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Solvent Effects on Complex Formation: Cobalt(II)–Thiourea in Ethyl Acetate, Propanol, Propylene Carbonate*

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The complex formation between cobalt(II) and thiourea was studied in solvents as ethyl acetate (Etac), propanol (PrOH) and propylene carbonate (PC). The stability order with respect to the solvent was PC > Etac > PrOH. This behaviour was discussed in terms of solvent properties as DN, AN, DEC. The influence of the donicity (DN) was the prevailing effect. The species formed when water is added to the solvent were also considered: $Co(H_2O)_4S_2^{2+}$ *seems to be formed when solvent is PrOH or PC, while* $Co(H_2O)_6^{2+}$ *when solvent is Etac. Some possible interpretations are proposed considering the acceptor ability (AN) of the solvents.*

Introduction

The formation of metal–ligand complexes has been investigated [1–9] in order to check the influence of the solvent on the stability of the systems. Many aspects are involved in a rigorous description of these relationships; however, a good approach seems to be offered by the empirical rules proposed by Gutmann and co-workers [10, 11].

In this paper the study of cobalt(II)–thiourea complex formation is reported in three different solvents. The cobalt(II) acceptor was chosen because of the colour displayed by its coordination compounds, making possible an easy spectrophotometric investigation. On the other hand this method is the most reliable one when studying ion concentrations in solvents different from water. The ligand was thiourea, elsewhere indicated as Tu, offering a high solubility in low polar solvents. Moreover the ionization of this ligand is not required to act as a complexing agent, thus avoiding dissociation problems. The chosen counterion of cobalt(II) was perchlorate, which offers the highest degree of ionization and lowest coordination ability [12].

Ethyl acetate, propanol and propylene carbonate, elsewhere indicated as Etac, PrOH and PC, respectively, were used as solvents. Their donicities (DN), acceptor properties (AN) and dielectric constants (DEC) are so different to allow some relationships with complex behaviour to be pointed out [11–13].

A comparison with the results reported for the same system in ethanol [14] was also made.

Experimental

All the products used were of analytical grade. The cobalt(II) perchlorate was dried at 90 °C to constant weight. It was also analyzed by complexometric metal titration. The initial water content of that salt and of solvents were determined by the Karl Fisher method [15]. The added water amounts were measured volumetrically taking into account also the crystallization water of the salt. Spectra were recorded at 25 ± 0.1 °C on a Perkin Elmer 320 spectrophotometer using 0.10, 1.00 and 5.00 cm quartz cells.

Results

The complexation reactions between cobalt(II) and Tu were studied in the solvents without using a possible interfering agent to fix the ionic strength of medium. The obtained results are quasi-thermodynamic values due to the low concentrations used (about 10^{-3} *M*).

Standard preliminary tests were performed on solutions of reagents and of complexes to check spectrophotometric stability for at least one day.

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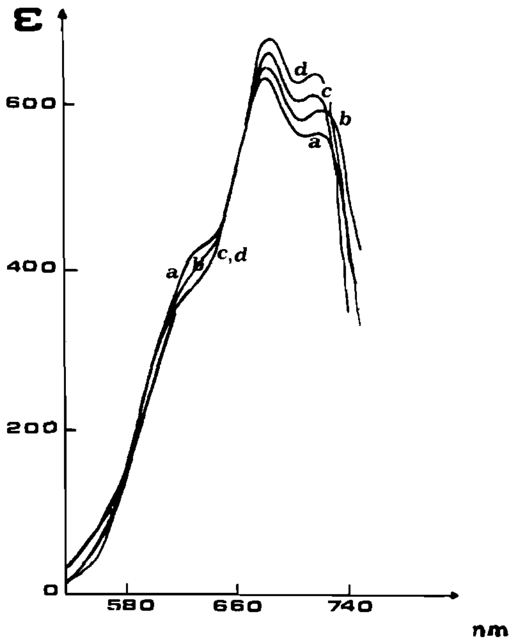

Fig. 1. Absorption spectra expressed as molar absorptivities, cm^{-1} $l mol^{-1}$, of cobalt(II) complexes with Tu (Tu/Co > 20) in various solvents: a) Etac, b) PrOH, c) PC, d) EtOH.

In addition the reaction was checked to be complete after a few seconds from the mixing of the reagents. In Fig. 1 the absorption spectra of complexes in ligand excess are reported, together with the same spectrum in ethanol, performed in the same conditions as reported by other authors [14]. Always with ligand excess, the absorbance, read at a wavelength corresponding to the maximum of each spectrum in the visible region is reported in Fig. 2 when varying the water amount present in the solvent. In calculating this amount the crystallization water of cobalt perchlorate was also considered.

From the data shown in Fig. 2 it was possible to obtain the minimum amount of water required to obtain no more absorbance variations, *i.e.* corresponding to the first horizontal portion of these curves. These amounts, expressed as v/v percent, were 0.6, 0,2, 0.5, for Etac, PrOH and PC, respectively.

From the same data the number of water molecules coordinated by the central metal ion when water concentration is increased, was calculated according to a previously described procedure [16]. This number, referred to as q, resulted 6, 4 and 4, respectively, for the above solvents in the same order.

To evaluate the concentration quotients at equilibrium, β_n, of the complex cobalt(II)–thiourea in the solvents under examination, the method of corresponding solutions [17] was applied in the metal concentration range 1×10^{-3} to 5×10^{-3} *M*.

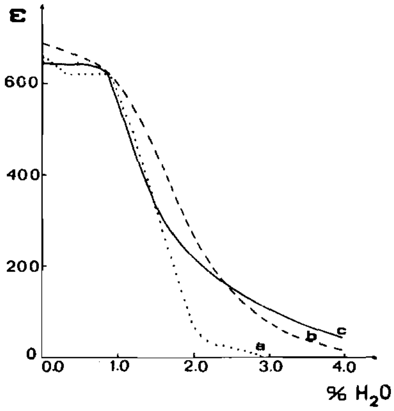

Fig. 2. Molar absorptivities at $\lambda = 685$ nm in cm^{-1} $l mol^{-1}$ of cobalt(II)–Tu system in various solvents with added water expressed as percent v/v: a) Tu/Co = 22, $C_M = 2.25 \times 10^{-3}$ *M*, solvent = Etac. b) Tu/Co = 36, $C_M = 2.25 \times 10^{-3}$ *M*, solvent = PrOH. c) Tu/Co = 20, $C_M = 2.25 \times 10^{-3}$ *M*, solvent = PC.

The calculated values of $\bar{n}$ *vs.* logTu are reported in Fig. 3. The values of β_n were graphically estimated by these curves. No iterative refinement of these values was attempted because of the very close values of the successive constants.

The obtained results are summarized in Table I.

Discussion

The absorption spectra of the complexes in the various solvents account for a tetrahedral coordination of the cobalt(II) [18]. Moreover, values of $\bar{n}$ higher than 4 were not observed.

Data obtained for the complex in ethanol, using the same working conditions, agree with data reported for $\log\beta_2$ and a virtual $\log\beta_6$ by other authors [14]. The values of 1.9 and about 4.0, the latter extrapolated using the estimate $\log K_5 = \log K_6 = 0.6$, agree with 1.7 and 4.0 reported. This can support the correctness of the used method, even if it is doubtful that species with coordination numbers higher than 4 may be detected using the corresponding solutions method. In fact these species must arrange cobalt(II) in a octahedral configuration, showing a molar absorptivity about 100 times lower than that displayed in tetrahedral form. In this way the trend of the absorbance *vs.* ligand concentration would not be monotonic as required by the corresponding solutions method.

Excluding ethanol, some considerations can be made on the complex stability in the considered solvents. As a measure of the overall stability $\Sigma_1^4 \log K_n$, reported in Table I, can be considered.

The stability sequence of the complexes in the solvents results to be PC > Etac > PrOH, that is the

TABLE I. Concentration Quotients at Equilibrium for $CoTu_n^{2+}$ Complexes with n = 1–4 in Several Solvents with Added Water (percent v/v). DN, AN and DEC reported as pure solvent parameters. The value q represents the number of water molecules entering the complex when water is increased up to 3–4%.

	Ethyl acetate	Propylene carbonate	n-Propanol	Ethanol
DN	17.1	15.1	19.6	24.0
AN	9.3	18.3	37.0	37.1
DEC	6.0	69.1	20.7	24.3
water %	0.6	0.5	0.2	5.0
q	6	4	4	
$\log K_1$	2.5	>3	2.6	>1
$\log K_2$	2.3	>3	2.1	0.9
$\log K_3$	2.2	2.6	1.9	0.7
$\log K_4$	2.2	2.0	1.8	0.7
$\sum_1^4 \log K_n$	9.2	10.6	8.4	3.3

reverse of DN values. This is consistent with the model that the coordination of the ligand by metal ion is more favoured when the competing solvent is weaker as donor agent.

With respect to AN values the main influence would be in solvating the ligand, thus reducing the complex formation ability when the solvent is characterized by a higher value of this parameter. While this is respected for the EtAc > PrOH and PC > PrOH couples, even if not so dramatic as the AN difference may suggest, the sequence is completely reversed when considering PC and Etac. The ligand solvation seems to be a second order effect with respect to solvent– ligand competition, both acting as donor towards metal acceptor, when complexation takes place.

The DEC values are uncorrelated with the stability of the complex, at least to a first approximation, according to the complete ionization of the cobalt(II) perchlorate and to the uncharged ligand.

In this way the DN, as suggested in previous work, seems to predominate in determining the complex stability in the solvents.

The obtained stability order of cobalt(II)–thiourea complexes also agrees with 'soft' interaction between divalent cobalt and sulphur donor atom. The coordination becomes stronger when the π-polarizability of the coordinated ligands increases, due to π-interactions with surrounding solvent. Considering molecular structures these interactions would decrease in the order PC > Etac > PrOH, in accord with the similar stability sequence found for the complexes. Moreover the DEC contribution seems to be not important accounting for a 'frontier control led' rather than a 'charge controlled' complex formation [19].

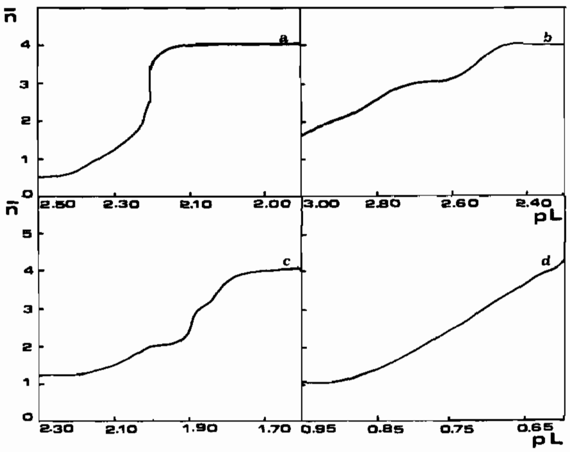

Fig. 3. Formation functions of cobalt(II)–Tu complexes in various solvents, pL = –log[Tu] : a) Etac, b) PrOH, c) PC, d) EtOH.

It is interesting, however, to note that the q values are 4 for PC and PrOH but 6 for Etac, having the lower AN. This implies, according to the proposed model [16], that when water is added the main reactions taking place are

$$CoTu_4^{2+} + 4H_2O + 2S \rightleftharpoons Co(H_2O)_4S_2^{2+} + 4Tu$$

when solvent S is PC or PrOH, and

$$CoTu_4^{2+} + 6H_2O \rightleftharpoons Co(H_2O)_6^{2+} + 4Tu$$

when the solvent is Etac.

The configuration change from tetrahedral to octahedral form is evident when examining spectra and absorptivity at low and high water concentration.

Spectra of cobalt(II) solutions with added water at the maximum concentration reported in Fig. 2 are not sensitive to Tu addition in the cobalt(II) absorption range (500–550 nm). So it is possible to confirm that the Tu is not involved in complexation when water is present in those amounts. Some measurements were made of molar absorptivities of cobalt perchlorate in the three solvents with water, added up to the maximum raised in Fig. 2, and in pure water. Values are 6.9 cm^{-1} l mol^{-1} for PC and PrOH, while 4.8 and 5.0 for pure water and Etac. This can be assumed as a support that the same species $Co(H_2O)_6^{2+}$ is present both in water and in Etac (taking into account the experimental error due to low concentrations and absorptivities), which is different from those present in the two other solvents.

Moreover, it is interesting to note that the same was observed by other authors [20] when considering cobalt(II)-water complexes in other solvents: the predominant species in similar concentration was $Co(H_2O)_6^{2+}$ just for n-eptanol, this being the only one among the pool of solvents having a low water solubility. In our case the Etac has the lowest water solubility with respect to the other two solvents.

This behaviour can also be related to low AN value considering that the solvent in the coordination sphere of the metal is not stabilized by an interaction with surrounding water implying that water acts as donor and the coordinated solvent as acceptor. This latter model can be related to the observed low solubility if considering that a low AN, regarded as a low donor–acceptor interaction of the solvent with water, may also suggest a low solvent–water solubility.

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