Inorganica Chimica Acta, 45 (1980) L173–L175

Microcalorimetric and Spectrophotometric Investigation on Cobalt(II)–Bromide System in Ethanol*

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Received July 18, 1980

Bromide complexes in ethanol were first studied by Bobtelsky and Spiegler [1] who made evidence for the species existing in solution. The relative values of formation constants (K_n) were determined by Libus *et al.* [2] and by Shchukarev and Lobaneva [3] using spectrophotometric methods. The latter Authors calculated the formation enthalpies ($\Delta H_{\beta n}$) using the Van't Hoff equation and these values are the only thermodynamic data on the subject quoted in the literature [4]. However, considering the method and the operative conditions there used, some uncertainties arose about the validity of the K_n values.

Moreover, the shape of the reported spectra [3] is typical of tetrahedral complexes [5] such as $CoBr^{3-}$ and $CoBr_4^{2-}$: so it seems unlikely to form the reported $CoBr_5^{3-}$. On the other hand, some inconsistencies were evidenced [5] also on the assignment of the complex species to the same system in acetone [6].

The direct determination of the formation heats by flow microcalorimetry can be a useful approach to study this problem. The directly measured reaction heats can be compared with values calculated using reported β_n and $\Delta H_{\beta n}$ ($\Delta H_n = \Delta H_1 + ... + \Delta H_n$) [3]. In addition spectrophotometric measurements may give further information to explain the reported results.

Experimental

$CoBr_2$ and LiBr anhydrous were purchased from Ventron-Alfa Division and absolute ethanol from Merck. All solutions were prepared as previously described [7].

The flow microcalorimeter LKB 10700-1 was equipped with silica syringes pump (Braun, Unita I) in order to avoid interferences by the peristaltic pump's plastic materials which may interact with ethanol. A measuring range of 10 ÷ 300 μV was used.

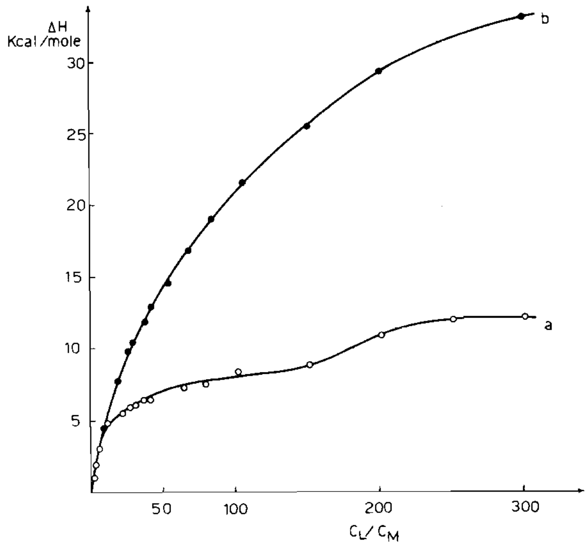

Fig. 1. Heat evolved per mole of cobalt(II) on mixing at 20 ± 0.1 °C solutions of $CoBr_2$ abd LiBr in ethanol at various bromide/cobalt(II) concentration ratios (C_L/C_M), $C_M = 8.5 \times 10^{-4}$ *M*. a) Experimental curve; b) Calculated curve.

Many preliminary experiments were carried out at various flow rates in order to check the full reaction signal and an operative flow rate of 0.5 ml/min was chosen. When increasing this flow rate up to 5 ml/min, no decrease in the heat evolved per mole of the reagents was observed, thus confirming that the reaction reaches the equilibrium and is completed in the calorimetric cell.

Beckmann DK-2A and Beckmann DU-2 spectrophotometers with quartz cells of 1.0 cm optical path were employed.

All calorimetric and spectrophotometric measurements were carried out at 20 ± 0.1 °C.

Results and Discussion

Evolved heats per mole of cobalt(II) were measured taking into account the dilution heats of the reagents. The experimental and the calculated curves are reported in Fig. 1.

The initial concentration of Co^{2+} was 8.5×10^{-4} M and that of Br^- was varied in the range $2.1 \times 10^{-3} \div 2.6 \times 10^{-1}$ *M*. The total enthalpy values plotted in the curve b were calculated according to the equation $\Delta H_{TOT} = \alpha_1 \Delta H_{\beta_1} + \alpha_2 \Delta H_{\beta_2} + ... + \alpha_n \Delta H_{\beta n}$, where α_n are the molar fractions of the respective n-complex species obtained from the reported formation constants [3] and actual reagent

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*Presented in part at 'VI Convegno del Gruppo di Termodinamica dei Complessi', Tabiano (Parma), June 1979.

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TABLE I. Apparent Molar Absorptivity Values at Various Metal and Ligand Concentrations for the System $CoBr_2$–LiBr in Ethanol at 20 ± 0.1 °C; λ = 710 nm; b = 1.0 cm.

C_M (M)	C_L (M)	ϵ' (M^{-1} cm^{-1})
5×10^{-4}	0.351	264
	0.101	156
	0.031	82
	0.011	44
	0.004	32
	0.002	20
10×10^{-4}	0.350	261
	0.100	146
	0.080	140
	0.030	86
	0.010	43
	0.003	24
20×10^{-4}	0.360	236
	0.105	144
	0.035	83
	0.010	38
	0.004	21
25×10^{-4}	0.360	231
	0.105	150
	0.035	81
	0.015	50
	0.005	20
30×10^{-4}	0.370	213
	0.110	134
	0.040	87
	0.015	35
	0.006	25
50×10^{-4}	0.370	178
	0.110	124
	0.040	70
	0.015	36
	0.010	27

concentrations. $\Delta H_{\beta n}$ values are the reported overall formation enthalpies [3] calculated on the basis of the Van't Hoff equation. On the other hand by combining the calculated α_n with the calorimetric results, it was not possible to determine the formation enthalpies ($\Delta H_{\beta n}$) relative to each complex. In fact, the obtained values are not consistent in the examined range, because of numerical uncertainty of data which do not reflect the assumed model of a stepwise complex formation. The same problems were found in determining the formation constants by calorimetry.

In order to plot a calibration curve of absorbances per mole of cobalt(II) *versus* C_L/C_M (initial molar concentration ratio of ligand and metal), several solutions were prepared with cobalt(II) concentration (C_M) equal to 8.5×10^{-3} M and bromide concentrations (C_L) varying in the range $1.7 \times 10^{-2} \div 3.8 \times 10^{-1}$ M.

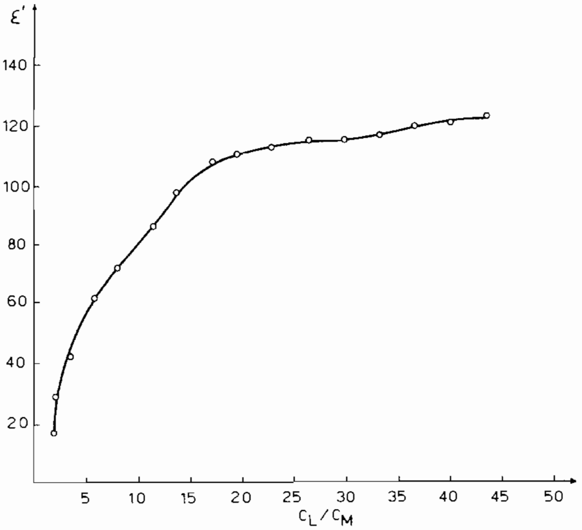

Fig. 2. Calibration curve for the system $CoBr_2$–LiBr in ethanol: $C_M = 8.5 \times 10^{-3}$ M; λ = 710 nm; b = 1.0 cm; t = 20 ± 0.1 °C.

Preliminary tests showed that the complex formation is instantaneous to the mixing time and that the formed species are inert over at least four hours. The calibration curve is plotted in Fig. 2. To apply the 'corresponding solutions method' [8] other solutions were prepared varying both the metal and the ligand concentrations, according to the values listed in the Table I. From these data it can be seen that the relative absorbance values are not consistent with those of the calibration plot (Fig. 2). In fact, this curve reaches a plateau, while the above absorbance values (Table I) are larger in many cases and they continuously increase without showing a limiting value. Nevertheless the trend of the formation function $\bar{n} = (C_L - [L])/C_M$ *vs.* logarithmic values of the free ligand concentration ($-\log$ [L]) was calculated for the corresponding solutions and the resulting plot shows so little trend (Fig. 3) that no more calculation is possible. Because of the great difference between the experimental and calculated curves (heats evolved *vs.* C_L/C_M, see Fig. 1), the validity of the stability constants and/or of formation enthalpy values [3] is very doubtful.

The numerical difficulties in obtaining univocal values of β_n and ΔH_n could be explained on the assumption that lithium bromide dissociation in ethanol is not complete at operative concentrations. In such a way the used model of a complex stepwise formation is not consistant with the experimental data.

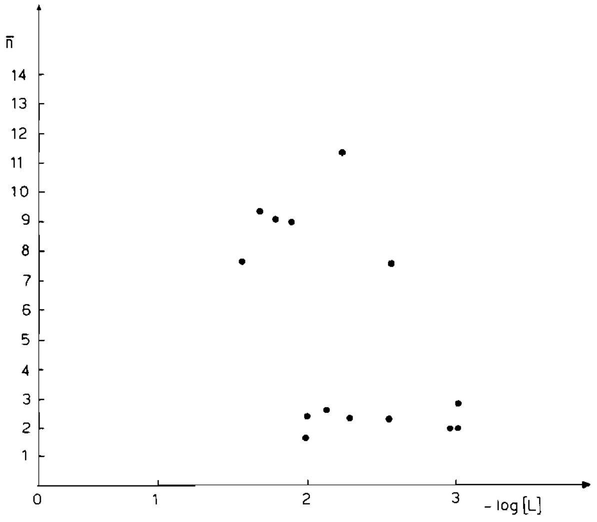

Fig. 3. Variation of the formation function $\bar{n} = (C_L - [L])/C_M$ depending on the free ligand concentration (–log [L]) for the system $CoBr_2$–LiBr in ethanol.

The assumption that LiBr dissociation in ethanol is not complete is supported by the considerable difference in the absorbance values between the corresponding solutions (Table I) and the calibration curve (Fig. 2). The formation functions values ($\bar{n}$) in the range 8 ÷ 10, at free ligand concentration ([L]) higher than 10^{-2} *M* (Fig. 3), also suggest that the considered total ligand concentration (C_L) is larger than the actual amount in solution. Moreover, in these conditions, configurational changes between tetrahedral and octahedral forms [9] must be taken into account, as they could be responsible, at each concentration, for the ΔH_n fluctuations, especially when n = 2, where the configurational change mainly occurs [10] with an equilibrium not shifted towards one of the two configurations. Both the tetrahedral and the octahedral forms of the $CoBr_2$ species contribute to the ΔH_2 value, depending on their relative concentrations, which are not only a function of free ligand in solution but also of the total amount of reagents with respect to the solvent.

In this way we could say that the reported thermodynamic quantities [3] are all lacking in correctness. This probably depends upon the operative conditions about which it is not possible to give an opinion because they are not completely described. For example, being the ethanol used not sufficiently anhydrous, the complete dissociation of LiBr might occur because of the presence of some water.

Furthermore it is worth considering that the complex species $CoBr_3^-$ and $CoBr_4^{2-}$ are strongly dissociated in ethanol, which is a solvent with good donicity (DN = 30, see reference 9). So the study of the equilibria at high C_L/C_M values seems to be incorrect and any pre-conceived model turns out to be unable to explain the cobalt(II)–bromide system experimental behaviour.

Acknowledgement

This work was carried out by the financial support of the Consiglio Nazionale delle Ricerche (Rome), which also gave a grant to one of us (R.B.).

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