

Complexation of Bi(III) with Chloride ion in non-aqueous medium

N.T. YATSIMIRSKAYA AND ARAIN RAFEE*

*Department of Analytical Chemistry, Moscow State University, Moscow.***Institute of Chemistry University of Sind Jamshoro. Pakistan.*

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Summary: The complexation of Bi(III) with chloride ion has been studied in non-aqueous medium. The state and behaviour of BiCl_3 and its higher complexes have been examined in organic solvents. This attempt is merely an addition to the study of Bi(III) complexes with potassium diphenyldiselenophosphate where Bi(III) forms complexes of definite (1:3) composition.

Introduction

In an earlier communication¹ the complexation of Bi(III) with potassium diphenyldiselenophosphate (dsp) was discussed which was carried out in chloride ion medium. In this regard the data had to be examined by taking into account the complexation of the metal with chloride ion present in the system. Therefore an attempt has been made to study the complexation of Bi(III) with chloride ion in non-aqueous solvents. This study is of considerable significance since chloride ion is a ligand which differs from dsp in the sense that it has a smaller radius and subsequently possesses high electron density and that it forms bonds of ionic character as it is a "harder anion"² compared to dsp. The following text is an attempt to discuss the pattern of complexation of Bi(III) with chloride ion in organic solvents, as the orientation of chloride ion is different from dsp.

Experimental

The absorbance of solutions was recorded on Hitachi EPS-3 spectro-photometer. All the measurements were made at $25 \pm 0.1^\circ\text{C}$ by providing thermostated camera for the cuvettes.

Results and Discussions.

Absorption spectra of Bi(III) chloride solutions in ethanol and DMF are presented in figure 1 (curve 1) and figure 2 (curve 1) (for off-setting the hydrolysis of Bi(III) a negligible amount of HCl was added to the solutions). Both these figures depict that the character of bismuth chloride spectra in ethanol and DMF is almost similar and are characterised by the presence of only one absorption band in the near UV region. This absorption is apparently due to charge transfer in bismuth(III) chloride. Figure 1 carries the absorption spectrum of

bismuth(III) in ethanol at various chloride concentrations. The addition of chloride ion brings about a change in the absorption spectrum of bismuth(III) chloride as has been reported earlier³ in case of aqueous solutions where the absorption maximum is shifted towards longer wavelengths. In the studied concentration interval of HCl two isospeptic points are observed at $\lambda = 298 \text{ nm}$ and $\lambda = 315 \text{ nm}$.

The dependence of absorbance on the concentration of chloride ion allows the calculation of step-wise stability constants of higher bismuth(III) chloride complexes. For calculating stability constants only that concentration range was selected in which only two forms of bismuth(III) chloride complexes exist- Bi(III) , BiCl_n and BiCl_{n+1} .

The presence of two types of complexes is evident from the two isospeptic points in the curve ($A - \lambda$) in the given concentration range. For all such series of curves the constant was calculated graphically taking the chloride concentration to be equal to the total HCl concentration, from the values of absorbances at 275 nm 317 nm, since the concentration of HCl was always in excess to that of Bi(III). Using the methods proposed by Rossotti⁴, we have:

$$A_x = A_o - K [L] (A_{\infty} - \bar{A}_x) \quad (1)$$

and the value of stability constant is calculated as the tangent of the slope from the co-ordinates $A_x - L(A_{\infty} - \bar{A}_x)$ (figure 3 a,b). The values obtained are $K_n = 8.1 \times 10^4 \text{ M}^{-1}$, $K_{n+1} = 46.6 \text{ M}^{-1}$ and $K_{n+2} = 2.9 \text{ M}^{-1}$.

The absorption spectra of bismuth chloride solutions in DMF at varying concentration of LiCl are shown in figure 2. Here too like ethanol the addition of chloride ion the absorption maximum is shifted to longer wavelength region of the spectrum. In the studied concentration range two isospeptic points at $\lambda = 306 \text{ nm}$ and $\lambda = 324 \text{ nm}$ are observed. The calculation of step-wise stability constant was carried out graphically⁴ from the

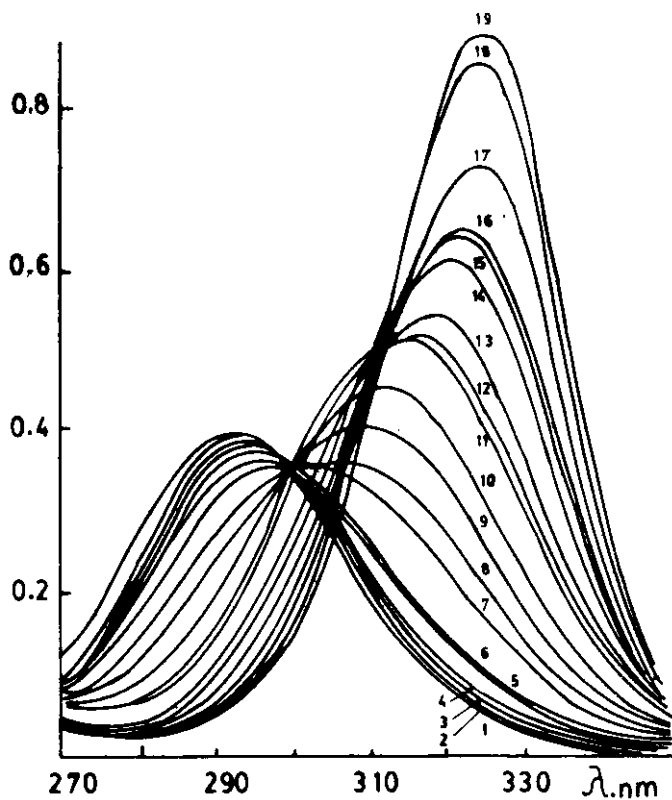
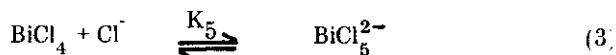
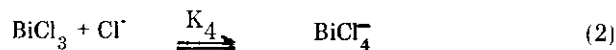


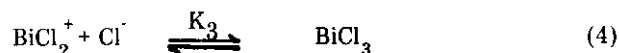
Figure 1: Absorption spectra of 6×10^{-5} M BiCl_3 at various HCl concentrations (in moles) in ethanol: (1) 6×10^{-5} (2) 4.6×10^{-4} (3) 9.2×10^{-4} (4) 1.8×10^{-3} (5) 2.8×10^{-3} (6) 3.7×10^{-3} (7) 7.4×10^{-3} (8) 1.16×10^{-2} (9) 2.1×10^{-2} (10) 4.6×10^{-2} (11) 0.11 (12) 0.16 (13) 0.35 (14) 0.46 (15) 0.58 (16) 0.67 (17) 0.93 (18) 1.04 (19) 1.16

values of absorbances at $\lambda = 330$ nm. The concentration range involved in the calculation corresponds to the presence of two types of complexes Bi , BiCl_m and BiCl_{m+1} . The value of stability constant is equal to the tangent of the slope from the co-ordinates $[(\bar{A}_x - A_0)/C_{\text{LiCl}}] - \bar{A}_x - (K_{m+1})$ and from the co-ordinates $[(\bar{A}_x - A_0)/(A_0 - \bar{A}_x)] - C_{\text{LiCl}} - K_m$ (figure 3 c,d). The values obtained are $K_m = 1.5 \times 10^4 \text{ M}^{-1}$ and $K_{m+1} = 38.5 \text{ M}^{-1}$.

An analysis of the values obtained for step-wise stability constants for higher chloride complexes of Bi(III) in methanol and DMF shows that the constants $K_n, K_m, K_{n+1}, K_{m+1}, K_{n+2}$ correspond to K_3, K_4 and K_5 . This conviction is further supported by comparing the values of these constants in water, ethanol and DMF. In fact the values of K_4 and K_5 should slightly depend upon the nature of the solvent because the left hand and the right hand side species of equations accounting for step wise constants have equal number of charge ions⁵:



Thus the values obtained for K_4 and K_5 in water⁵ should almost be equal to the values in ethanol and DMF. The results obtained in this work in conformity with one another. This is exactly the case when we compare the values in water K_4 equaling 89^6 is closer to the values calculated for K_{n+1} and K_{m+1} equaling 46.6 and 38.5 respectively. Similarly a satisfactory arrangement exists between the values of K_{n+2} , calculated in ethanol (2.9) and K_5 in water (3.2)⁶. On the other hand the constant K_3 accounting for the association of various ions forming uncharged molecules must strongly depend on the solvent⁵:



Hence the values of K_3 obtained are by no means less by one order of magnitude than in water (in literature K_3 for water is 2×10^3)^{7,8}.

The values of stability constants for the following equations:

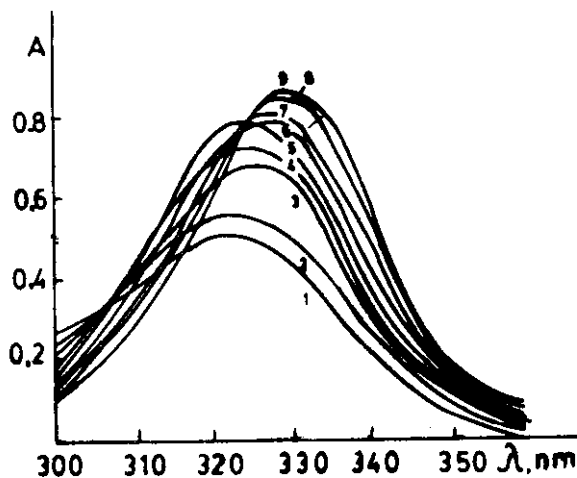
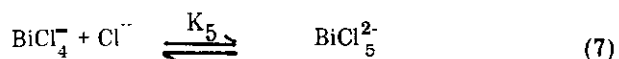
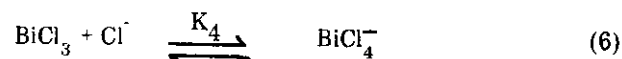
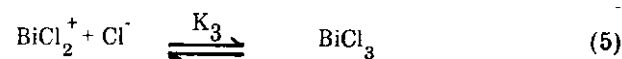


Figure 2: Absorption spectra of 8×10^{-5} M BiCl_3 at various LiCl concentrations in DMF: (1) 8×10^{-5} M (2) 1×10^{-4} M (3) 2×10^{-4} M (4) 6×10^{-4} M (5) 2×10^{-3} M (6) 2×10^{-2} M (7) 4×10^{-2} M (8) 6×10^{-2} M (9) 8×10^{-4} M.

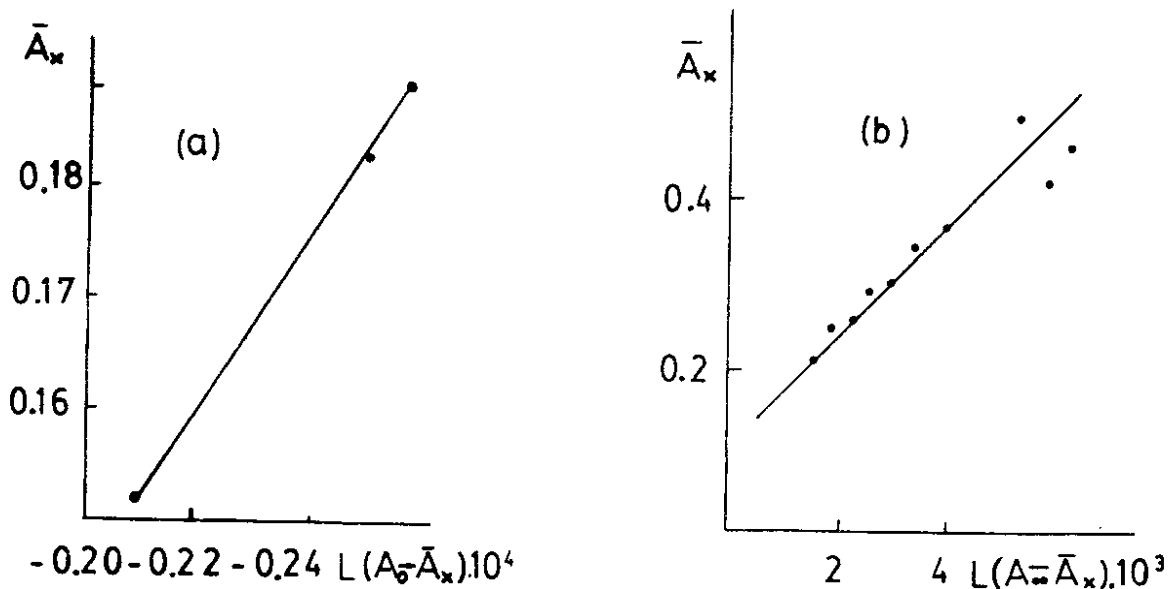


Figure 3 (a) and (b) : Calculation of stability constant in ethanol. (a)— K_3 and (b)— K_4

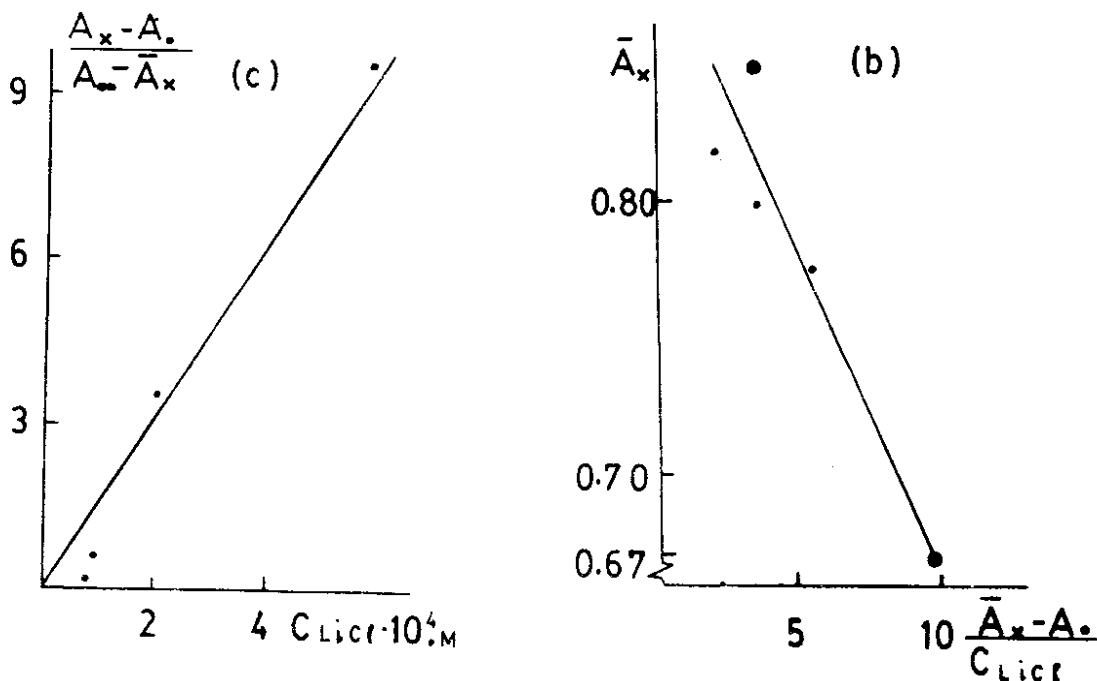


Figure 3 (c) and (d) : Calculation of stability constant DMF: (c)— K_3 and (d)— K_4

in ethanol, methanol DMF and water are summarised in table 1. The data in table 1 clearly shows that the solvent appreciably changes the stability constant -changing K_3 by forty times from ethanol to water. While the values of K_4 depend only slightly on the nature of the solvent and do not correlate with dielectric constant. Instead it

is expected that K_4 would depend, in principle, on the donor properties of the solvent if one takes into account the solvation of equation (6) expressed by the following equation:

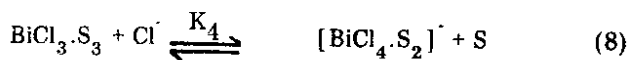


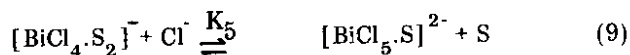
Table 1.

Step-wise stability constants of higher chloride complexes.

Solvent	K_3, M^{-1}	K_4, M^{-1}	K_5, M^{-1}
EtOH	$(8.1 \pm 0.4) 10^4$	47 ± 3	2.9 ± 0.3
MeOH*	$(3.0 \pm 0.3) 10^4$	40 ± 3	7.0 ± 0.5
DMF	$(1.5 \pm 0.2) 10^4$	38 ± 4	—
H ₂ O**	2×10^3	89	3.2

*data taken from⁶**data taken from^{5,7,8}

Apparently the contribution due to desolvation is not significant in this case, because the more closely bound molecules of the solvent remain attached. The process of attaching the next chloride ion can be expressed as:



The value of K_5 is almost equal for ethanol, methanol and water having closer donor strength (DN = 18-19).

The values of K_3 , K_4 and from table 1 can be used to calculate the relevant proportions of various chloride complexes of Bi(III). This is worked out as follows:

$$\frac{[\text{BiCl}_2^+]}{[\text{Bi(III)}]_0} = \frac{1}{(1 + 1/K_3 [\text{Cl}^-] + K_4 [\text{Cl}^-]) K_3 [\text{Cl}^-]} \quad (10)$$

$$\frac{[\text{BiCl}_3]}{[\text{Bi(III)}]_0} = \frac{1}{1 + 1/K_3 [\text{Cl}^-] + K_4 [\text{Cl}^-]} \quad (11)$$

$$\frac{[\text{BiCl}_4^-]}{[\text{Bi(III)}]_0} = \frac{K_4 [\text{Cl}^-]}{1 + 1/K_3 [\text{Cl}^-] + K_4 [\text{Cl}^-]} \quad (12)$$

For the solvents studied the value of $K_3 \geq 1 \times 10^4 M^{-1}$. Hence the factor $1/K_3 [\text{Cl}^-]$ while using a background concentration of 0.01M Cl⁻ does not exceed 0.01 that is it does not appreciably affect the overall values of equations 10-12. K_4 depends slightly on the nature of the and for all the investigated solvents falls within 38 to 47 M⁻¹. Substitution of these values in equations 10-12 shows that the relative portion of BiCl₂ is negli-

gibly small while BiCl₃ accounts for 70±2 % and BiCl₄⁻ for 30± 2%. Since the value of K_4 , responsible for the main contribution to the calculations according to equations 10-12 is almost constant (table 1) for all the solvents differing in their physico-chemical properties. The only conclusion that can be drawn is the starting species in all these cases contain 70±2 % of BiCl₃.

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