > 10. Also the determination of the ligand index confirms the hypothesis, which Fine could make only on the basis of the analogy of the spectrum of the same species in other solvents, since their calculation was not possible by the mole ratio method.

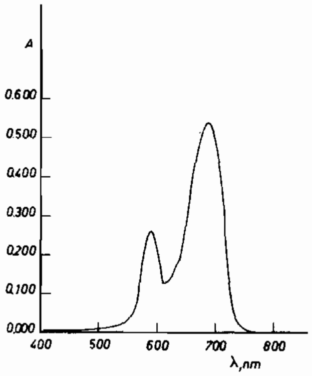

Figure 1. Absorption spectrum in 100% acetone of $CoCl_2$ 1.20×10^{-4}*M* - LiCl 4.81×10^{-4}*M* solution (blank: solvent, b = 10.00 cm, t = 25°C).

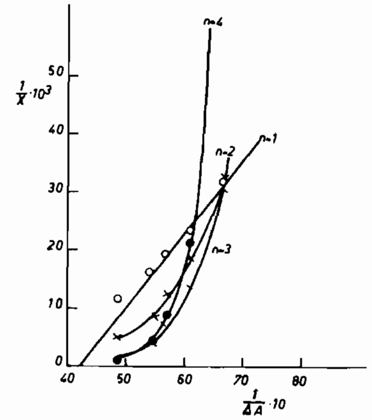

Figure 2. « Straight line » method with constant metal concentration for cobalt(II)-chloride system in 100% acetone with $C_M = 1.20 \times 10^{-4}$*M* and $C_L = (2.40\text{—}9.80) \times 10^{-3}$*M*, $X = \frac{C_L}{C_M} - 3$ ($\Delta A = A_{605} - A_{575}$, blank: solvent, b = 10.00 cm, t = 25°C).

Acetone-water Mixtures. The analysis of the species present in the Co^{II}—Cl system, when varying the composition of the water-acetone mixture, was carried out through absorption spectra.

Addition of water to the acetone solution containing constant amounts of $CoCl_2$ and LiCl($C_{Cl}/C_{Co} \simeq 50$) originates modifications in the absorption spectrum, which are markedly evident between 590 and 700 nm, as shown in Figure 3.

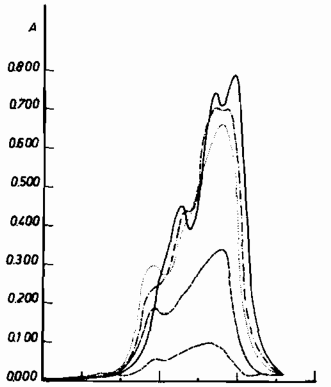

Figure 3. Absorption spectra of cobalt(II)-chloride system in water-acetone mixture at various ratios given in % weight acetone:

——————— 98
—·—·—·—·— 97
·················· 95
— — — — — — 88
·····—·····—····· 85

($C_M = 3.06 \times 10^{-4}$*M*, $C_L = 1.53 \times 10^{-2}$*M*, blank: solvent, b = 5.00 cm, t = 25°C).

An investigation has been carried out at the wavelengths corresponding to some singular points of the absorption spectrum with the precise aim of obtaining more detailed information about the solvent effect. The absorbance values at 690, 665, 625, and 595 nm are reported in Figure 4 at variable solvent composition.

Assuming that these variations are mainly due to a change in species distribution and not to molar absorptivity modifications of the single entities present in solution, an attempt to interpret the experimental optical behaviour can be made.

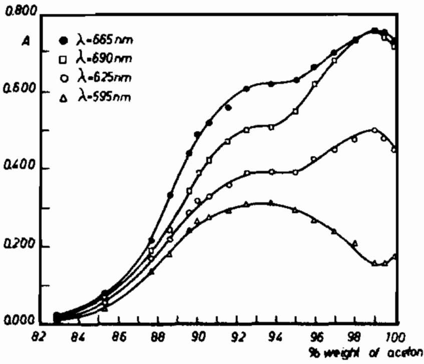

Figure 4. Absorbance values of cobalt(II)-chloride system in water-acetone mixture with $C_M = 3.06\times10^{-4}M$ and $C_L = 1.53\times10^{-2}M$ (blank: solvent, b = 5.00 cm, t = 25°C).

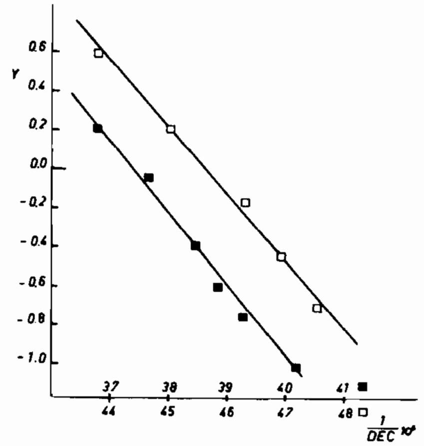

Figure 5. Variation of the function

$$Y=\log\frac{A-A^0_{n-q}}{A^0_n-A}$$

depending on DEC: ■ 87-92%, □ 95-98% weight acetone (blank: solvent, b = 5.00 cm, t= 25°C).

On examining Figure 4, it appears that by increasing the water content the absorbance at 690, 665, and 625 nm increases, reaches a maximum and then diminuishes through a horizontal inflection point down to negligible values, thus showing the disappearance of the tetrahedral species. The spectrum of the solutions (Figure 3) corresponding to the above mentioned maximum is that attributed to the 1:4 tetrahedral species and that of the inflection point to the 1:3 tetrahedral species. Moreover, in the 100%-92% acetone, the trend at 595 nm is opposite to that of the above wavelengths, according to the molar absorptivity ratios of 1:3 and 1:4 species, respectively.

It can be deduced that the reaction $(CoCl_4^{2-}) \leftrightarrows (CoCl_3^-)+(Cl^-)$ can explain the behaviour between 99% and 92% acetone, $(CoCl_3^- \rightleftharpoons (Co^{2+})+3(Cl^-)$ that between 92% and 83%, while the trend from 100% to 99% acetone is probably due to an indirect effect, as explained in the discussion section. Then, if we suppose that the solvent effect can be described by the dielectric constant variation of the binary mixture, the species distribution was analyzed at 665 nm, where the precision of the absorbance measurements is better than at the other wavelenghts, by plotting:

$$\log\frac{A-A_3^0}{A_4^0-A} \text{ versus } \frac{1}{DEC} \tag{7}$$

$$\log\frac{A-A^0}{A_3^0-A} \text{ versus } \frac{1}{DEC} \tag{8}$$

where A is the measured absorbance and A_4°, A_3°, and A° are the absorbance values at 99, 92, and 83% of acetone, respectively. The two functions are linear.

In our experimental conditions the least square method gives the expression $\log A-A_3^\circ/A_4^\circ-A=354/DEC+16.9$ in the DEC range 21.0-22.8 and $\log A-A^\circ/A_3^\circ-A=385/DEC+14.4$ in the range 24.8-27.2.

Discussion

The equilibrium of the reaction

$$CoCl_nD_m+qD \rightleftharpoons CoCl_{n-q}D_{m+q}+qCl \tag{9}$$

(where the charges are omitted) depends on several factors, such as the Co–Cl bond-breaking, the coordination power of solvent D, the anion solvation, the ions separation.

The linear correlations between species distributions and 1/DEC suggest that in our experimental conditions the solvent effect is exhibited mainly through the modification of dielectric constant.

Such a dependence is represented by expressions (7) and (8), which have been obtained on the basis of the following considerations.

In the concentration quotient at the equilibrium

$$K_n=\frac{[CoCl_n]}{[CoCl_{n-q}][Cl]^q} \tag{10}$$

$[CoCl_n]/[CoCl_{n-q}]$ ratio can be determined from optical density measures by assuming that any other absorbent species be present in negligible amount in the examined range.

The absorbances at a given wavelength of the $CoCl_n$ and $CoCl_{n-q}$ species, per unit path length, are

$$A^0_n=\varepsilon_n[CoCl_n] \tag{11}$$

$$A^0_{n-q}=\varepsilon_{n-q}[CoCl_{n-q}] \tag{12}$$

respectively. They are both extrapolated for values of the relative formation degree equal to the unit. If the examined reaction prevails all the others, the absorbance is

$$A=\varepsilon_n[CoCl_n]+\varepsilon_{n-q}[CoCl_{n-q}] \tag{13}$$

and the mass balance is

$$[CoCl_n]+[CoCl_{n-q}]=C^\circ \tag{14}$$

where C° is the total concentration of cobalt present in solution.

From the combination of relations (11), (12), (13), and (14)

$$\frac{[\mathrm{CoCl_n}]}{[\mathrm{CoCl_{n-q}}]}=\frac{\mathrm{A}-\mathrm{A}^{0}_{n-q}}{\mathrm{A}^{0}_{n}-\mathrm{A}} \tag{15}$$

is obtained, which, if replaced in (10), gives

$$\log\frac{\mathrm{A}-\mathrm{A}^{0}_{n-q}}{\mathrm{A}^{0}_{n}-\mathrm{A}}=q\log[\mathrm{Cl}]+\log \mathrm{K}_n \tag{16}$$

where $\log[\mathrm{Cl}]$ = constant since $[\mathrm{Cl}]\gg[\mathrm{Co}]$. A linear dependence is obtained between $\log \mathrm{A}-\mathrm{A}^{\circ}_{n-q}/\mathrm{A}_n^{\circ}-\mathrm{A}$ and I/DEC, when expressing $\log \mathrm{K}_n$ as a function of the dielectric constant according to Denison and Ramsey's relation[19]

$$\log \mathrm{K}=\log \mathrm{K}_0+\frac{\mathrm{B}}{\mathrm{DEC}} \tag{17}$$

where K_0 is related to the ionization process of the considered species and B is a proportionality constant depending on temperature, charges of species, and interatomic distances.

The absorbance variations which appear in the cobalt(II) - chloride system by varying DEC of the solvent mixture can be interpreted qualitatively by examining the following set of reactions.

$$\mathrm{LiCl}\rightleftharpoons\mathrm{Li^+}+\mathrm{Cl^-} \tag{18}$$

$$\mathrm{CoCl_4Li_2}\rightleftharpoons\mathrm{CoCl_4Li^-}+\mathrm{Li^+} \tag{19}$$

$$\mathrm{CoCl_4Li^-}\rightleftharpoons\mathrm{CoCl_4^{2-}}+\mathrm{Li^+} \tag{20}$$

$$\mathrm{CoCl_4^{2-}}+\mathrm{D}\rightleftharpoons\mathrm{CoCl_3D^-}+\mathrm{Cl^-} \tag{21}$$

$$\mathrm{CoCl_3D^-}+\mathrm{D}\rightleftharpoons\mathrm{CoCl_2D_2}+\mathrm{Cl^-} \tag{22}$$

$$\mathrm{CoCl_2D_2}+4\mathrm{D}\rightleftharpoons\mathrm{CoD_6^{2+}}+2\mathrm{Cl^-} \tag{23}$$

Neglecting ionic radius variations, the increase of DEC facilitates the reactions of heteronomous charge separation (18), (19), (20), and (23), while the separation reaction of homonimous charges (21) decreases, and reaction (22), which does not bring to the separation of charges, remains scarcely unaffected by DEC variation. By assuming that the dissociation of LiCl (18) in pure acetone is not complete,[20] the initial increase of DEC facilitates it and it causes also an increase in the dissociation constant of (19) and (20), whereas it reduces the dissociation constant of (21); reactions (22) and (23) are initially negligible because of LiCl excess. Moreover, the mass effect due to the formation of $\mathrm{Li^+}$ and $\mathrm{Cl^-}$ from (18) opposes (19) and (20) and reduces (21). The result is an increasing effect on the formation of Co/Cl = 1:4 species which explains the initial absorbance increase (Figure 4).

When increasing the dielectric constant beyond the values at which reaction (18) is complete, the mass effect due to $\mathrm{Li^+}$ and $\mathrm{Cl^-}$, which are in constant excess with respect to the total amount of cobalt, is missing.

If the charge density of $\mathrm{CoCl_4^{2-}}$, higher than that of $\mathrm{CoCl_3D^-}$, is considered, the dissociation constant increase in reactions (19) and (20) should be prevaling whith respect to the decrease in (21). The mass effect due to the formation of $\mathrm{CoCl_4^{2-}}$ from reaction (20) makes reaction (21) shift to the right, thus going against its dissociation constant decrease. The absorbance decrease is probably due to the formation of $\mathrm{CoCl_3^-}$ species from $\mathrm{CoCl_4^{2-}}$ and $\mathrm{CoCl_4Li^-}$.

From the above considerations about reactions (20) and (21) it follows that the concentration quotient $\mathrm{K_4}$ is given by the expression

$$\mathrm{K_4}=([\mathrm{CoCl_4^{2-}}]+[\mathrm{CoCl_4Li^-}])/[\mathrm{CoCl_3^-}][\mathrm{Cl^-}]$$

The values calculated from $(\mathrm{A}-\mathrm{A_3^{\circ}})/(\mathrm{A_4^{\circ}}-\mathrm{A})$ divided by the constant chloride concentration correspond to the above expression with the assumption that molar absorptivities of $\mathrm{CoCl_4^{2-}}$ and $\mathrm{CoCl_4Li^-}$ are equal.[21]

After the complete formation of Co/Cl = 1:3 species a further increase in DEC values causes a correspondent increase in the dissociation constant of reaction (23), while reaction (22) is not mainly affected by DEC variations. Hence, calculated quotient β_3 is referred to reactions (20) and (21), but since $\mathrm{CoCl_2}$ species shows a non-negligible molar absorptivity at the examined wavelenght, (A–Å) / $(\mathrm{A_3^{\circ}}-\mathrm{A})$ ratio is equal to $[\mathrm{CoCl_3^-}]/[\mathrm{Co^{2+}}]$ only when the absorption of $\mathrm{CoCl_2}$ species can be neglected. With the above reservations, the extrapolation of $\mathrm{K_4}$ and β_3 to the pure solvents can only give values non consistent with those found directly in these two solvents.

By adding water to the solvent mixture, the increase in $\mathrm{Cl^-}$ solvation[22] can also qualitatively explain the trend of Figure 4. While solvation has not the same influence as DEC on the single reactions from (19) to (23), the overall effect can be the same. The increase in LiCl disociation takes place by making (19), (20), and (21) shift to the left. Also the absorbance is increased. When LiCl dissociation is completed, further water additions shift to the right first reaction (21) and then reactions (22) and (23), thus decreasing the absorbance through the two observed steps. Both DEC and solvation play an important role in determining species distribution while a separation of the two effects seems impossible.

In can be also observed that reaction (23) undergoes a configurational transformation. This is confirmed by the absorption decrease in the 600-700 nm region and by the appearance of bands in the 500-550 nm region typical of octahedral cobalt complexes. Therefore, it can be deduced that the octahedral structure of cobalt in water-acetone is stable at 25°C only when at least two $\mathrm{Cl^-}$ are present in the coordination sphere of cobalt, thus confirming that $\mathrm{Cl^-}$ causes cobalt to undergo the octahedral-tetrahedral transformation.[23]

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The proposed set of reactions for the $CoCl_2$–LiCl system in various water-acetone mixture can also explain the results obtained by other authors. The conductivity of the acetone solutions of $CoCl_2$[1,24] increases upon addition of LiCl up to $CoCl_2/LiCl = 1$, *i.e.*, Co/Cl = 1:3, then it gradually decreases. Gröh explains this effect by the formation of the 1:4 species,[24] while Wormser[1] excludes such a possibility. Not taking into account the different charge densities of $CoCl_4^{2-}$ and $CoCl_3^-$, the latter author assumes that the $CoCl_4Li_2$ and $CoCl_3Li$ dissociations are equal. In this way the formation of the 1:4 species would result in an increase in solution coductivity. Furthermore, Wormser has examined $CoCl_2$ in acetone solution without addition of LiCl. In these conditions the 1:3 species was found prevailing.

The observed low stability of the 1:4 species can explain these results. In the absence of LiCl excess only the 1:3 species could be determined. The decrease in conductivity in the $LiCl/CoCl_2 = 1-5$ range, then, confirms the partial LiCl dissociation.

Our proposed scheme justifies also what Katzin and Gebert reported[2] on the absorbance variations of $CoCl_2$ acetone solution, without LiCl excess by water addition. They found an absorption decrease in the entire spectrum which can be attributed to the increase in the dissociation constant of reaction (23). Moreover, the spectrum approaches that of $CoCl_3^-$. This effect can be understood when considering that, for the above mentioned reasons, the dissociation constant of reaction (22) does not vary with DEC or, at least, does not increase in the same entity as that of (23). Moreover, the mass effect caused by addition of LiCl excess gives more evidence to the spectrum of the 1:3 species rather than to that of the 1:2 species.

The 1:4 species in acetone has been also found by Katzin and Gebert by the continuous variation method at 620 nm, despite the low stability of this species and the fact that the above method does not necessarily solve a system where several species are present.

Finally, our results in pure acetone, where reaction (23) is less extensive because of low DEC values, have allowed the identification of reaction (22) independently from (23). On the contrary, DEC increase upon water addition makes reactions (22) and (23) not to be distinguished.

Experimental Section

All the solutions were prepared in a dry box under dry nitrogen atmosphere, using analytical grade products, which were previously dried. Acetone was dehydrated and purified in the usual manner.[25] Anhydrous cobalt(II) chloride was obtained by dehydration of $CoCl_2 \cdot 6H_2O$ at 110°C for 16 hours.

The water content of the used solutions was determined by the dead stop end point method using Karl Fischer reagent[26] and resulted to be less than 0.05%, except when water was added.

Visible spectra were recorded at 25±0.1°C on Beckman DU and DK-2A spectrophotometers using 5.00 and 10.00 cm quartz cells.

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