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Coordination of Water by Cobalt(II) Ion in Acetone[*]

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The cobalt(II) perchlorate–water system in acetone has been studied in order to investigate the exchange between water and acetone in the coordination sphere of the metal. Concentration quotients at equilibrium were determined by spectrophotometric measurements in the visible region at four different temperatures. NMR measurements reveal that coordination to cobalt is dominated by water molecules even in the presence of large excess of acetone. Little variation of the equilibrium concentration quotients with temperature is in agreement with low enthalpy variation in the water–acetone exchange. This behaviour agrees with the very close DN_{SbCl_5} *values of the two solvents.*

Introduction

In a solvent mixture with high water content the hydration of an acceptor is altered with respect to that occurring with single H_2O entity [1]. Both hydrogen bonds and entropic effects account for the variation of water donicity. Gutmann has pointed out that the water donicity, measured by ΔG of VO(acac)$_2$[*] hydration [2], gives a value of 'bulk donicity' which is higher than the donor number DN_{SbCl_5}[**] in 1,2-dichloroethane [1]. Moreover, to get a complete idea about the reaction, the anionic solvation must also be taken into account [1, 2]. In our previous papers [3–6] we studied solvent effects in metal ion coordination, taking into account the donicity and dielectric properties of solvents. To get further information about water donicity with respect to its DN value, we have now studied the hydration of cobalt(II) ions in acetone with low water concentrations (thus limiting 'bulk' contribution). The choice of acetone system was due to the following considerations: i) the high solubility of the reactants in acetone, ii) the nearly ideal water–acetone mixture behaviour, iii) the acetone DN value very close to that of water, which avoids the variations of equilibrium constants with temperature (if DN reflects enthalpic changes). The perchlorate was chosen as counterion of cobalt(II). Due to its very low coordination power in aqueous solutions [7] as well as in other solvents [1], the competition between this anion and the studied donors may be neglected.

The study of cobalt(II) perchlorate–water system in acetone has been carried out by visible spectrophotometry, using NMR for complementary informations. Taking into account the low amount of water present in the solvent mixture, a tentative approach was made considering water as a simple coordinating agent, rather than a solvent.

Experimental

All the reagents used were of analytical grade. The cobalt(II) perchlorate was dried at 90 °C to constant weight (24 hours). It was analysed by complexometric metal titration. The initial water content of solutions and reagents were determined by the Karl Fisher method as previously reported [3]. The added water amounts were measured volumetrically. The spectrophotometric apparatus was the same as described in the previous work [3]. The study was performed at a constant metal concentration by varying the water content. NMR measurements were performed on a Varian A-60 spectrometer at 25 °C. Temperature was kept constant within ±0.1 °C.

Results

A linear correlation between absorbance and cobalt(II) concentration has been observed both in

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[*] acac = acetylacetonate.

[**] Hereafter indicated shortly as DN.

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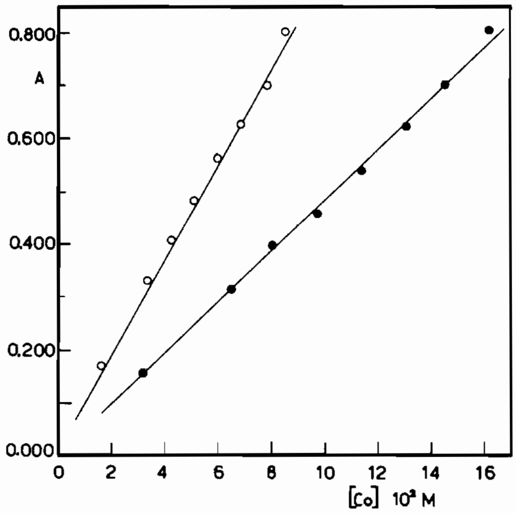

Fig. 1. Absorbance values of solutions containing variable amounts of cobalt(II) perchlorate exahydrate in water and in acetone. λ = 510 nm; path length = 1.00 cm; T = 25 °C; ● in water; ○ in acetone.

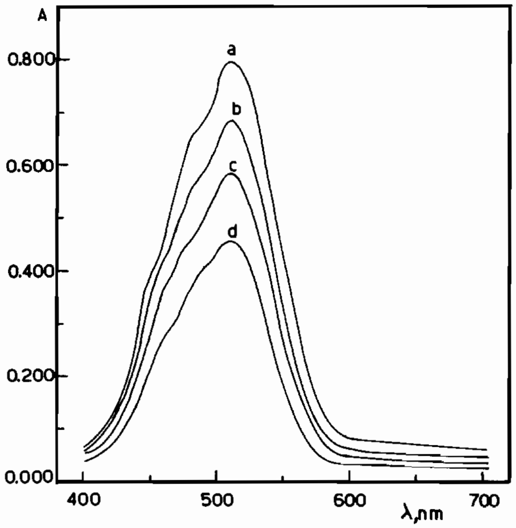

Fig. 2. Absorption spectra of cobalt(II) perchlorate exahydrate in acetone at different ratios. R = mol of added water/mol of cobalt(II); T = 25 °C; path length = 1.00 cm; C_{Co} = 8.6 × 10^{-2} *M*; a) R = 0; b) R = 3.3; c) R = 12.9; d) R = 90.6.

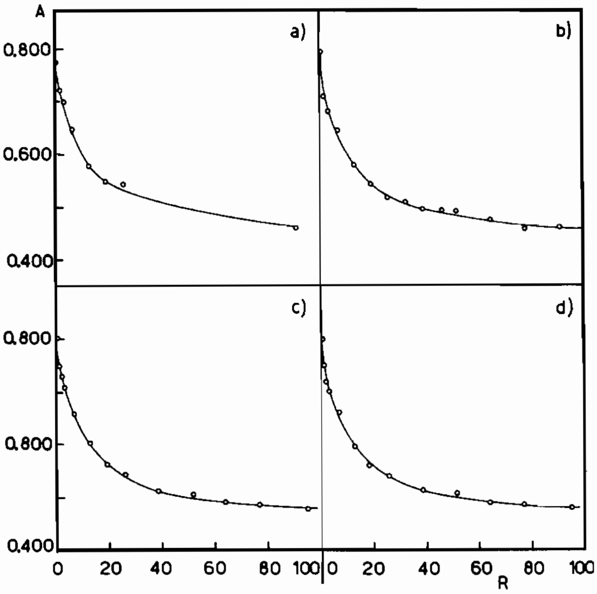

Fig. 3. Absorbance values with constant metal concentration and variable amounts of added water at different temperatures; solvent: acetone; λ = 510 nm; path length = 1.00 cm.
a) [Co] = 8.6 × 10^{-2} *M*; [H_2O] = (0 ÷ 7.8)*M*; T = 5 °C.
b) [Co] = 8.6 × 10^{-2} *M*; [H_2O] = (0 ÷ 7.8)*M*; T = 25 °C.
c) [Co] = 8.6 × 10^{-2} *M*; [H_2O] = (0 ÷ 8.2)*M*; T = 35 °C.
d) [Co] = 8.6 × 10^{-2} *M*; [H_2O] = (0 ÷ 8.2)*M*; T = 45 °C.
R = mol of added water/mol of cobalt(II).

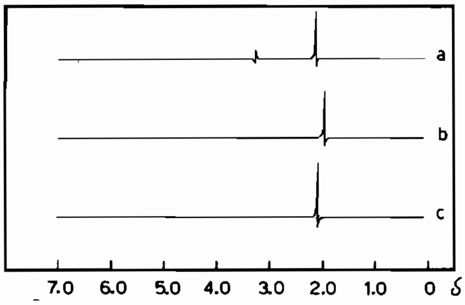

Fig. 4. NMR spectra (60 MHz) at 25 °C of acetone solutions containing: a) water 5.4% (w/w); b) $Co(ClO_4)_2 \cdot 6H_2O$ 25 mg/ml; c) $Co(ClO_4)_2 \cdot 6H_2O$ 25 mg/ml and water 5.4% (w/w).

water and acetone (Fig. 1). The molar absorptivity values in these solvents at λ_{max} = 510 nm are 4.9 and 9.1 l mol^{-1} cm^{-1}, respectively. On adding water to acetone solutions of cobalt(II), the absorbance decreases while the spectrum trend does not change (Fig. 2). At other temperatures (namely 5, 25, 35 and 45 °C) little variation in the apparent molar absorptivities was observed and the spectrum remained unaltered. This confirmed that no configurational change had occurred [8]. Figure 3 shows variation of the absorbance values at λ = 510 nm with water content at the above temperatures. When the water concentration is about 100 times greater than the concentration of cobalt, the absorbance approaches a constant value, equal to that observed when dissolving cobalt(II) perchlorate in pure water at the same concentration. Figure 4 shows NMR spectra at 25 °C for three acetonic solutions, containing a) water; b) $Co(ClO_4)_2 \cdot 6H_2O$; and c) $Co(ClO_4)_2 \cdot 6H_2O$ and added water.

Modelling and Calculations

If we express the concentration of species involved as 'conditional', the overall reaction is represented by the equation

$$ML_{n-q} + qL \rightleftarrows ML_n \qquad \text{(I)}$$

where the solvent molecules have been neglected. When q varies from 1 to n in equilibria up to the coordination number n, we get the conditional constant

$$K'_{n-q,n} = \frac{[ML'_n]}{[ML'_{n-q}]\,[L']_q} \qquad \text{(II)}$$

Knowing the ratio $[ML'_n]/[ML'_{n-q}]$ and $[L']$, $K'_{n-q,n}$ may be calculated. Two cases are possible: i) only two complex species are responsible for the change in the absorbance, or ii) many species, with close reaction constants, contribute to the absorbance, *i.e.* a 'mixed' system is involved. In the latter case the solution of the system is often very difficult and results are highly sensitive to small variations of experimental values (mathematically ill-conditioned matrices of data are obtained). This needs very accurate measurements and methods employing logarithmic variables have to be preferred. In fact logarithmic determinations of concentrations or activities (as in potentiometric methods), allow us to obtain data with a constant relative precision in a wide range of concentrations ($\Delta \log x \cong \Delta x/x$). This is not the case of linear measurements (as in spectrometric methods) which are to be applied in small concentration ranges. On the contrary, when couples of prevailing species may be identified in selected concentrations ranges (which is equivalent to the mathematical effort to separate the matrix of data into blocks), spectrophotometric methods allow a very accurate determination of parameters in a simple manner. Another important feature of the latter methods is the possibility to be applied to systems having the optical properties even if the potentiometric model is difficult to be described, as in solvents other than water. The possibility of identifying concentration ranges according to the above stated conditions generally cannot be fixed *a priori* without knowledge of the examined system. However it is always possible to make assumptions and verify them after system solution, using iterative processes. In a reaction of the type described by (I), the absorbance variations with concentrations, may be represented by:

$$A = \epsilon_n[ML'_n] + \epsilon_{n-q}[ML'_{n-q}] + \epsilon_c C \qquad \text{(III)}$$

where path length is assumed to be unit (or normalized absorbance) and ligand L is assumed to be transparent (or absorbance can be corrected for ligand absorption measured separately). $\epsilon_c C$ includes the contributions of all ML_x ($x \neq n$, $x \neq n-q$) species. The total metal concentration is given by

$$C_M = [ML'_n] + [ML'_{n-q}] + C \qquad \text{(IV)}$$

The problem becomes simple if ϵ_c and C remain constant. The chemical sense of this assumption can be summarized in two cases: i) when q = 1, the concentrations of the species other than ML_n and ML_{n-1} must be negligible, and ii) when q = 2, the concentrations of the species other than ML_n, ML_{n-1}, ML_{n-2} must be negligible; in addition the sequence $K_{n-2} > K_{n-1} < K_n$ must occur to maintain a low relative concentration of ML_{n-1}, or reactants concentrations must be chosen very close to the maximum formation of ML_{n-1} (in this way small shifts around this value do not determine appreciable variations in ML_{n-1} concentration).

When q > 2, the ϵ_c and C values have a very low probability of being constants, due to the general trend of ϵ_i and K_i values.

In the two first cases listed above, which are not so infrequent, combining the expression III and IV we obtain

$$\frac{[ML'_n]}{[ML'_{n-q}]} = \frac{A - A_o}{A_\infty - A} \qquad \text{(V)}$$

where $A_o = \epsilon_{n-q}(C_M - C)$ and $A_\infty = \epsilon_n(C_M - C)$.

For weak complexes, where $[L'] \cong C_L$, it is possible to combine II and V in logarithmic form to get

$$\log \frac{A - A_o}{A_\infty - A} = \log K_{n-q,n} + q \log C_L$$

In this case the plot of

$$\log \frac{A - A_o}{A_\infty - A} \ \textit{vs.}\ \log C_L$$

will result in a straight line with an integer angular coefficient equal to q. Our experimental points have been treated in this manner for a system containing two absorbing species. This assumption has been verified by a method [9] based on the determination of the rank of the matrix describing absorbance at various wavelengths and concentrations. The plot has been checked with the water/cobalt ratios as abscissae, instead of the absolute value of C_L, owing to the fact that the total cobalt concentration is constant ($C_{Co} \equiv C_M$, $C_{H_2O} \equiv C_L$).

Then we get

$$\log \frac{A - A_o}{A_\infty - A} = \log K'_{n-q,n} + q \log C_{Co} + q \log \frac{C_{H_2O}}{C_{Co}}$$

TABLE I. Water Molecules (q) Involved in the Reaction I, Molar Absorptivities in $mol^{-1}\ l\ cm^{-1}$ at $\lambda_{max} = 510$ nm for Cobalt(II) Perchlorate in Acetone (ϵ_5) and for Cobalt(II) Perchlorate–Water System in Acetone (ϵ_6) with Molar Ratio $C_{H_2O}/C_{Co} \cong 100$ and Concentration Quotients K'_6 at Equilibrium at Different Temperatures.

T (°C)	5	25	35	45
q	1.1	1.0	1.1	1.0
ϵ_5	9.1	9.2	9.2	9.2
ϵ_6	5.2	5.3	5.4	5.4
log K'_6	0.0	0.1	0.0	0.1

The water/cobalt ratio is obtained by adding, to the actual value of added water $C^o_{H_2O}$, six times the total cobalt concentration (water of crystallization of the employed cobalt perchlorate) and subtracting the amount bound to cobalt in n–q ratio, *i.e.*:

$$\frac{C_{H_2O}}{C_{Co}} = \frac{C^o_{H_2O}}{C_{Co}} + 6 - (n - q)$$

In this way q and n have been determined iteratively and values of 1 and 6 have been found respectively at all examined temperatures. Molar absorptivity $\epsilon_{n-q} = \epsilon_5$ and $\epsilon_n = \epsilon_6$ has been obtained by A_0 and A_∞ measurements (Fig. 3) with the C constant equal to zero (see expression V). Results obtained are listed in Table I, including calculated log $K'_{n-q,n}$ = log K'_6 values. NMR spectra showed that in the presence of cobalt perchlorate the peak of water at 3.2 ppm disappears, indicating a water–cobalt binding [10].

Discussion

The linear correlation between absorbance and cobalt(II) concentration (Fig. 1) shows no appreciable complexation between cobalt(II) and perchlorate ions: otherwise one should have observed some inflection of the curve in the concentration range examined. Equation I thus satisfactorily represents the present system. The evidenced species, when water is in excess, shows the same spectral behaviour and molar absorptivity as that obtained when dissolving cobalt(II) perchlorate in pure water. The spectral trend accounts for the coordination number six assigned to cobalt(II). The spectrum of tetracoordinated cobalt(II) was never observed during our experiments [3]. On the basis of these considerations it may be assumed that $Co(H_2O)^{2+}_{n-q}$ in acetone is $Co(H_2O)_5(Me_2CO)^{2+}$ (Me = methyl group).

NMR data also confirmed Co–H_2O association in the acetone solution. The value of q in equilibrium I has been found to be one. Thus, the prevailing reaction is of the type

$$Co(H_2O)_5(MeCO)^{2+} + H_2O \rightleftarrows Co(H_2O)_6^{2+} + Me_2CO$$

The magnitude of experimental error involved in the determination of K′ (defined by II) did not permit observations in the variation of log K′ with temperature. However some considerations may be made about the magnitude of enthalpy variation associated with the reaction. If considering that DN corresponds to –ΔH of the reaction

$$SbCl_5S + X \rightleftarrows SbCl_5X + S$$

where S = 1,2-dichloroethane and X = donor species, it is possible to estimate the enthalpy change of the reaction

$$SbCl_5(MeCO) + H_2O \rightleftarrows SbCl_5H_2O + Me_2CO$$

as the difference between DN (acetone) and DN (water), which is of the order of –1 Kcal/mol. In this way other enthalpic contributions, such as the heat of solution of water in acetone and differences in species heat of solvation, are neglected. With the same assumption the reaction

$$Co(H_2O)_5(Me_2CO)^{2+} + H_2O \rightleftarrows Co(H_2O)_6^{2+} + Me_2CO$$

must have about the same value of enthalpic variation because no significant difference in solvation between $Co(H_2O)_5Me_2CO/Co(H_2O)_6$ couple with respect to $SbCl_5Me_2CO/SbCl_5H_2O$ is likely to be expected. When the temperature values vary in the range 5 ÷ 45 °C, the log K'_6 variation (evaluated by Van't Hoff relationship with ΔH = –1) is 0.1 unit, *i.e.* of the same order of magnitude as the error which affects the experimental measurements. Thus, the constancy of experimental K'_6 values with temperature confirms that the ΔH of the reaction is about the same as expected when considering the DN values. The same agreement does not result in the stoichiometry of the exchange reaction; in fact, we could have expected a lower number of water molecules in the coordination sphere of cobalt. Higher entropic contributions to the stability of cobalt–water complexes may account for the formation of the above described species instead of cobalt–acetone ones.

References

1 U. Mayer and V. Gutmann, 'Phenomenological Approach to Cation–Solvent Interactions', in Structure and

Bonding, J. D. Dumtz *et al.* editors, vol. 12, Springer – Verlag, New York, 1972.

2 U. Mayer and V. Gutmann, *Mh. Chem.*, *101*, 912 (1970).

3 V. Carunchio, U. Biader Ceipidor and A. Messina, *Inorg. Chim. Acta*, *6*, 613 (1972).

4 U. Biader Ceipidor, V. Carunchio and G. Pascucci, *Ann. Chimica*, *66*, 727 (1976).

5 U. Biader Ceipidor, V. Carunchio, L. Pagnoni and M. Tomassetti, *Ann. Chimica*, *69*, 557 (1979).

6 U. Biader Ceipidor, V. Carunchio, G. D'Ascenzo and M. Tomassetti, *Thermochim. Acta*, *35*, 197 (1980).

7 J. M. Smithson and R. J. P. Williams, *J. Chem. Soc.*, 457 (1958).

8 H. C. A. King, E. Körös and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

9 R. Siefker, *Anal. Chim Acta*, *52*, 545 (1970).

10 J. Beech and Miller, *J. Chem. Soc., Dalton*, 801 (1972).