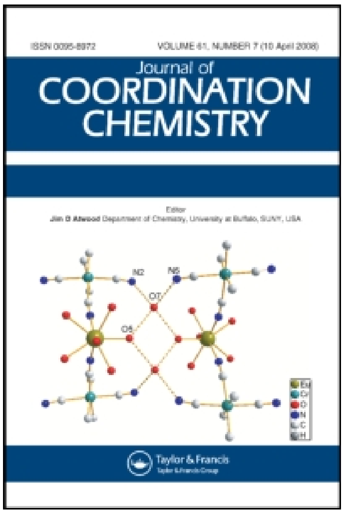

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EQUILIBRIA INVOLVING COBALT(II) HALIDES AND PHOSPHINE OXIDES I. A SPECTROPHOTOMETRIC STUDY OF THE COBALT(II) CHLORIDE – TRIPHENYLPHOSPHINE OXIDE SYSTEM IN ACETONE MEDIUM

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KEY WORDS: Cobalt(II) Chloride; Triphenylphosphine Oxide; Acetone; Spectrophotometry; Stability Constants.

The $CoCl_2$–triphenylphosphine oxide system was studied in anhydrous acetone medium, at 25.00 ± 0.05°C, by spectrophotometry. It was found that the system comprises at least three complex species, whose over-all stability constants are: $\beta_1 = (1.40 \pm 0.10) \cdot 10^4\ M^{-1}$, $\beta_2 = (6.77 \pm 0.95) \cdot 10^6\ M^{-2}$, $\beta_3 = (1.77 \pm 0.40) \cdot 10^9\ M^{-3}$. The composition of the system as well as the values of the stability constants of the complex species are in a marked disagreement with the literature data. The compatibility between the experimental data and the results obtained in the present work was confirmed by different methods.

INTRODUCTION

In 1969, Sheka *et al.*[1] studied the binary complex systems of $CoCl_2$ with triphenylphosphine oxide (TPPO) and butyldiphenylphosphine oxide in anhydrous acetone and tetrahydrofuran solutions. They stated that the metal salt, in the solvents used, was in the form of $CoCl_2(solv.)_2$ and in the light of some experimental data, it was established that for the above mentioned systems only two complex species existed in solution and were formed by progressive substitution of the solvent by the ligand under investigation. The over-all stability constants determined by these authors for the $CoCl_2$–TPPO system in acetone, at 20 ± 1°C, applying Yatsimirskii's spectrophotometric method[2-4] were: $\log \beta_1 = 2.64$ and $\log \beta_2 = 4.25$.

Solid complexes of some metal salts with phosphine oxides have been systematically studied in this laboratory.[5-10] The authors of the present work initiated an investigation on binary systems involving Cobalt(II) halides and benzyldiphenyl, dibenzylphenyl and tribenzylphosphine oxide, in acetone medium, with the main purpose of determining the stability constants of the complex species formed, as well as their molar absorptivities. The determinations were carried out according to Yatsimirskii's method, both in the experimental part and computation technique. For the calculations, it was assumed that each system comprised only two complex species. For none of the referred systems was it possible to obtain convergent values for the constants, due, mainly, to difficulties found in the graphical extrapolations. It was decided that the same method should be applied to the $CoCl_2$–TPPO system, in acetone medium, this time, using the experimental data obtained by Sheka *et al.*[1] In this case, the several cycles of successive approximations – performed as specified by the authors[1] – furnished values very different from each other, clearly indicating non convergence. In none of the attempts could the published stability constants be obtained.

The mentioned facts seemed to reveal an incompatibility between the referred constants and the experimental data from which they were estimated. This evidence was strengthened by comparing the experimental formation curve with the calculated one (Figure 1, curve 1).

In view of the striking discrepancies found, a re-study of the mentioned system was judged advisable. The results obtained in the present

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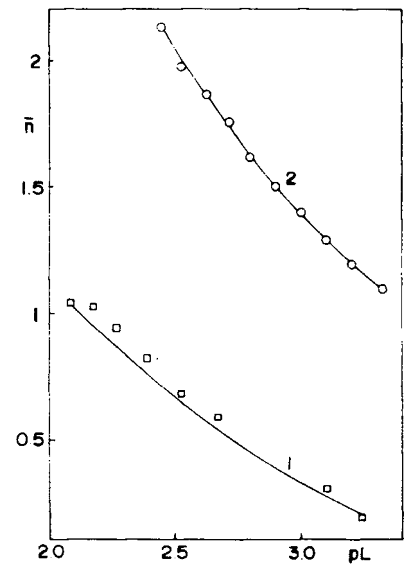

FIGURE 1 $CoCl_2$ – TPPO system, in acetone medium. Formation curves. Curve 1: obtained from data of Sheka *et al.*[1]. Curve 2: obtained from data given in Tables II and III. Squares and circles: experimental values. Full curves: calculated from β_n.

investigation were very different from those reported by Sheka *et al.*,[1] concerning both the number of complex species in solution and the orders of magnitude of the formation constants.

EXPERIMENTAL

Symbols

The following symbols are used: A, measured absorbance; A_{iJ}, absorbance value of a particular solution numbered J at a specified wavelength, numbered i; α_n, fraction of Me in the form of MeL_n; b, length of the optical path; β_n, over-all stability or formation constant of MeL_n (M^{-n}); C_{Me}, total concentration of $CoCl_2$; C_L, total concentration of TPPO; ϵ, mean molar absortivity = $A/b.C_{Me}$ ($M^{-1} \cdot cm^{-1}$); ϵ_n, molar absorptivity of MeL_n ($M^{-1} \cdot cm^{-1}$); F_n, Fronaeus' functions[11]; K_n, step stability constant of MeL_n; λ, wavelength; L, free TPPO; M, molar concentration; Me, free $CoCl_2$; n, number of ligands in mononuclear complex MeL_n; 1:n, central group to ligand proportion in mononuclear species; N, maximum value of n; R, number of absorbing species in solution; $\bar{n}$, average number of ligands bound to one central group.

Materials and Solutions

Pure anhydrous acetone was obtained following the directions of Jervis and Neelakantan.[12] TPPO, obtained from Koch-Light laboratories, was recrystallized from anhydrous acetone to a constant melting point (157–8°C). This m.p. is in good agreement with literature data.[13] Acetone solutions of known concentrations of the above substance were made up by direct weighing of the anhydrous product into calibrated measuring flasks.

An anhydrous stock solution of $CoCl_2$ in acetone was prepared according to the following procedure: a weighed quantity of $CoCl_2 \cdot 6H_2O$ (Merck) was dissolved in anhydrous acetone ($CoCl_2$ concentration of *ca.* 0.1 M). Triethylorthoformate (BDH) was added in a small excess (in proportion to the amount of water expected) and the resulting solution slowly evaporated on a hot plate until its volume was reduced to *ca.* 30% of the original (total evaporation was avoided as it was found to produce a sparingly soluble residue). More acetone was added and the above procedure repeated until the temperature of the liberated vapour assumed a constant value, corresponding to the boiling point of the pure acetone. By using this procedure, the excess triethylorthoformate and the products of its reaction with water were eliminated. The resulting solution, diluted with anhydrous acetone, was standardized by complexometric titration.[14] Working solutions were prepared from this solution as required.

Equipment

Spectrophotometric measurements were carried out with a Varian, model 635 spectrophotometer using matched silica cells of 1.00 cm optical path. A device for spectrophotometric cells thermostatization was used allowing temperature control within 0.05°C The photometric scales of the apparatus were tested for reliability according to the method recommended by Haupt.[15] It was found that the mean relative error did not exceed one per cent for the absorbance scales used to perform the present work.

Conductivity measurements, at 25.00 ± 0.05°C, were made with a Metrohm model E365B apparatus, using a cell with a constant of 0.785 cm^{-1}. A programmable Hewlett-Packard model 9810A eletronic calculator was used for all computations.

Methods

The method developed by Coleman *et al.*[16] was used to determine the number of light-absorbing species in solution. The symbols used were the same as those proposed by these authors. The stability constants were determined by combining the spectrophotometric method of corresponding solutions[17–20] (which makes it possible to obtain $\bar{n}$ and [L] pairs of values) with the computation technique of Fronaeus.[11]

RESULTS AND DISCUSSION

Preliminary Data

Conductivity measurements of $CoCl_2$ solutions and $CoCl_2$–TPPO mixtures in anhydrous acetone confirmed the data presented by Sheka *et al.*:[1] the metal salt and the complex species in solution are almost undissociated. In addition to these data, the conductivity of a solution in which $C_{Me} = 2.05$ mM and $C_L = 36.0$ mM was measured. The value obtained for this solution and the one found for a $CoCl_2$ solution ($C_{Me} = 2.05$ mM) were almost the same, furnishing additional proof that the TPPO, even present in considerable excess, does not displace the chloride from the internal coordination sphere of the complex. Thus, the $CoCl_2$ may be considered as a central group in the above mentioned conditions, and the equilibria in the system can be represented (without taking into account the solvation on the involved compounds), generically, by the equation:

$$CoCl_2 + n(TPPO) \rightleftharpoons CoCl_2(TPPO)_n$$

and the over-all stability constants defined by $\beta_n = [CoCl_2(TPPO)_n]/[CoCl_2] \cdot [TPPO]^n$.

The constancy of absorbances as a function of time, for any fixed ligand and metal salt concentrations, indicates that the attainment of equilibria is rapid relative to the time necessary to prepare a sample for examination. In addition, the absorption spectra of $CoCl_2$ – TPPO mixtures, covering the 550–710 nm range (Figure 2) show the occurrence of complex formation and indicate the feasibility of a spectrophotometric study of the system.

The aborbances (A_{ij}) listed in Table I were obtained with the purpose of determining the number of absorbing species in solution according to the method of Coleman *et al.*[16] Figure 3 shows plotted curves obtained by applying this method (for R = 3) to the matrix M′ data. Straight lines are not obtained, which clearly indicates that the system comprises more than three absorbing species; as one of these species is the $CoCl_2$, it leads to the conclusion that the number of complex species is higher than two.

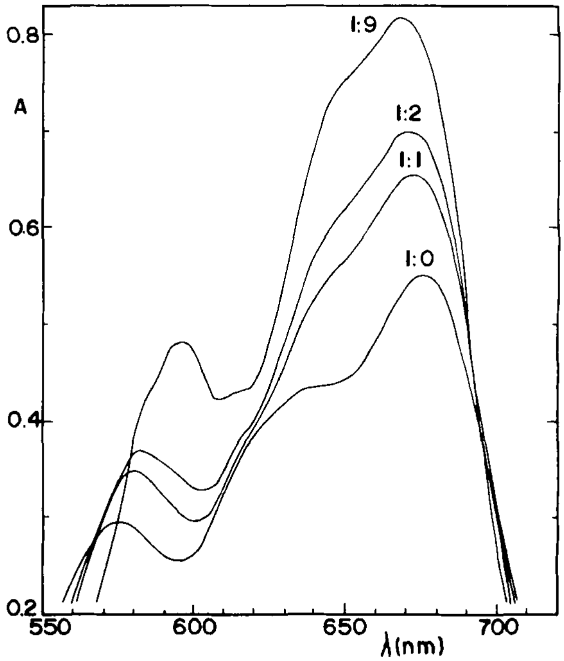

FIGURE 2 $CoCl_2$–TPPO system, in acetone medium, at 25°C. Absorption spectra of metal salt: ligand mixtures in different proportions. $C_{Me} = 2.00$ mM.

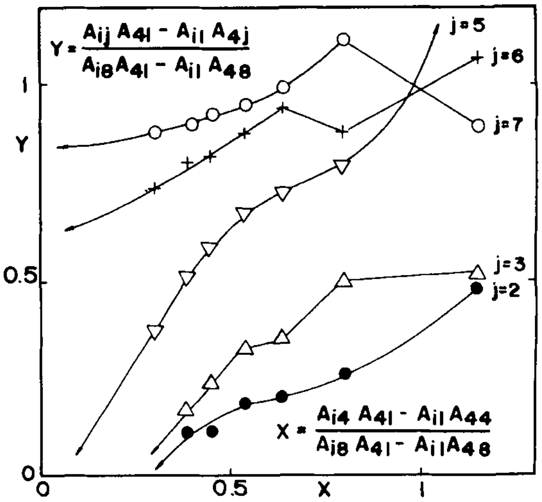

FIGURE 3 $CoCl_2$–TPPO system, in acetone medium, at 25°C. Test for three absorbing species based on the M′ aborbance matrix of Table I.

This result is in disagreement with the findings of Sheka *et al.*[1] At this point it seems appropriate to emphasize that the C_{Me} value as well as the range of

TABLE I

CoCl$_2$ TPPO system in anhydrous acetone. Absorbance matrices C_{Me} = 2.05 mM; t = 25.00 ± 0.05°C

		C_L (mM)														
		0	0.317	0.630	0.938	1.240	1.538	2.963	4.286	5.517	6.667	7.742	8.750	9.697	10.59	11.43
		Soln. no., J														
		Matrix M′														
			1		2		3	4	5		6		7			8
		Matrix M″														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wavelength nm	i	$A.10^3$														
630	1	452	480	487	495	501	508	534	552	564	573	581	587	592	596	600
635	2	466	509	521	533	542	553	587	616	635	647	656	667	672	679	686
640	3	477	531	546	563	574	588	635	671	693	715	722	734	741	749	757
645	4	480	545	564	584	598	615	670	707	735	754	767	779	786	795	800
650	5	486	560	581	602	618	634	693	733	761	779	792	804	813	822	826
655	6	503	581	604	625	643	660	718	758	785	803	815	828	837	845	850
660	7	535	612	635	656	674	691	746	786	813	831	844	856	865	873	877
665	8	571	647	671	688	705	722	777	815	838	857	870	882	889	898	902
670	9	605	676	696	715	730	744	795	830	853	870	882	892	900	907	912
675	10	622	686	706	722	736	748	793	822	842	854	864	874	880	887	890
680	11	615	670	687	701	712	722	759	778	793	802	807	814	821	824	827

C_L values associated with the curves of Figure 3 are very close to those of the above mentioned authors.

In view of the peculiarities of the system under investigation, it was decided to determine the stability constants of the complex species formed through spectrophotometric data. Among the available methods, the one of corresponding solutions[17–20] seemed to be adequate as it is almost the only spectrophotometric method that will generate a formation curve (or, at least, a portion of it) for a series of complexes.[20] By applying this method, no previous assumptions regarding the number of complex species present in solution need to be made.

Evaluation of the Stability Constants

The absorption spectra (figure 2) show that the 630–680 nm range is the most appropriate for an investigation of the system. Figure 4 shows the dependence between ϵ(at 677 nm) and C_L, for three fixed C_{Me} values. The curves indicate an asymptotic ϵ value in the vicinity of 450. ϵ_0 was experimentally determined by measuring the absorbances of $CoCl_2$ solutions of $C_{Me} = 1.01 - 3.80$ mM. Beer's law was found to apply at least to the highest mentioned C_{Me} value. Table II lists the ϵ values interpolated from the curves of Figure 4, the corresponding $\bar{n}$ and [L] values as well as the Fronaeus' functions, obtained by graphical integration of the $\bar{n}$/[L] *vs.* [L] curve as recommended by Ahrland.[21] From Table II it can be seen that $\bar{n}$ attains values of 1.98 and 2.13 for ϵ values reasonably lower than the asymptotic one, providing further indication of the existence of more than two complex species in the system; the last column of this Table shows that the F_3 function attains a range of near constancy, indicating that the system comprises *at least* three complex species in the experimental range studied.

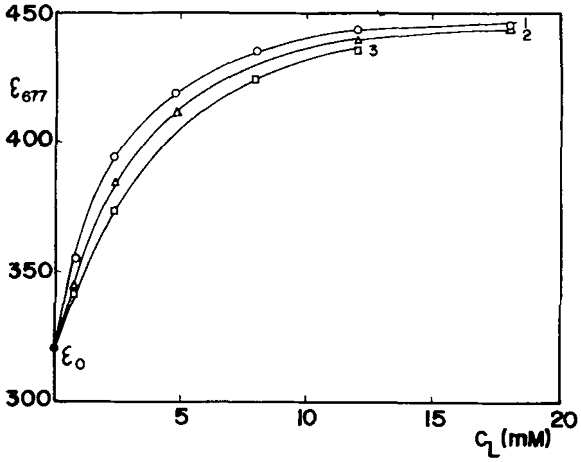

FIGURE 4 $CoCl_2$–TPPO system, in acetone medium, at 25°C. Dependence of the mean molar absorptivity on total ligand concentration. 1 – C_{Me} = 1.01 mM; 2 – C_{Me} = 1.53 mM; 3 – C_{Me} = 2.02 mM.

The stability constants and the molar absorptivities of the species found in the system are given in Table III. A good agreement is shown between the stability constants calculated from the Fronaeus' functions and those computed by assuming three complex species in solution. Also, a quite good agreement is revealed by comparing the ϵ_0 value

TABLE II

$CoCl_2$–TPPO system in anhydrous acetone. Concentration variables ($\bar{n}$, [L]) and Fronaeus' functions.[11] t = 25.00 ± 0.05°C.

ϵ^a	[L], mM	$\bar{n}$	$\bar{n}$/[L]	F_0	$F_1 .10^{-4}$	$F_2 .10^{-6}$	$F_3 .10^{-9}$
365^b	0.19	0.82	4,310	3.89	1.52	6.32	–
370^b	0.26	0.90	3,460	5.11	1.58	6.92	0.56
375^b	0.36	1.00	2,780	6.99	1.66	7.22	1.25
380	0.48	1.09	2,270	9.48	1.77	7.71	1.96
385	0.63	1.19	1,890	13.0	1.90	7.94	1.86
390	0.80	1.29	1,610	17.4	2.05	8.13	1.70
395	1.00	1.40	1,400	23.5	2.25	8.50	1.73
400	1.25	1.50	1,200	32.6	2.53	9.04	1.82
405	1.58	1.62	1,020	47.0	2.91	9.56	1.77
410	1.90	1.76	926	64.1	3.32	10.1	1.75
415	2.35	1.86	791	94.4	3.97	10.9	1.76
420	2.92	1.98	678	144	4.90	12.0	1.79
425	3.59	2.13	593	–	–	–	–

^{a}–interpolated values

^{b}–Values not used for the calculations owing to the greater uncertainty in this portion of the ϵ *vs.* C_L curves.

TABLE III

$CoCl_2$–TPPO system in ahydrous acetone. Stability constants and molar absorptivities. t = 25.00 ± 0.05°C.

		n			
		0	1	2	3
β_n	(*a*)	1	$(1.40 \pm 0.10).10^4$	$(6.77 \pm 0.95).10^6$	$(1.77 \pm 0.40).10^9$
	(*b*)	0.83	$1.44.10^4$	$6.73.10^6$	$1.79.10^9$
$\log \beta_n$	(*a*)	0	4.15 ± 0.03	6.83 ± 0.06	9.25 ± 0.10
	(*b*)	−0.08	4.16	6.82	9.25
K_n	(*a*)	1	$1.40.10^4$	483	261
ϵ_n	(*c*)	320	378	430	450

[a] Constants obtained by application of Fronaeus' method.[11] The indicated limits of error were calculated from the uncertainty limits (see original) of the experimental points shown in figure 4.

[b] Constants obtained by fitting the polynomial: $F_0 = \Sigma_0^3 \beta_n[L]^n$ to the experimental data of Table II.

[c] Molar absorptivities (677 nm) obtained by solving simultaneous equations of the type: $\Sigma_0^3 \epsilon_n \beta_n [L]^n = \epsilon \Sigma_0^3 \beta_n [L]^n . \beta_n(a)$ and ϵ data in the range of 380–425 (Table II) were used.

computed from the stability constants and the one determined experimentally (319).

So far the discussion has been based on the sole existence of mononuclear complexes in solution. Polynuclear species can be excluded almost with certainty only in such cases where measurements at several wavelengths yield results in close agreement.[18–20] In the present work, the constants were calculated from measurements carried out at a single wavelength (677 nm) since the results obtained during the investigation seemed to point to the absence of polynuclear species, for the fixed experimental conditions. Thus, the good agreement between the experimental and calculated formation curves (Figure 1, curve 2) confirm the compatibility between the stability constants and the experimental data; furthermore, this agreement furnishes an evidence indicating the absence of polynuclear species, within the experimental limits fixed for the present work.

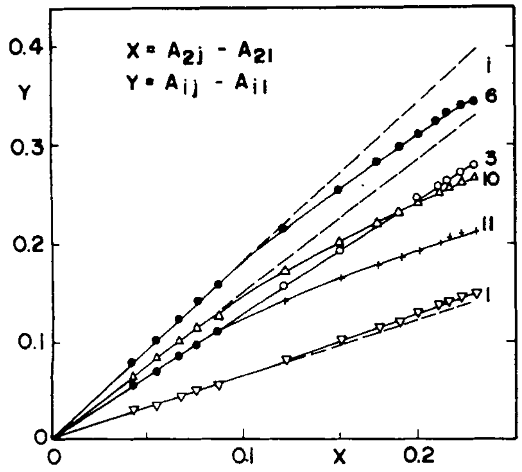

FIGURE 5 $CoCl_2$–TPPO system, in acetone medium, at 25°C. Test for two absorbing species based on the M″ absorbance matrix of Table I.

Figure 5 shows the curves obtained by applying the test of Coleman *et al.*,[16] assuming R = 2, to the M″ absorbance matrix (Table I). All these curves present a linear portion, passing through the origin, for X values associated to the 0–1.538 mM C_L range. The upper C_L limit of this range corresponds, approximately, to pL = 4.1 (it is helpful to note that the X values change only with J and, for the absorbance matrix considered, the consecutive numerical values of J are associated with increasing C_L and, therefore, [L] values). This result seems to reveal that up to the mentioned pL value the system comprises almost only two absorbing species. In fact, this is shown by the distribution diagrams Figure 6, (for pL = 4.10, α_2 = 0.02 and $\alpha_3 \simeq$ (0) providing further support concerning the validity of the stability constants estimated in this work.

The linear portions shown in Figure 5 correspond to C_{Me}/C_L ratios in the 1.3–6.5 range. On the other hand, an experiment was designed in which absorbances were measured in the 630–680 nm range for a series of solutions with constant C_L and variable C_{Me}(C_L = 0.109 mM; C_{Me} = 0.134–2.33 mM). By applying the test of Coleman *et al.* to the resulting absorbance matrix (assuming R = 2) a family of straight lines is obtained (Figure 7). The referred absorbance matrix was set up in such a way that the consecutive numerical values of J are associated with

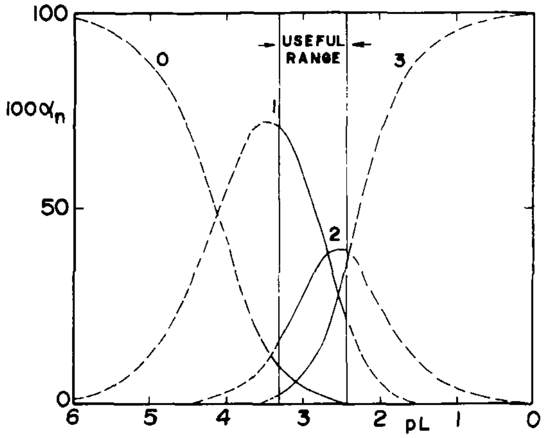

FIGURE 6 $CoCl_2$–TPPO system, in acetone medium, at 25°C. Distribution diagrams calculated from β_n values given in Table III.

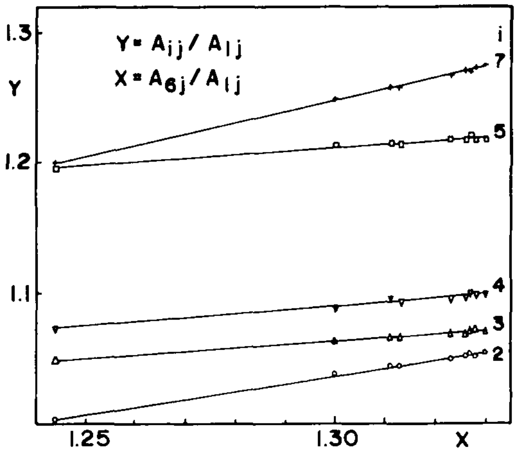

FIGURE 7 $CoCl_2$–TPPO system, in acetone medium, at 25°C. Test for two absorbing species. Solutions in which $C_L = 0.109$ mM and $C_{Me} = 0.134 - 2.33$ mM. $\lambda = 630–680$ nm.

increasing values of C_{Me}; the same is true relative to i and λ values. Linearity holds for the entire C_{Me}/C_L range (1.2–21.4). The association of results from both experiments (Figures 5 and 7) indicate that one of the absorbing species found is certainly $CoCl_2$ and the other, with great probability, is $CoCl_2(TPPO)$. It should be noted that the experimental conditions established for the last mentioned experiment are those in which the formation of polynuclear species would be very favoured.

Previous to the determination of the formation constants through the method of corresponding solutions, several attempts at determining β_1 were made by applying some spectrophotometric methods available for this purpose.[22,23] No consistency of results was found (values of log β_1 in the range of 3.5–4.2 were obtained). In one such attempt, a method described by Rossotti and Rossotti[22] (amongst other authors) was used. For the application of this method to the system under study, only data for C_{Me}, C_L and measured absorbances are, in principle, required. By working with $C_L = 1.09.10^{-4}$ M and $C_{Me} = 4.87.10^{-4} - 1.18.10^{-3}$ M, several difficulties appeared in connection with the computations. Precise values could not be obtained and the results pointed to a log β_1 between 3.8 and 4.0. Some advantages and limitations of this method were briefly discussed by Beck[23] and Mc Bryde;[20] it is known, for instance, that for β_1 values to be well-defined, $(C_{Me} + C_L)$ and β_1^{-1} must be of comparable magnitude.[20] By taking as correct the β_1 value obtained in this work, *via* the method of corresponding solutions, the lack of precision is to be expected as, in the fixed experimental conditions, $(C_{Me} + C_L) \gg \beta_1^{-1}$. On the other hand, the above mentioned condition is reasonably fulfilled, for most of the examined solutions, when the value for β_1 presented by Sheka *et al.*[1] is assumed ($\beta_1 = 437$), suggesting that the true constant must be higher than the one published by the cited authors.

The distribution diagrams (Figure 6) reveal that in most of the useful pL experimental range the 1:1 complex predominates; at the upper [L] limit of the indicated range (pL = 2.45), the 1:2 and 1:3 complexes occur in almost identical proportion, whereas the concentration of the 1:1 complex is still very significant. The 1:2 complex is the one that has been obtained in the crystalline state.[1,8,24,25] Partly from this fact, Sheka *et al.*[1] inferred that the mentioned complex is the highest in the $CoCl_2$–TPPO system, in acetone medium. Nevertheless, it is generally accepted that the crystallization of a particular complex from a system where several coexist, is due mainly to a lower recticular energy of that complex. So, the fact does not necessarily provide evidence that the 1:2 species is the highest one in the mentioned system, as was demonstrated in the course of the present work.

The body of experimental evidence shows, once more, the inadvisability of applying methods in which the computation of stability constants is dependent on the fixation of N. It appears that if, for any reason, an assumption concerning N has to be made, it must be based on adequate experimental support.[16,26] In connection with this statement, the method devised by Coleman *et al.*[16] seems to be of great value, as it was possible to demonstrate in the present investigation.

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