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A New Method for the Determination of Equilibrium Constant and Molar Extinction Coefficient of 1 : 1 Type Complex

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Job's method of continuous variation has been reinvestigated with respect to the formation of 1 : 1 type complex from the view point of (i) geometrical significance of the Job curve, (ii) developing a method for determining the equilibrium constant and molar extinction coefficient of the complex. A mathematical analysis of the method of continuous variation as applied to the formation of strictly 1 : 1 type complex shows that the Job curve is a hyperbola obeying the equation

$$\frac{(d-\beta)^2}{a^2}-\frac{(C_M^\circ/\lambda-1/2)^2}{b^2}=1,$$

where d is the corrected optical density, C_M° is the initial concentration of the metal ion in solution, λ is a constant equal to the sum of the concentrations of the metal and the ligand in solution, β is the ordinate of the local origin of the hyperbola referred to the conventional framework of the Job curve, a and b represent respectively the semi-major and semi-minor axes of the hyperbola. The equation has been recast into the form $x=A_3d^2+A_2d+A_1$, where $x=(C_M^\circ/\lambda-1/2)^2$ and A_3, A_2, and A_1 are the appropriate coefficients. A parabolic fit of this equation between x and d by the least square deviation method using the computer B-6800 system enables one to find the coefficients A_3, A_2, and A_1 from which K and ε are evaluated. This equation has been tested with literature data on a variety of 1 : 1 type metal complexes whose formation constants and extinction coefficients as calculated by the present method agree closely with those determined by other methods. The promising features of the equation have been discussed.

There are various methods for ascertaining the composition of complexes, of which the most noteworthy is the method of continuous variation introduced by Job.[1] The simplicity of the method has made it very attractive and it is widely used in the evaluation of spectrophotometric data. Beck[2] has listed several limitations of the method and has cautioned that they have to be considered before it is applied to the study of complexes. The method works well if only one complex is formed in the system, although Voshburgh and Cooper[3] as well as Katzin and Gebert[4] applied it to the study of stepwise complex formation. For a very stable complex the curve of absorbance (or other suitable measured property) *versus* mole fraction (X) of one of the two components of the complex consists of two strictly linear intersecting portions.[2] In the case of moderately stable complexes there is no such linearity, and from the deviation of the curve and that constructed by extrapolation from the slopes near the extreme values of x, the value of the equilibrium constant can be calculated. There are, however, other methods[2,5,6] for determining the equilibrium constant of metal-chelate formation reactions from spectral data. A critical analysis of the principle of continuous variation method shows that the geometrical significance of the Job curve as observed in the case of 1 : 1 complex has not been elucidated, not to mention of those found in the case of higher order complexes. The purpose of the present investigation is to elucidate the geometrical nature of the conic, and to develop therefrom a general method for determining the stability constant and molar extinction coefficient of 1 : 1 complexes.

Principle

The stability constant for an 1 : 1 type complex, ML, formed between a metal ion and a ligand is given by

$$K_c=\frac{C_{ML}}{(C_M^\circ-C_{ML})(C_L^\circ-C_{ML})}, \tag{1}$$

where C's are the concentrations of the various species at equilibrium, the superscript zero refers to the initial concentrations. The optical density (corrected for absorption, if any, by the metal and the ligand) of a solution containing the complex, the free metal and the ligand is

$$d=\frac{1+K_c(C_L^\circ+C_M^\circ)-[\{K_c(C_L^\circ-C_M^\circ)\}^2+2K_c(C_L^\circ+C_M^\circ)+1]^{1/2}\varepsilon l}{2K_c}, \tag{2}$$

where ε is the effective extinction coefficient of the complex ($\varepsilon=\varepsilon_{ML}$ only when the complex alone absorbs at the wavelength of measurement), l is the path length. In Job type experiment the sum total of the concentrations of the metal and the ligand is held constant, *i.e.*, $C_M^\circ+C_L^\circ=\text{constant}=\lambda$ (say). Under this condition Eq. 2 reduces to the equation of the hyperbola

$$\frac{(d-\beta)^2}{a^2}-\frac{(C_M^\circ/\lambda-1/2)^2}{b^2}=1, \tag{3}$$

where $a^2=\dfrac{1+2K_c\lambda}{m^2}$, $b^2=\dfrac{1+2K_c\lambda}{4K_c^2\lambda^2}$, $\beta=\dfrac{1+K_c\lambda}{m}$, and

$$m=\frac{2K_c}{\varepsilon l}.$$

Here a and b represent respectively the semi-major and semi-minor axes of the hyperbola; β is the ordinate of the local origin of the hyperbola referred to the conventional framework of the Job curve.

In Job type experiment we plot customarily d along the y-axis and C_M°/λ in the abscissa. According to Eq. 3 a plot of d against C_M°/λ should be a hyperbola and it is evident that the axes of the hyperbola are not the axes in our original framework of the coordinate system but some axes which are parallel and interchanged with respect to the original axes.

The eccentricity of the hyperbola is related to a and b of the hyperbola and to the physical parameters of the complex by the relation

$$e^2 = 1 + \frac{b^2}{a^2} = 1 + \frac{1}{\lambda^2\varepsilon^2 l^2}, \tag{4}$$

which shows that the nature of the hyperbola depends on the extinction coefficient and on the total molar concentration of the solution but not on the equilibrium constant of the complex.

Determination of K_c and ε. Equation 3 can be written in the following form

$$x = A_3 d^2 + A_2 d + A_1, \tag{5}$$

where $x = (C^\circ_M/\lambda - 1/2)^2$, $A_3 = \frac{b^2}{a^2}$, $A_2 = -2\left(\frac{b^2}{a^2}\right)\beta$, and

$$A_1 = b^2\left(\frac{\beta^2}{a^2} - 1\right).$$

The coefficients A_3, A_2, and A_1 of Eq. 5 can be found out by making a parabolic fit between x and d by the least square deviation method. The extinction coefficient, ε, of the complex is evaluated from A_3 by using the relation

$$\varepsilon = \frac{1}{\lambda l A_3^{1/2}}. \tag{6}$$

The stability constant K_c of the complex is determined from a knowledge of all three coefficients using Eq. 7

$$K_c = \frac{1 \pm (1+4S)^{1/2}}{4\lambda S}, \tag{7}$$

where $S = (A_2^2/4A_3) - A_1$. Only the admissible value of K_c is accepted. K_c can also be calculated by utilizing A_2 and A_3 only. This yields a unique value of K_c since the equation in K_c is not quadratic in nature. K_c obtained by this method agrees with that calculated from Eq. 7.

For a very stable complex the curve of absorbance *vs.* mole fraction of one of the two components of the complex consists of two strictly linear intersecting portions. This can be explained with the help of Eq. 5 which can be written in the following form

$$x = \left[A_3^{1/2} d + \frac{A_2}{2A_3^{1/2}}\right]^2 - b^2, \tag{8}$$

where $b^2 = A_1 - (A_2^2/4A_3)$ and is negligible for a complex of high stability constant so that Eq. 8 splits into Eqs. 9 and 10 respectively.

$$d = \frac{1}{A_3^{1/2}}\left(\frac{C^\circ_M}{\lambda}\right) - \left[\frac{A_3^{1/2} + A_2}{2A_3}\right], \tag{9}$$

$$\text{and}\quad d = -\frac{1}{A_3^{1/2}}\left(\frac{C^\circ_M}{\lambda}\right) + \left[\frac{A_3^{1/2} - A_2}{2A_3}\right]. \tag{10}$$

Equation 9 describes the left hand portion of the Job curve and for a complex with very high formation constant it represents a straight line passing through the origin since the term $\frac{A_3^{1/2} + A_2}{2A_3}$ is practically zero. Similarly Eq. 10 describes the right hand portion of the Job curve and represents a straight line with negative slope and positive intercept.

The principle of the method as embodied in Eq. 5 is valid for complexes whose stoichiometry is strictly 1: 1 (*i.e.*, $m = n = 1$ where m and n refer to the mole numbers of the metal and the ligand respectively).

Results and Discussion

The principle of the method, *viz.*, Eq. 5 has been tested with literature data on a variety of 1: 1 metal complexes formed by Al^{3+}, Ga^{3+}, Fe^{3+}, La^{3+}, Cu^{2+}, and Pd^{2+} with one or more of the following ligands such as salicylic acid (SA), sulfosalicylic acid (SSA), *p*-aminosalicylic acid (PAS), 2-quinizarinsulfonic acid, 1-(*p*-nitrophenylazo)chromotropic acid, and Chromeazurol S. The compositions of the complexes were ascertained by Job's method of continuous variation. The optical density data necessary for our purpose have, therefore, been read from the Job curves of the complexes available in the literature. A perusal of the literatures concerned reveals that Job's experiments involving these complexes were performed at constant pH's and at constant values of λ but not at constant ionic strength. The ligand Chromeazurol S forms with Pd^{2+} a violet coloured 1: 1 chelate which is stable between pH 3.5 and 8.0 with an absorption maxima at 585 nm.[7] 2-Quinizarinsulfonic acid forms a blackish violet water soluble complex with Fe^{3+} in 1: 1 mole ratio.[8] La^{3+} forms with 1-(*p*-nitrophenylazo)chromotropic acid (abbreviated as CTB) a reddish violet chelate which is stable between pH 5 and 12.5 and has an absorption maxima at 340 nm.[9] In these three cases metal ion was used as its chloride salt. Iron(III) forms a violet complex with PAS at pH 2.5.[10] While Al^{3+} and Ga^{3+} form colourless complexes with SA and SSA,[11,12] complexes of copper with these reagents[13] are olivegreen in colour. In the study of these latter complexes perchlorates of the respective metals were used. The violet complex of Fe^{3+} with PAS has been reinvestigated by us. Stability constants and molar extinction coefficients of the complexes have been calculated from the Job data with the help of Eq. 5. A special computer program has been written to solve Eq. 5. In solving Eq. 5 two additional points corresponding to mole-fractions of zero and unity have been considered. Experience suggests that inclusion of these two points improves the final results appreciably. The computer Burroughs 6800 has been used for the purpose. The results are shown in Table 1 where other experimental details such as wavelength of measurement, total molarity of the solution, pH values, *etc.*, are also recorded. The formation constants recorded in column 5 and extinction coefficients shown in column 7 of the complexes calculated by Eq. 5 agree fairly well with those (vide columns 6 and 7 of Table 1) determined by other methods. The agreement is noticeable, particularly, in the case of iron (III) *p*-aminosalicylate complex. The variations in K_c values noted in some cases, particularly with wavelength, may be traced to the fact that ionic strength of the medium was not maintained constant in Job's experiments done at constant pH's and at constant values of λ.

An attempt has been made to test approximately the validity of Eqs. 9 and 10 with data on complexes which are not very strong. According to these equations the magnitude of the slope of the plot d *vs.* C°_M/λ is

TABLE 1.

System	Wavelength nm	Total molarity mol l^{-1}	pH	K_c l mol^{-1}	K_c l mol^{-1} (Reported)	ε l mol^{-1} cm^{-1}
Iron(III)	500	3.596×10^{-4}	2.5	3.07×10^4	$(2.21—3.06)\times10^4$	
p-aminosalicylate		4.795×10^{-4}		2.4×10^4		1606 (1675)
		7.192×10^{-4}		2.5×10^4		
—[a]		7.0×10^{-4}		2.5×10^4		1589
Iron(III)	570	1.0×10^{-3}	2.45	1.02×10^3	$(4.34—5.41)\times10^3$	796 (726)
2-quinizarinsulfonate		5.0×10^{-4}		7.57×10^3		
complex	580	1.0×10^{-3}		2.78×10^3		
		5.0×10^{-4}		2.85×10^3		728
		6.66×10^{-4}		3.89×10^3		(602)
Aluminium	310	2.0×10^{-4}	4.0	6.46×10^4	$(1.68—7.04)\times10^4$	2282
sulfosalicylate		3.0×10^{-4}		3.22×10^4		(2277)
	320	2.0×10^{-4}		6.44×10^4	$(1.73—7.31)\times10^4$	3015
		3.0×10^{-4}		4.5×10^4		(2716)
Gallium sulfosalicylate	315	3.0×10^{-4}	3.0	5.76×10^4	2.43×10^4 at 310 nm	1666 (1564)
Gallium salicylate	310	3.0×10^{-4}	3.5	6.46×10^4	$(1.34—9.43)\times10^4$	1304 (1355)
Copper(II) sulfosalicylate	750	9.0×10^{-3}	4.5	5.82×10^2	$(1.07—3.88)\times10^2$	47 (34)
		1.2×10^{-2}		1.54×10^2		
Copper(II) salicylate	750	1.287×10^{-2}	4.5	1.32×10^2	$(1.52—2.04)\times10^2$	20 (21)
		1.716×10^{-2}		0.86×10^2		
Lanthanum(III) 1-(*p*-nitrophenylazo) chromotropate complex	590	2.0×10^{-4}	6.0 ± 0.2	2.26×10^4	3.162×10^4	5226 (—)
Palladium(II) chromeazurol S Complex	585	1.66×10^{-4}	4.0	1.56×10^5	1.58×10^5	—

a) Investigated by us.

$1/A_3^{1/2}$ from which the extinction coefficient of the complex can be estimated. With iron(III) *p*-aminosalicylate complex studied by Das and Aditya[10] the extreme left and right wings of the Job curve correspond approximately to straight lines from whose slopes the average extinction coefficient of the complex is found to be 1634 which is in fairly good agreement with the reported value, considering the approximations made in deriving Eqs. 9 and 10.

Furthermore, the formation constant of the iron(III) *p*-aminosalicylate complex calculated from the intercept of the straight line drawn through the right wing portion of the Job curve for the system is 5.13×10^4 which is in fairly good agreement with the value obtained by using Eq. 7.

The present treatment of the principle of continuous variation has several promising features of which the most important is that it determines simultaneously the relative composition, the stability constant and the extinction coefficient of a complex from the same experimental data by considering all the points of the Job curve. In this respect the present method is advantageous over the one based on the measurement of the deviation between the experimental Job curve and that constructed by extrapolation from the slopes near the extreme values of mole-fraction.[14] The latter method considers only a single point corresponding to the maximum in the Job curve and it involves an element of arbitrariness in drawing tangents to the Job curve because experimental data near the extreme values of mole-fraction which should be most imprortant in drawing tangents to the Job curve are wanting in most cases. These demerits are obviously absent in Eq. 5. Moreover, the proposed method does not require a prior knowledge of extinction coefficient of a complex, which is required in other methods[2,5,6,14] for computing the formation constant of a complex. Another fruitful result obtained from Eq. 5 is that it explains quantitatively the nature of the Job curve in the case of complexes with very high formation constant. It yields two Eqs. 9 and 10 which can profitably be used to compute the stability constant and extinction coefficient of such complexes.

The errors in A_1, A_2, and A_3 have been calculated for the various systems investigated. The sequence of errors is $\Delta A_1<\Delta A_2<\Delta A_3$. The error in A_1 hardly exceeds 4%, that in A_2 is within 10%, while the error in A_3 is somewhat large. In some cases it is observed to be about 16 to 20%. The estimated error in ε in such cases hardly exceeds 10%, particularly, when the extinction coefficient of the complex is large. The error in K, however, lies within 10% in any case. The analysis of errors in A_1, A_2, and A_3 does not warrant the presence in solution of complexes having stoichiometries other than 1:1. It is felt that the theory developed here be tested with precise Job data on many more systems.

References

1) P. Job, *Ann. Chim. Phys.*, **9**, 113 (1928).

2) M. T. Beck, "Chemistry of Complex Equilibria," Van Nostrand Reinhold, London (1970), Chap. 5, pp. 86—89.

3) W. C. Voshburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 427 (1941).

4) L. J. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5455 (1950).

5) S. K. Banerjee and A. K. Dey, *Z. Anorg. Allg. Chem.*, **309**, 226 (1961).

6) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

7) S. P. Sangal and A. K. Dey, *J. Indian Chem. Soc.*, **40**, 464 (1963).

8) D. P. Joshi and D. V. Jain, *J. Indian Chem. Soc.*, **41**, 33 (1964).

9) S. P. Sangal, S. C. Srivastava, and A. K. Dey, *J. Indian Chem. Soc.*, **40**, 275 (1963).

10) R. C. Das and S. Aditya, *J. Indian Chem. Soc.*, **37**, 557 (1960).

11) R. K. Nanda and S. Aditya, *J. Indian Chem. Soc.*, **40**, 660 (1963).

12) R. C. Das, R. K. Nanda, and S. Aditya, *J. Indian Chem. Soc.*, **40**, 739 (1963); R. K. Nanda and S. Aditya, *ibid.*, **40**, 755 (1963).

13) R. C. Das and S. Aditya, *J. Indian Chem. Soc.*, **42**, 15 (1965); R. C. Das, R. K. Nanda, and S. Aditya, *ibid.*, **42**, 307, (1965).

14) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants and other Equilibrium Constants in Solution," McGraw-Hill, London (1961), Chap. 3, pp. 47—53.