The Concept of Theoretical Molar Absorptivity for Photometric Determination of Trace Amount of Metal & Thermodynamic Formation Constants of Mo(VI) Complexes with Disodium cis-1,2-Dicyanoethylene-1,2-dithiolate*

SASWATI P. BAG & ANIL K. CHAKRABARTI

Department of Chemistry, Jadavpur University, Calcutta 700032

A new concept on theoretical molar absorptivity for the Mo-MNT complex has been given utilizing photometric law and free-ligand concentrations. Also, a new photometric method has been described for the evaluation of stepwise and successive formation constants for the 1:4 metal-ligand system. The overall formation constant can be termed as thermodynamic stability constant for a $10^{-4}M$ solution of molybdenum-MNT chelate complex. Different photometric procedures have been included for the calculation of overall formation constants including that of extrapolation of log K values against α and compared with each other. Log k_1, log k_2, log k_3, log k_4 and log β_4 have been found to be 4·46, 2·68, 2·91, 2·72 and 12·75 respectively. The log K values from Harvey-Manning's equation, mole-ratio plot and extrapolation method are found to be 15·85, 15·85 and 18·25 respectively at $25° \pm 0·1°$. The theoretical molar absorptivity (TMA) and the calculated molar absorptivity values are $5·80 \times 10^3$ and $5·87 \times 10^3$ litre mole^{-1} cm^{-1} respectively. The free energy change for the reaction comes out to be $-17·5$ kcal mole^{-1} (log $K = 12·75$) at 25°.

DISODIUM cis-1,2-dicyanoethylene-1,2-dithio-late (Na$_2$MNT) has been found to form coloured complexes with molybdenum(VI), tungsten(VI), vanadium(V) and many platinum group metals in 50% acetonitrile-water mixed solvent[1]. Previously, a green complex of molybdenum in the mixed solvent (λ_{max}, 665 nm) has been utilized for a selective photometric estimation of the metal in alloy steels[2]. In the present investigation, a new concept on theoretical molar absorptivity (TMA) has been evaluated on the basis of photometric law, composition and graphical extrapolation method. The metal to ligand ratio from both the continuous variation and mole-ratio methods has been found 1:4 with varied metal ion concentrations.

pH-metric methods for formation constants are often applied in many metal-chelate systems giving rarely unusual and abnormal results. However, with Mo(VI) chelates some unusual behaviour is often encountered due to redox reactions and H-bonding. Further, Mo(VI) complexes are supposed to be reduced to Mo(V) by thiols and the determination of stepwise formation constants is invariably difficult, and more so in case of high dissociation. Previously, it has been observed that a same degree of accuracy is achieved by two distinctly different photometric procedures when applied to Mo(VI)-thiol chelate with high metal-ligand ratio[3]. In the present investigation with molybdenum-MNT system the degree of complex formation function and subsidiary functions has been considered because of greater accuracy claimed in the method. The log K (K = overall formation

constant) values obtained employing subsidiary functions, Harvey-Manning's equation, mole-ratio plot and extrapolation methods was found to differ by logarithmic units. The results obtained by different methods have been compared and discussed. The successive formation constants (β_1, β_2, β_3, β_4) have been obtained from intercepts given by photometric method of extrapolation. The Ψ functions are plotted against and extrapolated to zero free-ligand [L].

Materials and Methods

Molybdenum solutions ($4·168 \times 10^{-3}M$) were obtained by proper dilution of the stock solution of known strength. Reagent solutions of equimolar strength were prepared from extremely pure form of Na$_2$MNT, to study the effect of varying metal to ligand ratio[4]. For this reason the reagent was purified three times from ethanol-ether mixture. Higher concentrations of freshly prepared solutions of reagent were utilized for mixing incomplementary proportions (6 ml). Pure acetonitrile (Riedel) was further purified by distillation over P$_2$O$_5$.

All spectral measurements were made with a Unicam SP600 spectrophotometer in 1 cm glass cells.

Determination of the metal-ligand composition — The composition of the molybdenum-MNT complex in mixed solvent was determined by method of continuous variation[5] and verified by mole-ratio method[6]. Equimolar solutions of metal and reagent were utilized in the final volume of 25 ml and mixed in complementary proportions (6 ml). After addition of required amount of acid (HCl), reagent solutions of higher concentrations were added and acidity was maintained at $3M$ HCl. The curves have been obtained by plotting absorbances (measured at 665 nm)

against mole fraction of metal. For constant metal ion ($2 \cdot 084 \times 10^{-3}M$ and $4 \cdot 164 \times 10^{-3}M$), mole-ratio plot indicated the composition to be 1:4 (molybdenum: MNT).

Photometric procedure — A suitable aliquot of Mo(VI) solution was taken and to this was added varying amounts of reagent solutions and hydrochloric acid so as to maintain acidity at $3M$ HCl in a total volume of 25 ml. The turbidity of solution was removed by adding 12·5 ml of purified acetonitrile. After thorough mixing the solution was allowed to attain normal room temperature. The absorbances measured at 665 nm were plotted against mole fraction of molybdenum. The photometric titration data (Table 1) have been utilized for evaluation of formation constants as well as theoretical absorbance.

Calculations — The theoretical molar absorptivity (TMA) of complex species was evaluated from photometric titration results[7]. A series of absorbance values were determined considering amount of metal complexed from Beer's law. Since molybdenum species absorbed strongly at wavelength maxima the different absorptivities were expressed as $e = \text{absorbance}/C_M$ and the average value was found for solution comprising only single coloured species. Principle of the method of obtaining TMA of the complex involved extrapolation of absorptivities at several points in photometric titration curve. The e values were plotted against Y where Y stands for inverse of free-ligand concentration [L]. The intercept gives TMA at almost infinite amount of free-ligand concentrations, i.e. in the presence of large excess of ligand (Na$_2$MNT).

Successive and stepwise formation constants of molybdenum-MNT complex species were obtained considering the equation $M + nL \rightleftharpoons ML_n$ ($n = 4$). Since overall concentration of metal in solution (C_M) is sum of the concentrations of complexes, it follows that

$$\varphi = \frac{C_M}{[M]} = 1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4$$

where β_1, β_2, β_3 and β_4 are the successive formation

constants[8]. The degree of complex formation function (φ) has been calculated on the basis that the composition was 1:4 even in the presence of insufficient ligand concentration. In this procedure a series of subsidiary functions were constructed and extrapolated to zero value of the variable [L]. The function ψ_1 can be constructed and defined as follows:

$$\psi_1 = \frac{\varphi - 1}{[L]} \text{ and } \underset{[L] \to 0}{\text{Lim}} \psi_1 = \underset{[L] \to 0}{\text{Lim}} \frac{\varphi - 1}{[L]} = \beta_1$$

$$\underset{[L] \to 0}{\text{Lim}} \psi_2 = \underset{[L] \to 0}{\text{Lim}} \frac{\psi_1 - \beta_1}{[L]} = \beta_2 = k_1 k_2$$

$$\underset{[L] \to 0}{\text{Lim}} \psi_3 = \underset{[L] \to 0}{\text{Lim}} \frac{\psi_2 - \beta_2}{[L]} = \beta_3 = k_1 k_2 k_3$$

$$\underset{[L] \to 0}{\text{Lim}} \psi_4 = \underset{[L] \to 0}{\text{Lim}} \frac{\psi_3 - \beta_3}{[L]} = \beta_4 = k_1 k_2 k_3 k_4$$

In general, $\underset{[L] \to 0}{\text{Lim}} \psi_n = \underset{[L] \to 0}{\text{Lim}} \frac{\psi_{n-1} - \beta_{n-1}}{[L]} = \beta_n$

(where $n = 2, 3, 4$ and $k_1, k_2, k_3, k_4 = $ stepwise formation constants).

Thus, the values for β_1, β_2, β_3 and β_4 are obtained by plotting the functions ψ_1, ψ_2, ψ_3, ψ_4 against the variable and extrapolated to zero free-ligand concentration [L]. Knowing the metal-ligand composition, the free-metal and free-ligand concentrations for each of the solutions are calculated from Beer's law data. The metal is bound to ligand in 1:4 ratio even in the absence of sufficient amount of equimolar reagent concentrations. So, once the amount of metal complexed is known the free-metal can be calculated. Also, the free-ligand concentration is obtained considering amount of ligand complexed in the complex species. The successive formation constants have been found directly from intercept values.

The free-energy change for the reaction has been calculated from the equation

$$\Delta F^\circ = -RT \ln K$$
$$= -17 \cdot 5 \text{ kcal mole}^{-1} (\log K - 12 \cdot 75) \text{ at } 25^\circ$$

Results and Discussion

In Fig. 1, e values with different free-ligand concentrations have been plotted against y, i.e. $1/[L]$. The curve is extrapolated to y tending towards zero and the intercept gave for TMA a value of $5 \cdot 80 \times 10^3$ litre mole^{-1} cm^{-1} ($5 \cdot 87 \times 10^3$ litre mole^{-1} cm^{-1}, cf. Beer's law). In the presence of sufficient reagent in excess Mo-MNT complex appeared to be a strong one. TMA obtained by extrapolation method ($5 \cdot 80 \times 10^3$) was almost similar to that given by Beer's law data ($5 \cdot 87 \times 10^3$) and lies within highest experimental accuracy as revealed by the data in Table 1. The concept of TMA has already been followed with different metal-ligand ratios. Since absorbance corresponds directly to the amount of molybdenum complex formed, [L] is found using established composition and photometric law. The TMA concept appeared to be important. Because the actual analytical concentration of metal ion involved for high dissociating complexes can be

TABLE 1 — ABSORBANCE, FREE-LIGAND CONCENTRATIONS AND THE MOLAR ABSORPTIVITY VALUES OF MOLYBDENUM-MNT SYSTEM IN 50% AQUEOUS ACETONITRILE AT $25^\circ \pm 0 \cdot 1^\circ$

$[M = R = 4 \cdot 168 \times 10^{-3} M]$

Total ligand conc. ($C_L \times 10^4$, M)	Absorbance	Free-ligand conc. ([L] $\times 10^4$, M)	Molar absorptivity litre mole^{-1} cm^{-1} ($e \times 10^{-3}$)	$Y = 1/[L]$ ($\times 10^{-3}$)
6·601	0·760	1·285	4·559	7·782
8·337	0·860	2·321	5·159	4·308
9·870	0·885	3·678	5·309	2·718
11·672	0·920	5·228	5·520	1·913
13·339	0·925	6·867	5·549	1·456
15·007	0·930	8·495	5·580	1·177
16·674	0·930	10·162	5·580	0·984
18·341	0·930	11·830	5·580	0·845
20·009	0·930	13·497	5·580	0·740
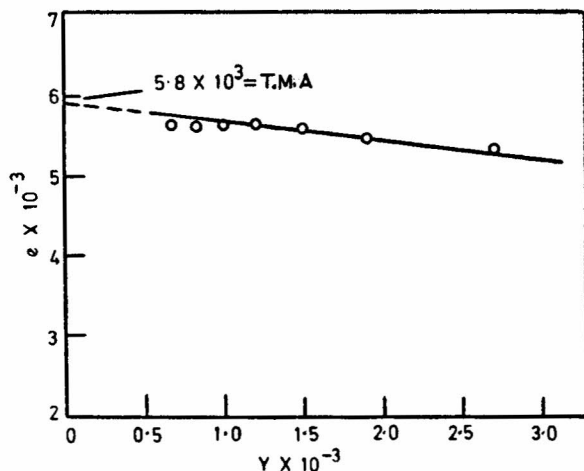
Fig. 1 — Average molar absorptivity e as a function of the reciprocal of the free-ligand concentration

Fig. 2 — Subsidiary functions Ψ_1, Ψ_2 as a function of free-ligand concentration [L]

Fig. 3 — Subsidiary functions Ψ_3, Ψ_4 as a function of free-ligand concentration [L]

accurately evaluated from theoretical absorbance. In the present system, the concentration of molybdenum obtained from observed absorbance and theoretical absorbance (cf. TMA) are the same. From Fig. 1 the immediate conclusion regarding nature of complex species is that four to five times equimolar excess of MNT solution was enough to form a strong complex with negligible degree of dissociation. Utilizing TMA it would be possible to design and choose a sensitive and selective reagent for a particular metal ion system in a particular solvent. The concept of TMA is useful for molybdenum-MNT system for accuracy involved during selective determination of trace quantity of the metal. Also, since the intercept gives TMA at excess of free-ligand degree of dissociation (α) is minimum lowest possible.

Figs. 2 and 3 illustrate the plots of Ψ function against free-ligand [L]. In the range of reagent concentrations employed between $8\cdot337 \times 10^{-4}M$ and $15\cdot01 \times 10^{-4}M$ in the final volume the different subsidiary functions have been constructed. The functions near the vicinity of 1:4 metal to ligand ratio were most suitable to give intercepts that are accurate and reproducible. From Table 2 it is evident that the φ value increases with decrease in free-metal (uncomplexed). A general trend has been maintained with Ψ functions plotted against
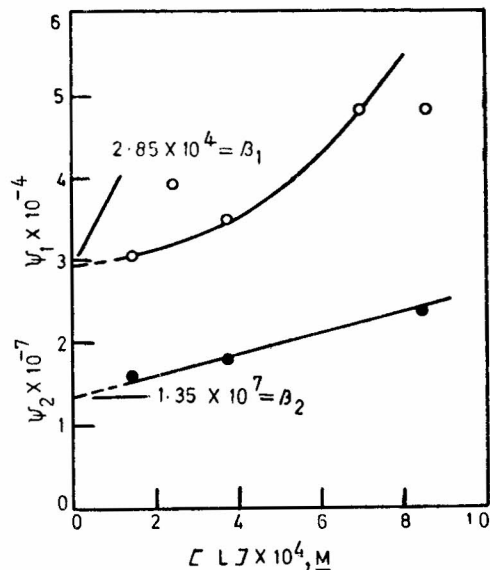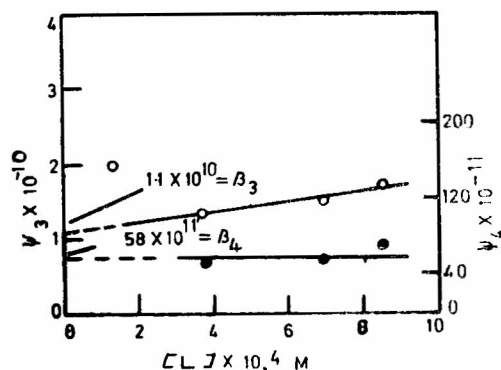
[L]. However, $\log k_1$ (4·46) $>$ $\log k_3$ (2·91) $>$ $\log k_4$ (2·72) and $\log k_1 > \log k_2$ (2·68?) $< \log k_3$. Overall formation constant (K) has been calculated considering TMA as absorbance maximum. α from the relation, $\alpha = \text{TMA} - \text{absorbance}_{\text{stoichiometric}}/\text{TMA}$ was found to be 0·1827. Thus, $\log K$ utilizing Harvey-Manning's method[9] comes out to be 15·85. The $\log K$ evaluated by photometric method is found

TABLE 2 — ABSORBANCE, FREE-LIGAND CONCENTRATIONS AND DEGREE OF COMPLEX FORMATION FUNCTIONS OF MOLYBDENUM-MNT SYSTEM IN 50% AQUEOUS ACETONITRILE AT 25° ± 0·1°

[M = R = $4\cdot168 \times 10^{-3}M$; final volume = 25 ml]

Total ligand conc. ($C_L \times 10^4$, M)	Absorbance	Equilb. ligand conc. ([L]$\times 10^4$, M)	Equilb. metal conc. ([M]$\times 10^5$, M)	Conc. of metal complexes ($\times 10^4$, M)	Degree of complex formation function, $\varphi = C_M/[M]$	ψ_1 ($\times 10^{-4}$)	ψ_2 ($\times 10^{-7}$)	ψ_3 ($\times 10^{-10}$)	ψ_4 ($\times 10^{-12}$)
6·601	0·760	1·285	3·384	1·329	4·926	3·056	1·603	1·97	67·70
8·337	0·860	2·321	1·634	1·504	10·20	3·964	4·794	14·86	593·1
9·869	0·885	3·678	1·194	1·548	13·96	3·523	1·829	1·30	5·437
11·672	0·920	5·228	0·574	1·610	29·04	5·363	4·806	6·61	105·4
13·39	0·925	6·867	0·494	1·618	33·75	4·769	2·801	1·48	5·535
15·007	0·930	8·485	0·394	1·628	42·31	4·863	2·369	1·71	7·063

to be 12·75. The overall stability constant has also been calculated employing extrapolated curve in mole-ratio plot. The basis for the procedure is that the ratio of true absorbance to the extrapolated absorbance in mole-ratio plot is mole fraction of the molybdenum complex actually formed ($abs_{stoich}/abs_{extrapt} = ML_4/C_M$). The value of α has been considered further to be 0·1383 ($\alpha = abs_{extrapt} - abs_{stoich}/abs_{extrapt}$) for Harvey-Manning's equation. Thus, log K (average) from mole-ratio plot is found to be 15·85 ($C_M = 1·667 \times 10^{-4}M$).

In extrapolation method, α values obtained from points above stoichiometric break are found to be 0·1162, 0·1412, 0·1739, 0·1783 and 0·1827. log K values from corresponding α in titration curve was found to give an increasing trend with α. The plot is linear having a negative slope. It increases sharply with more of free-ligand, indicating some dissociation of Mo-MNT complex around equal molar proportions of reagent. log K (= 18·25) obtained by extrapolation to zero α was found to to differ from that given directly by Harvey-Manning's method (15·85).

Difference in log K by several units, photometric 12·75; Harvey-Manning 15·85; mole-ratio plot 15·85 and graphical extrapolation 18·25 supported a dissociative nature of molybdenum thiolate complex in the absence of sufficient amount of reagent. In the presence of excess of reagent the dissociation is checked and com-plete formation of the complex is ensured. In photo-metric method evaluation of φ involved lower concen-tration of the coloured species which contributed a value much lower than theoretical absorbance. On the other hand, α has been calculated consi-dering the complete formation of the species. With very dilute solutions of $10^{-4}M$ molybdenum and MNT, both ionic strength and the salt effect in the acetonitrile-water solvent have not necessarily been considered. Actually, the formation constant can be termed thermodynamic stability constant.

References

1. CHAKRABARTI, A. K., *Complexes of less-common metals (Studies on formation constants and analytical applications)*, Ph.D. thesis, Jadavpur University, 1971.
2. CHAKRABARTI, A. K. & BAG, S. P., *Talanta,* **19** (1972), 1187.
3. BAG, S. P. & CHAKRABARTI, A. K., *J. Indian chem. Soc.,* **51** (1974), 474.
4. DAVISON, A. & HOLM, R. H., *Inorganic syntheses*, Vol. 10 (McGraw-Hill, New York), 1967, 11.
5. VOSBURGH, W. C. & COOPER, G. R., *J. Am. chem. Soc.,* **63** (1941), 437.
6. YOE, J. H. & JONES, A. L., *Ind. Engng Chem. (Anal. edn),* **16** (1944), 111.
7. CHAKRABARTI, A. K. & BAG, S. P., *Talanta,* **23** (1976), 736.
8. BAG, S. P. & CHAKRABARTI, A. K., *J. Indian chem. Soc.,* **52** (1975), 492.
9. HARVEY, A. E. & MANNING, D. L., *J. Am. chem. Soc.,* **72** (1950), 4488; **74** (1952), 4744.