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Spectrophotometric study of cobalt(II) chloride complexes in ethanol and propan-2-ol

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Abstract

A spectrophotometric investigation of cobalt(II) chloro complexes was carried out in ethanol and propan-2-ol at 25 °C and at constant ionic strength of 1 mol l⁻¹. Three mononuclear complexes are identified in both the solvents: CoCl⁺, CoCl₂ and CoCl₃⁻ and the respective apparent overall stability constants are calculated. The calculated values in ethanol are: log β₁=1.3, log β₂=2.8, log β₃=4.1; in propan-2-ol: log β₁=1.7, log β₂=3.3, log β₃=4.7. Stability is higher in the higher alcohol. Individual electronic spectra of all species in both the solvents are calculated and reported here for the first time.

Introduction

The colour change of cobalt(II) chloride solutions from pink to blue is well known and numerous qualitative studies of this phenomenon are widely used to demonstrate the principle of Le Chatelier. We cite here only some of the recent studies on the qualitative aspects of this system [1–3].

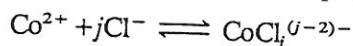
Quantitative investigations were undertaken by Katzin and Gebert in solution [4] and in the solid state [5], who reported the presence of two complexes in solution: the di- and the trichloro complex with the possibility of the presence of the tetrachloro complex in solution of excess chloride concentration. They assigned different bands to specific complexes and concluded that various blue forms have tetrahedral groupings. Identical complexes but with different absorption bands assigned to them have been reported by Fine [6] who also calculated their stepwise formation constants. Cotton *et al.* [7] studied Co(OH)₂ in concentrated alkali metal hydroxides concluding that [CoX₄]²⁻ ions are not obtained, or only partially obtained, in aqueous solutions of cobalt(II), even when saturated with HX or LiX (X=Cl, Br, I). Trutia and Musa [8] have shown that Co²⁺ is tetrahedrally coordinated in ethanol, and in methanol Bkouche-Waksman correlates polarisation properties in terms of stability of compounds of the form CoCl₂ [9].

Benali-Baitich and coworkers [10] have studied in detail the chloro complexes of transition metals in perchloric acid aqueous medium and report four species: {Co(H₂O)₆}²⁺, Cl⁻, Co(H₂O)₆²⁺ absorbing at 340 nm, {Co(H₂O)₆}²⁺ absorbing at 360 and 315 nm, [Co(H₂O)₅Cl]⁺ with absorption bands at 530, 480, 250 and 208 nm, and [CoCl₄]²⁻ which absorbs at 690, 665 and 625 nm. They calculated the formation constant of the first complex, whose value is quite different from that calculated by Fine. They also indicate that [CoCl₄]²⁻ formed in solution does not exceed 2.5%, even in concentrated solutions. Zeltmann *et al.* [11] have also postulated, in addition to the hexaaqua ion, four complexes viz. [Co(H₂O)₅Cl]⁺, [Co(H₂O)₄Cl₂]⁺, [Co(H₂O)₃Cl₃]⁺ and [CoCl₄]²⁻ in hydrochloric acid solutions up to 16 molality. Bjerum and coworkers [12, 13] studied this system in strong aqueous chloride solutions, identifying four cobalto complexes and calculated the stability constants. For the first complex their value of log K₁=1.34 is nearly the same as calculated by us in ethanol. On the other hand, Licheri *et al.* [14] in an X-ray diffraction study of MeCl₂ solutions (Me=Co, Ni) characterise only the complex [Me(H₂O)₅Cl]⁺ with the possible presence of higher complexes.

We have already reported the results of chloro complexes of copper(II) in different protic and aprotic solvents and more recently in a specific class of solvents

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such as alcohols [15–18]. In this paper, we present the results of cobalt(II) chloro complexes in ethanol and propan-2-ol at constant ionic strength of 1 mol l⁻¹ and at 25 °C. Apparent overall stability constants, β_j , have been calculated for the equilibrium



$$\beta_j = \frac{[\text{CoCl}_j^{(j-2)-}]}{[\text{Co}^{2+}][\text{Cl}^-]^j}$$

from a spectrophotometric study in the UV and visible region.

Although this solution equilibrium has already been studied before, this work presents a first quantitative attempt at determining the stability constants as well as the electronic spectra of all species present in solution. The complexes have been studied specifically in alcoholic medium with a view to compare, eventually, their stability and spectra with those of the copper(II) and nickel(II) chloro complexes. The latter are under investigation in our laboratory whereas we have already reported the results of copper(II) chloro complexes. These complexes especially in the alcohols are actually been studied in medical circles in connection with Wilson's disease concerning the fixation of copper in liver.

Experimental

Ethanol and propan-2-ol pro analysis (Merck) were used without further treatment. Stock solutions of salts were prepared from LiCl, LiClO₄ and Co(ClO₄)₂·6H₂O, all Fluka, p.a. products and the preparation of mixtures was carried out by dilution. The presence of a small amount of water due to cobalt perchlorate hexahydrate has no appreciable effect on the absorption spectra. The absorption variations were measured with a Beckman UV 5230 spectrophotometer and the spectrophotometric reference solution was 1 mol l⁻¹ LiClO₄ in ethanol and in propan-2-ol. The analytical concentration of the metal with respect to that of the ligand was kept very low and the possibility of the formation of polynuclear complexes is thus neglected. The final analytical concentration of cobalt was fixed at 5 × 10⁻³ mol l⁻¹, that of ligand varied from 2.5 × 10⁻⁴ to 1.0 mol l⁻¹. The numerical calculations based on least-squares method were carried out on an IBM 3090 computer at the Université Louis Pasteur, Strasbourg.

Results and discussion

The experimental spectra of the cobalt(II) chloride solutions in ethanol and propan-2-ol are shown in Figs. 1 and 2, respectively.

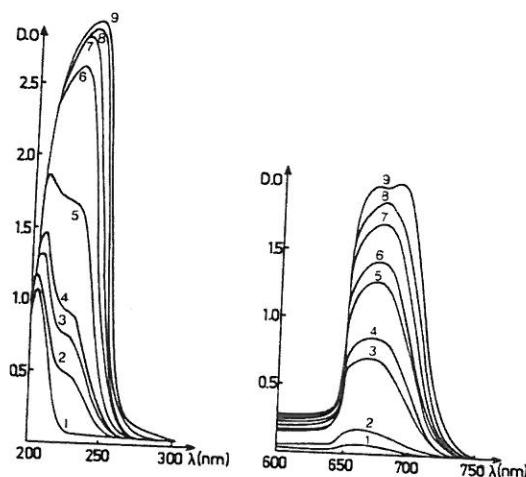


Fig. 1. Absorption spectra of cobalt(II)-Li⁺(Cl⁻, ClO₄⁻) 1 M solutions in ethanol: [Co^{II}] = 5 × 10⁻³ mol l⁻¹, *l*_{cuve} = 1 cm. [Cl⁻] (mol l⁻¹): (a) UV: 1, 0; 2, 0.005; 3, 0.008; 4, 0.01; 5, 0.02; 6, 0.03; 7, 0.04; 8, 0.08; 9, 1.0; (b) visible: 1, 0.01; 2, 0.02; 3, 0.04; 4, 0.05; 5, 0.08; 6, 0.1; 7, 0.2; 8, 0.6; 9, 1.0.

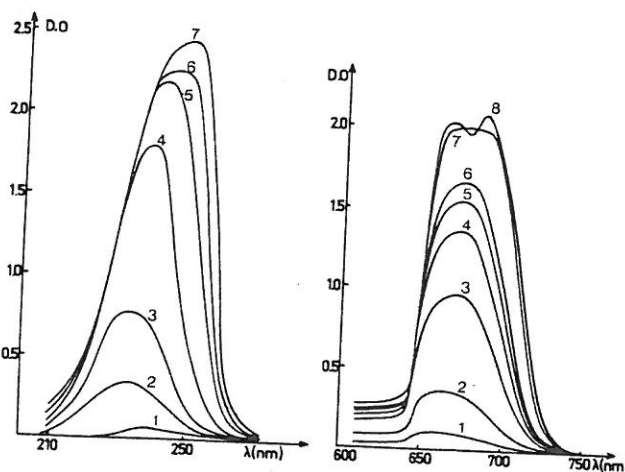


Fig. 2. Absorption spectra of cobalt(II)-Li⁺(Cl⁻, ClO₄⁻) 1 M solutions in propan-2-ol: [Co^{II}] = 5 × 10⁻³ mol l⁻¹, *l*_{cuve} = 1 cm. [Cl⁻] (mol l⁻¹): (a) UV: 1, 0.001; 2, 0.005; 3, 0.01; 4, 0.02; 5, 0.05; 6, 0.1; 7, 1.0; (b) visible: 1, 0.01; 2, 0.02; 3, 0.04; 4, 0.06; 5, 0.08; 6, 0.1; 7, 0.4; 8, 0.8.

In ethanolic solutions the maximum absorption band of cobalt(II) is located at 210 nm. With the addition of ligand a shoulder peak is formed at about 240 nm and both these maxima fuse into one asymmetric absorption band undergoing a bathochromic shift up to 255 nm. In the visible region the 660 nm absorption of the solvated cobalt(II) ion increases in intensity with increasing ligand concentration finally splitting, for *C* = 1.0 mol l⁻¹, into two bands at 665 and 695 nm.

The propanolic solutions exhibit nearly the same evolution in the visible spectrum. In the UV range, however, there appears an intense band at 235 nm, displaced up to 250 nm for higher ligand concentrations.

A matrix rank treatment method was used to determine the minimum number of species present in the solution [19] which requires a set of $N \times L$ data where N is the number of solutions and L the number of wavelengths. The result of this analysis indicated the presence of at least three complexes in both the solvents — ethanol and propan-2-ol. The theoretical expressions and the mathematical treatment have been given in our earlier publications [20, 21].

The numerical treatment was carried out on the {1, 2, 3} and the {1, 2, 3, 4} models, i.e. models with three and four successive mononuclear complexes. The best results, summarized in Table 1, were obtained for models with three complexes and it is observed that the stabilities of these complexes are higher in propan-2-ol than in ethanol. It is quite probable that the stability of the cobalto complexes increases with the number of atoms of carbon in the alcohol as is the case with the corresponding copper complexes which we have described earlier [18].

The absence of the fourth complex, $[\text{CoCl}_4]^{2-}$, is notable. The tetracoordinated complex is always formed in appreciable quantities in all solvents in copper solutions but with cobalt as the central metal ion this does not seem to be the case. Although the formation of the tetrachloro cobaltate has been reported by different authors, Cotton *et al.* think that $[\text{CoX}_4]^{2-}$ ions are hardly obtained in aqueous solutions and for Benali-Baitich even in concentrated solutions the formation of $[\text{CoCl}_4]^{2-}$ does not exceed 2.5%. We believe that in this system, the fourth complex may be formed in significant quantities only in some aprotic organic solvents at higher concentrations of cobalt [22].

The stability constants determined earlier were used to calculate the electronic spectra of the three complexes in the two alcohols. Figures 3 and 4 show these spectra in ethanol and propan-2-ol, respectively, and Table 2 summarizes the characteristic absorption bands of each complex in the two solvents.

The distribution curves for the complexes in the two solvents follow identical patterns and are represented by the curves in ethanol, Fig. 5. It can be noted that whatever the concentration, there is always the simultaneous presence of at least two species.

TABLE 1. Overall stability constants of the cobalt(II) chloride complexes in ethanol and propan-2-ol

Constant	Solvent	
	Ethanol	Propan-2-ol
β_1 (log β_1)	20 (1.3)	50 (1.7)
β_2 (log β_2)	570 (2.8)	1.8×10^3 (3.3)
β_3 (log β_3)	1.2×10^4 (4.1)	4.5×10^4 (4.7)
σ UV-Vis	0.095	0.080

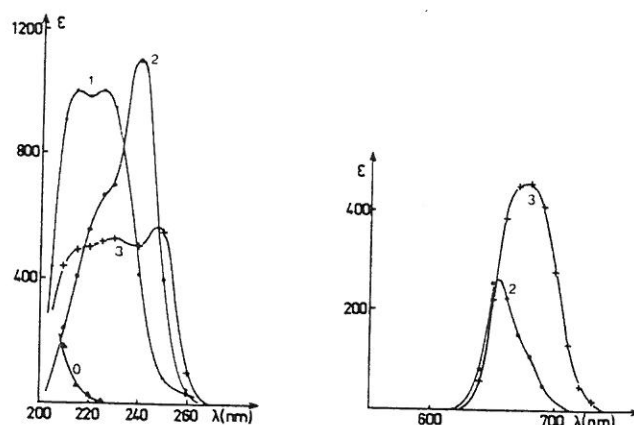


Fig. 3. Calculated electronic spectra of cobalt(II) chloro complexes in ethanol: 0, Co^{2+} ; 1, CoCl^+ ; 2, CoCl_2 ; 3, CoCl_3^- .

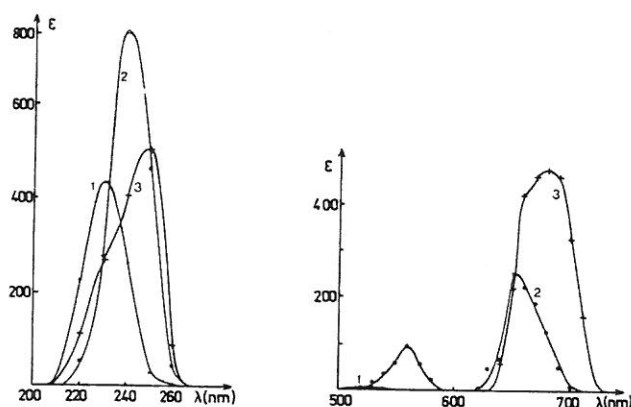


Fig. 4. Calculated electronic spectra of cobalt(II) chloro complexes in propan-2-ol: 1, CoCl^+ ; 2, CoCl_2 ; 3, CoCl_3^- .

TABLE 2. Characteristic absorption bands of the three complexes in the two solvents^a

Complex	Solvent	
	Ethanol λ_{max} (nm) (ϵ_{max} (l mol ⁻¹ cm ⁻¹))	Propan-2-ol λ_{max} (nm) (ϵ_{max} (l mol ⁻¹ cm ⁻¹))
CoCl^+	215 (1000)	
	226 (1000)	230 (435) 510 (15)
CoCl_2	225 sh	
	240 (1180)	240 (805) 560 (95)
	652 (260)	652 (255)
CoCl_3^-	213 sh	
	238 (428)	230 sh
	248 (568)	249 (510) 660 sh(420)
	675 (455)	680 (475)

^ash = shoulder peak.

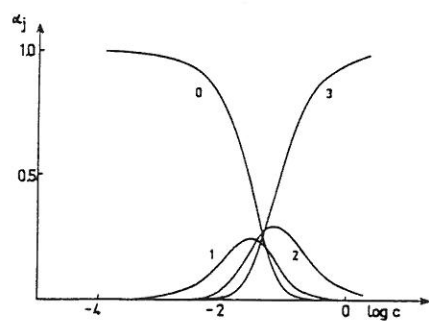


Fig. 5. Formation curves of chloro complexes of cobalt(II) in ethanolic solutions (α = degree of formation; c = free ligand concentration): 0, Co^{2+} ; 1, CoCl^+ ; 2, CoCl_2 ; 3, CoCl_3^- .

The characteristic absorption maxima for CoCl^+ (228 ± 2 nm), CoCl_2 (240 and 652 nm) and CoCl_3^- (248 and 675–680 nm) are identified in ethanol as well as in propanol. It is very interesting to notice that in the UV region there is always one absorption band more in ethanol than in propanol whereas in the visible region it is in propanol that there is always one maximum of absorption more than in the lighter alcohol. The investigation of this system in methanol could throw more light on this strange behaviour and at the same time give an idea on the evolution of stabilities of these complexes in alcoholic media.

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