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Continuous variation data: 1:1 or 2:2 weak complexes?

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Abstract

An attempt to distinguish between 1:1 and 2: 2 weak complexes from continuous variation data is given. A modification of the Heller and Schwarzenbach's method which involves the use of the absorbance ratio $y = A/A_{\text{lim}}$ (once the limiting absorbance, A_{lim} is known) may be applied to 1:1 weak complexes. This allows checking if the slope obtained is close to the theoretical value of -0.25. A curvature appears and the residuals have a pattern when a wrong 1: 1 model is selected for a true 2:2 stoichiometry.
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1. Introduction

The method of continuous variation, often called Job's method (Dimitrovska et al., 1996; Huang et al., 2003), provides a means of establishing the ratio of the substrate S and ligand L within the complex SL. The experimental procedure consists of preparing a series of solutions of S and L subject to the condition that the sum of the total substrate and ligand concentration is constant (Bruneau et al., 1992). Some property whose values changes in forming the SL complex, is measured (Ikeda et al., 2004; Masson et al., 2003; McBryde, 1974). The extremum of the property is related to the stoichiometric ratio (Connors, 1987). A question nevertheless remain concerning the existence of either 1:1 or 2:2 complexes and an attempt to give an answer to this question is intended in this paper.

2. Theory

For a 1:1 S + L = SL complex, in term of absorptiometric quantities we get (McBryde, 1974)

$$\beta_{11} = \frac{|\text{SL}|}{|\text{S}||\text{L}|} = \frac{A/\varepsilon}{(T_\text{S} - (A/\varepsilon))(T_\text{L} - (A/\varepsilon))} \qquad (1)$$

where A represents the measured absorbance (1-cm cells) at a given wavelength and T_S and T_L the total concentrations of the S and L, respectively, and ε is the molar absorptivity of the SL complex. Eq. (1) may be rearranged to give an expression similar to Heller and

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Schwarzenbach (1951)

$$\frac{X(1-X)}{A}=\frac{1}{2A_{\text{lim}}}\left(\frac{1}{T_0\beta_{11}}+1\right)-\frac{A}{4A^2} \tag{2}$$

where

$$X=\frac{T_\text{S}}{T_\text{S}+T_\text{L}}=\frac{T_\text{S}}{T_0} \tag{3}$$

and

$$A_{\text{lim}}=A_{\text{lim},X=0.5}=\frac{\varepsilon T_0}{a+b} \tag{4}$$

a and b are the stoichiometric coefficients of the S_aL_b complex ($a=b=1$). Thus, a representation of the left hand of Eq. (2) against A should gave a straight line ($Y=a_0+a_1x$) from which by least squares analysis

$$A_{\text{lim}}=\frac{1}{2}\sqrt{\frac{-1}{a_1}} \tag{5}$$

From Eq. (2) and (4) we get the absorbance ratio y as a function of X and $\beta_{11}T_0$

$$y=\frac{A}{A_{\text{lim}}}=\left(\frac{1}{T_0\beta_{11}}+1\right)-\sqrt{\left(\frac{1}{T_0\beta_{11}}+1\right)^2-4X(1-X)} \tag{6}$$

Fig. 1(left) shows an example for plots obtained using a normalised scale y based on using the A/A_{lim} quotients. All normalized Job curves are identical for a particular value of the $\beta_{11}T_0$ product. The smaller $\beta_{11}T_0$, the more curved is the plot obtained. The plot approaches two straight lines if the $\beta_{11}T_0$ product is large. In the case of the complexes of low and moderate stability the experimental curve can be quite flat in the vicinity of the maximum.

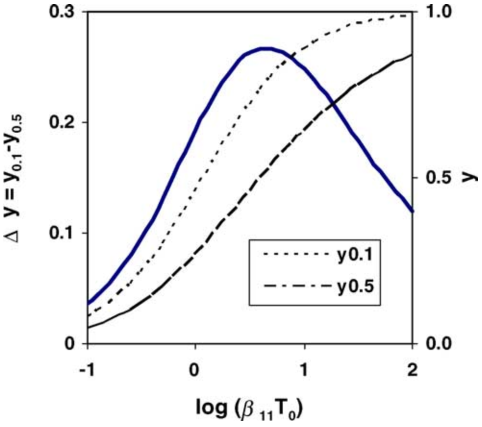

Fig. 2. Degree of complexation as a function of $\log(\beta_{11}T_0)$.

The degree of complexation at a given X value may be calculated from

$$y_x=\frac{A}{A_{\text{lim},X}}=\frac{y}{2X} \tag{7}$$

where

$$A_{\text{lim},X}=\varepsilon T_0X \tag{8}$$

At the point $X=0.5$, we get $y_{0.5}=y$. The plot of $y_{0.1}-y_{0.5}$ difference as a function of $\log(\beta_{11}T_0)$ is depicted in Fig. 2. The most accurate values of the stability constants are obtained when the difference between the degrees of complexation at $X=0.1$ and $X=0.5$ is

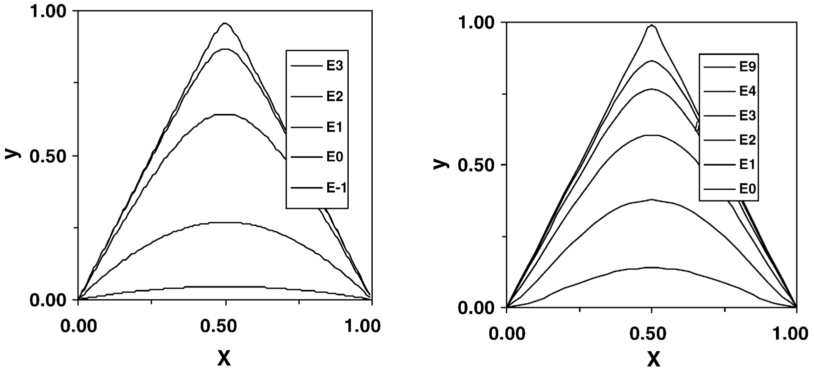

Fig. 1. Left: absorbance ratio y against X for 1:1 complexes with $\log(\beta_{11}T_0)$ included in the legend; right: absorbance ratio y against X for 2:2 complexes with $\log(\beta T_0^3)$included in the legend.

maximum; this corresponds to values of $\beta_{11}T_0$ in the range of 0.5−50, i.e., −0.3 to 1.5 for $\log(\beta_{11}T_0)$. Many inorganic (metal ligand) or organic (charge transfer, hydrogen bonding or host-guest) equilibria are likely to fall within this range. If the complex is too stable, it is possible to decrease the conditional constant by selecting a certain pH or adding a complexing agent. Previous results (Likussar, 1973; Likussar and Boltz, 1971; Slovak and Borak, 1974) have been discussed only on the basis of the degree of complexation at $X = 0.5$.

For a 2:2 dimeric complex species, $2S + 2L \rightleftharpoons S_2L_2$, we have

$$\beta_{22} = \frac{|S_2L_2|}{|S|^2|L|^2} = \frac{A/\varepsilon}{(T_S - 2A/\varepsilon)^2(T_L - 2A/\varepsilon)^2} \tag{9}$$

and then from Eq. (4) with $a = b = 2$ and (9) we may obtain the absorbance ratio $y = A/A_{\mathrm{lim}}$ as a function of X and $\beta_{11}T_0^3$

$$y^4 - 4y^3 + 4y^2(1 + 2X(1 - X)) - 4y\left(4X(1 - X) + \frac{1}{\beta_{22}{T_0}^3}\right) + 16X^2(1 - X)^2 = 0 \tag{10}$$

A family of curves for 2:2 complexes obtained by solving (Texas Instrument Tl-85 pocket calculator; POLY function) Eq. (10) for varying values of $\beta_{22}T_0^3$, the values of X ranging from 0.05 to 0.95 (spaced by 0.05X units) are depicted in Fig. 1(right). Alternatively, making the variable change

$$z = X(1 - X) \tag{11}$$

we get

$$16z^2 + 8y(y - 2)z - 4y \times \left(\frac{-y^3}{3} + y^2 - y + \frac{1}{\beta_{22}T_0^3}\right) = 0 \tag{12}$$

given the properties of symmetry of the 2:2 continuous variation curves. A second-degree equation in z may be solved from which the value of X may be obtained by solving the second-degree equation obtained rearranging Eq. (11). This task is easily accomplished even with a single calculator.

When the complexation interaction is weak, it is more reasonable to expect that 1:2 and 2:1 complexes (in excess of L or S, respectively) are also present in a solution that contains 2:2 complexes. In those cases, continuous variation curve losses its symmetric character, indicating simultaneous equilibria, which prevents to apply the formulation devised above.

3. Application to literature data

In terms of the absorbance ratio y, Eq. (2) may be rewritten as

$$\frac{X(1 - X)}{y} = \frac{1}{2}\left(\frac{1}{T_0\beta_{11}} + 1\right) - \frac{y}{4} \tag{13}$$

A representation of $X(1 - X)/y$ against y (least squares analysis) for a series of 1:1 complexes originates a series of parallel straight lines ($Y = a_0 + a_1x$) with −0.25 slope from which

$$\beta_{11} = \frac{1}{T_0(2a_0 - 1)} \tag{14}$$

A single straight line must be obtained for a given complex system from absorbance data measured at varying wavelengths. Deviations of slope from its nominal value could indicate a problem with the model; for example, multiple equilibria.

Eq. (2) and (13) were consecutively applied to several systems of varying stability described in the chemical literature: Ag(I)–dithizone (Likussar and Boltz, 1971), Zn–MBPT (methylglyoxal bis(4-fenil-3-thiosemicarbazone) (Herrador et al., 1987), Fe(III)–chromotropic acid (Heller and Schwarzenbach, 1951), Fe(III)–thiocyanate and Fe(III)–8-hydroxyquinoleine (Brewer, 1980), as shown in Fig. 3. Results are in agreement with the theory described above thus indicating the existence of single 1:1 complexes in all cases (Table 1). The standard deviation of the $\log\beta_{11}$ parameter was calculated by applying the random error propagation law (Asuero et al., 1988):

$$s^2_{\log\beta_{11}} = \left(\frac{\partial(\log\beta_{11})}{\partial\beta_{11}}\right)^2 s^2_{\beta_{11}} = \frac{1}{\ln^2 10\beta_{11}^2} s^2_{\beta_{11}} = \frac{1}{\ln^2 10\beta_{11}^2}\left(\frac{\partial\beta_{11}}{\partial a_0}\right)^2 s^2_{a_0} \tag{15}$$

from which

$$s_{\log\beta_{11}} = \frac{2s_{a0}}{\ln 10(2a_0 - 1)} \tag{16}$$

Table 1
Stability constants of the 1:1 weak system complexes

System.	λ (nm)	Data points	Slope Eq. (10)	$\log \beta_{11}$[a] ± $s(\log\beta_{11})$	$\sim\beta_{11}T_0$
Ag(I)–dithizone	485	9	−0.2498	6.00 ± 0.08	50
Zn(II)–MGBPT	460	5	−0.2502	5.36 ± 0.05	15
Fe(III)–chromotropic acid	655	9	−0.2502	3.68 ± 0.01	4
Fe(III)–SCN^-	500	7	−0.2499	3.53 ± 0.01	2
Fe(III)–8-hydroxyquinoleine	645	5	−0.2501	2.96 ± 0.01	1

[a] Reference values: Ag(I)-dithizone, 5.98; Zn(II)-MGBPT, 5.55; Fe(III)-chromotropic acid, 3.69.

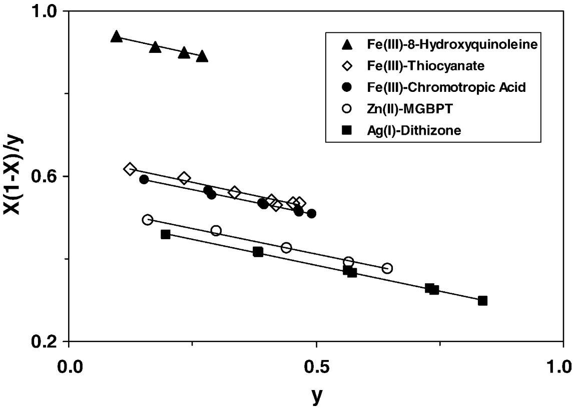

Fig. 3. Application of Eq. (13) approach (this paper) to literature data.

Eq. (13) was then applied to synthetic (X, y) data for varying values $\beta_{22}T_0^3$ (10^9 to 10^1) and X (0.05–0.5); $N = 10$ (Fig. 4 left and right). Varying slopes of −0.25, −0.2612, −0.2914, −0.4353 and −1.5708 were obtained for $\beta_{22}T_0^3$ values of 10^9, 10^4, 10^3, 10^2 and 10^1, respectively (with corresponding R^2 values of 1, 0.9996, 0.9955, 0.9614, and 0.8423). The differentiation of 1:1 and 2:2 complexes of high stability fails (Havel et al., 1977) because of the limited precision of experimental data which makes the sum of least squares very similar for both models. However, the residual analysis of the results obtained for theoretical data (with five significative numbers) based on the application of Eq. (13) by assuming 1:1 complex formation for 2:2 complexes, clearly indicates (Fig. 5) a pattern for values of $\beta_{22}T_0^3$ of 10^4 to 10^3, whereas for lower values of $\beta_{22}T_0^3$ the pattern is easily detected visually in the graph (Fig. 4(right)). For 1:1 complexes the residuals are distributed randomly instead.

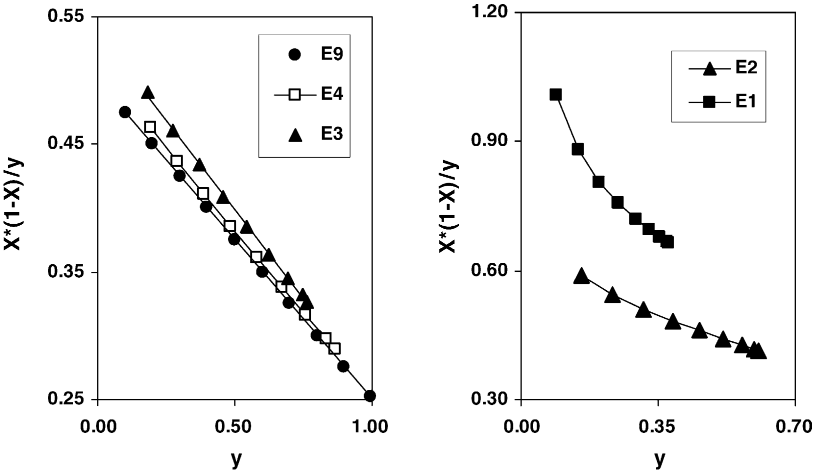

Fig. 4. Application of 1:1 Eq. (13) approach (this paper) to theoretical data for 2:2 complexes with $\beta_{22}T_0^3$ values given in the graph (left and right).

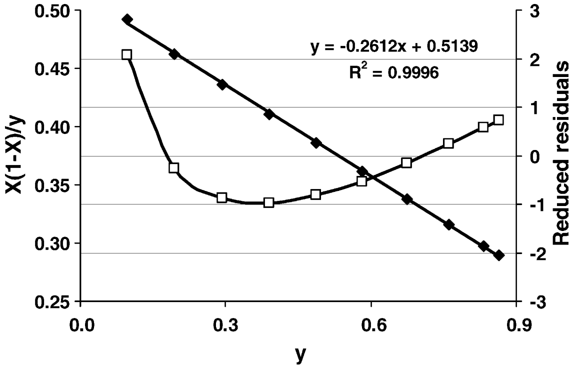

Fig. 5. Residual analysis based on the application of Eq. (13) to a 2:2 complex with $\beta_{22}T_0^3 = 10^4$.

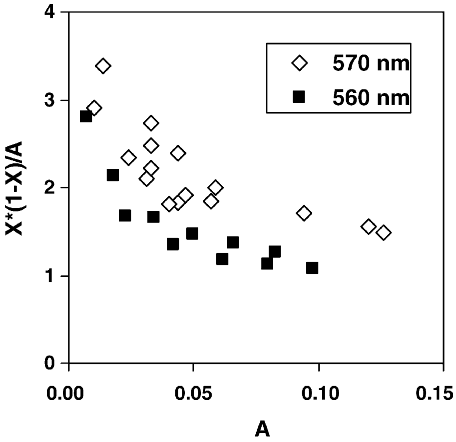

Fig. 6. Application of modified Heller and Schwarzenbach approach to the 2:2 complexes Fe(III)–chrome azurol S (◇) and Fe(III)–eriochromocyanine R (■).

The plots based on Eq. (2) and data from Marcantonatos et al. (1970) and Klausen and Langmuir (1963), corresponding to 2:2 weak complexes, show noticeable non-linearity (Fig. 6), in concordance with results depicted in Fig. 4(right).

4. Conclusion

The familiar continuous variation method goes on generating literature. The topic is recurrent and from time to time new papers appear in scene (Bruneau et al., 1992; Facchiano and Ragone, 2003; Vives et al., 2000). A discussion is carried out in this paper with the aim of distinguish 1:1 from 2:2 complexes. The approach applied implies the use of normalized graphs based on the absorbance ratio A/A_{lim}. A 1:1 weak complex system must show a slope value close to the theoretical one of -0.25 and no pattern in the sequence of the residuals.

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