On the Use and Misuse of the Spectrophotometric Method

for the Study of Inner- and Outer-sphere Complexes

in Solution

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When complex formation is studied by spectrophotometry, ab-
sorbance is often measured as a function of ligand concentration.
Theory as well as experiment shows that this method is very likely
to give results that seem to be reliable but are in fact completely
erroneous. Thus β_1 may come out low by a factor of ten or more.
Serious misinterpretations of such spurious results have been done
in connexion with outer-sphere complex formation.

The use of this unreliable method should be discouraged.

An inherent difficulty in spectrophotometric studies of complex formation
lies in the fact that n complexes introduce up to $2n+2$ unknown constants.
The problem can be dealt with in different ways. *E.g.*, the metal ion con-
centration can be varied keeping the ligand concentration very low (below
called the M-method). Only the first complex is then formed, its stability con-
stant being safely determined.[1,2] The ingenious method of corresponding so-
lutions [3] eliminates the unknown absorption coefficients and yields the average
ligand number $\bar{n}$ as a function of ligand concentration, whence the various
stability constants can be computed. Both methods mentioned require optimal
conditions, such as suitable strengths of the complexes and high solubility of
the metal ion in order to be fully applicable. The first method yields in any case
only the first stability constant, the second method often only the first few.

Since it is normally very desirable to gain information about higher com-
plexes as well, it has often seemed natural to extend the measurements and
measure the light absorption also as a function of ligand concentration (L-
method). Indeed, on some systems this method has yielded valuable and ac-
curate information about the complex formation (as judged from results of
independent methods). However, most often the results are erroneous, due to
certain more or less evident pitfalls in the data interpretation. Some of these
risks have been pointed out several times by various authors.[4-10] Quite ob-

viously, many workers in this field are nevertheless unaware of the hazards of this seemingly straightforward method, and dubious results continue to appear in the literature (examples, p. 3574). Therefore it seems proper to illustrate the mentioned risks further, theoretically and experimentally.

THEORY

We consider a situation when we study the apparent absorption coefficient, ε, of a solution of mononuclear complexes as a function of ligand concentration, [L]. If possible, the wavelength should be chosen so that the ligand has negligible absorption. Then, ε is constituted as follows

$$\varepsilon = \frac{A}{C_M} = \frac{\sum\limits_{n=0}^{N} \varepsilon_n \beta_n [L]^n}{\sum\limits_{n=0}^{N} \beta_n [L]^n} \tag{1}$$

If the ligand absorbs, a correction may be applied in the following way [3]

$$\varepsilon = \frac{A - \varepsilon_L C_L}{C_M} = \frac{\sum\limits_{n=0}^{N} (\varepsilon_n - n\varepsilon_L) \beta_n [L]^n}{\sum\limits_{n=0}^{N} \beta_n [L]^n} \tag{1a}$$

A is the measured absorbance (in 1 cm cells); L stands for ligand, M for metal ion; ε_i and β_i are the molar absorption coefficients, and overall stability constants, respectively, of the species ML_i ($\beta_0 = 1$); N is the maximum coordination number.

If, for instance, $N = 1$ eqn. (1) becomes

$$\varepsilon = \frac{\varepsilon_0 + \varepsilon_1 \beta_1 [L]}{1 + \beta_1 [L]} \tag{2}$$

Eqn. (2) may be rearranged to linear relationships (plots $vs.$ ε or $vs.$ [L], respectively)

$$\frac{\varepsilon - \varepsilon_0}{[L]} = \varepsilon_1 \beta_1 - \varepsilon \beta_1 \tag{3}$$

or
$$\frac{[L]}{\varepsilon - \varepsilon_0} = \frac{1}{(\varepsilon_1 - \varepsilon_0) \beta_1} + \frac{[L]}{\varepsilon_1 - \varepsilon_0} \tag{4}$$

Eqns. (3) and (4) yield reliable values of β_1 if the condition, $N = 1$, is really fulfilled (*e.g.* for monoprotic acids).

Neglect of higher complexes. When $N > 1$ (the normal situation in metal ion chemistry) confidence should be placed in eqns. (3) and (4) only if it is known *a priori* that complexes higher than the first one can be neglected in eqn. (1) in the numerator as well as in the denominator. Stoichiometric absence is not sufficient, since often $\varepsilon_{n+1} > \varepsilon_n$. On the other hand, when we do not know the strengths of the higher complexes, it is most important to realize that linear

relationships (eqns. (3) or (4)) do not prove their absence. Nor do such relationships necessarily give a correct β_1. Olerup[4] plotted $(\varepsilon - \varepsilon_0)/[L]$ $vs.$ ε ($cf.$ eqn. (3)) and showed that even the limiting slope (the plots being straight or curved) when [L] approaches zero is affected by complexes higher than the first one. The slope is not $-\beta_1$, as expected, but

$$\text{limiting slope} = -\left(\beta_1 - \frac{(\varepsilon_2 - \varepsilon_0)\,\beta_2}{(\varepsilon_1 - \varepsilon_0)\,\beta_1}\right) \tag{5}$$

This quantity might well be > 0, thus giving a negative apparent β_1.[4] It can moreover be shown that if the last term of eqn. (5) is not negligible it is actually also impossible to perform measurements at so small [L] that, in eqn. (1), higher complexes than the first one can be neglected.

$Reduction$ of $eqn.$ (1). As mentioned, plots according to eqns. (3) or (4) may be $linear$ even if higher complexes exist in appreciable amounts. In the first place, it is quite obvious that if the numerator and denominator of eqn. (1) just happen to have a common factor f of the type

$$f = \sum_{n=0}^{N-1} r_n[L]^n \tag{6}$$

eqn. (1) reduces to

$$\varepsilon = (\varepsilon_0 + p[L])/(1 + q[L]) \tag{7}$$

or (rearranged)

$$\varepsilon = \varepsilon_0 + p'[L]/(1 + q'[L]) \tag{7a}$$

($cf.$ eqn. (2)). p, q, $etc.$, are constants. The $N - 1$ conditions necessary for this reduction to occur can be elucidated directly or by studying derivatives.[5,9] Regardless of the value of N, eqn. (7) takes the form

$$\varepsilon = \varepsilon_0 + \frac{(\varepsilon_1 - \varepsilon_0)\,\beta_1\,[L]}{1 + \left(\beta_1 - \frac{(\varepsilon_2 - \varepsilon_0)\beta_2}{(\varepsilon_1 - \varepsilon_0)\beta_1}\right)[L]} \tag{7b}$$

$Cf.$ eqns. (2) and (5).

The described reduction should be a rather rare event, bearing in mind that the various ε_i and β_i have to be connected by a number of relationships. When it occurs, however, the effect is disastrous. Higher complexes escape discovery; β_1 is assigned too low a value (eqn. (7b)). In this case the same erroneous result will evidently come out, even if we start the calculations without any presumptions about the number of complexes (if we, $e.g.$, use one of the several computer programs available for the analysis of eqn. (1)).

It may be noted, though, that with the method of corresponding solutions[3] higher complexes would readily be detected.

$Approximations$ and $experimental$ $errors$. Apparently linear relationships may also be obtained for less obvious but probably more common reasons.

The plots may be approximately linear in some part of the range of [L]. Measurements only in this region may then easily be misinterpreted. $E.g.$, if the first and second complexes (or any two adjacent complexes) dominate in the studied region, eqn. (1) takes the form

$$\varepsilon = \frac{\varepsilon_1 \beta_1 [L] + \varepsilon_2 \beta_2 [L]^2}{\beta_1 [L] + \beta_2 [L]^2} = \frac{\varepsilon_1 \beta_1 + \varepsilon_2 \beta_2 [L]}{\beta_1 + \beta_2 [L]}$$

which is again of the same form as eqn. (7).

Moreover, we have so far assumed the various ε_i and β_i to be truly constant. Often, however, large parts of the inert salt used have to be replaced by ligand, in order to study a range of [L] as broad as possible. It is well known that this may bring about changes in activity factors and hence also in the stability constants. The question if the absorption coefficients are sensitive to medium changes is open to discussion,[11,14] but cannot be excluded.

The effects of a possible complex formation involving the inert salt are discussed in the succeeding paper.[15]

These possible changes in β_i and ε_i might well act in such a way that slightly curved plots are "straightened".

Finally we have to consider the experimental random errors. A slight curvature in a plot is often effectively obscured by the scatter caused by these errors. Or, on the other hand, of a deviation from linearity is actually seen one might tend to ascribe it to the random errors. These inevitable errors thus strongly increase the risks that the complex formation is interpreted as being simpler than it actually is.

Wavelength dependence. The possibility to vary the wavelength provides us with a good criterion on reliability. If the stability constants vary with the wavelength, this strongly indicates that the data interpretation is erroneous. However, if measurements at sufficiently different wavelengths, if possible in different absorption bands, give the same stability constants, these may on the other hand be regarded with much more confidence.

ILLUSTRATIONS

Coen$_3^{3+}$ – I$^-$-system. This system (en = ethylenediamine) was studied at 25°C using the spectrophotometric M- and L-methods (p. 3569), and solubility measurements, in 0.5, 1.0, 2.0, and 4.0 M media (Na$^+$ and ClO$_4^-$ being the inert ions). The measurements are described in detail in a succeeding paper.[15]

The L-method was used in 1, 2, and 4 M media. It was first attempted to fit all data in 4 M medium (300, 340, 400, and 470 nm) to a single set of stability constants, using the computer program Letagrop Spek.[16] No acceptable fit was obtained, however. When the data from each wavelength were run separately, it appeared that the best fit was obtained assuming only the first complex to be formed. The error square sum was, however, rather insensitive to the choice of complexes and their stability constants. Only the product $\varepsilon_1 \beta_1$ was obtained with good precision. The data from 1 M and 2 M media were analyzed graphically, with plots according to eqn. (3). At all wavelengths, the plots were linear, *within the experimental errors*. As a typical example, data from 1 M medium and 300 nm are given in Table 1 and Fig. 1. The values of $\varepsilon_1 \beta_1$ and β_1 as obtained from the intercepts and slopes, respectively, of the plots are summarized in Table 2. The values of β_1 thus obtained show a clear variation with the wavelength. Moreover, these "constants" are an order of

Table 1. Absorbances (referred to 1 cm cells; corrected for the slight absorption by I^-) *vs.* C_L at 300 nm, 25°C and 1 M ionic strength.

C_L M	$10^3 \times C_M$ M	A	ε cm^{-1} M^{-1}	$(\varepsilon - \varepsilon_0)/[L]$
0.0000	10.00	0.108	10.8	—
0.0400	10.00	0.580	58.0	1199
0.1000	10.00	1.276	127.6	1185
0.2000	10.00	2.405	240.5	1165
0.300	5.00	1.768	353.6	1150
0.400	5.00	2.298	459.6	1127
0.500	5.00	2.800	560	1102
0.600	2.000	1.332	666	1093
0.700	2.000	1.526	763	1076
0.800	2.000	1.714	857	1059
0.900	2.000	1.894	957	1041
1.000	2.000	2.070	1035	1025

magnitude lower than the concordant values obtained by the reliable M-method and the solubility method (also shown in Table 2). Referring to the facts discussed in the previous section, it is quite clear that the L-method, despite the approximately linear plots, gives a completely erroneous picture of the complex formation. The reason is the formation of higher complexes and probably also medium effects. The solubility method does indeed show [15] that at least the complex ML_3 if formed besides ML.
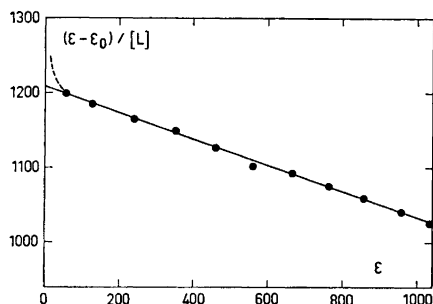

Fig. 1. $(\varepsilon - \varepsilon_0)/[L]$ *vs.* ε at 300 nm, 25°C and 1 M medium. Dashed curve: see text.

Returning to Fig. 1, we see that the points might well be fitted with a slightly curved function. Further, although the values of $\varepsilon_1\beta_1$ obtained by the L- and M-methods are *approximately* equal (Table 2) there is a systematic discrepancy of a few per cent, the L-method giving lower values. For low ε, where the low precision in $(\varepsilon - \varepsilon_0)/[L]$ does not allow meaningful measurements, the curve therefore probably has the form suggested by dashes in Fig. 1.

Other cobaltammine systems. As the study just described shows, the use of the L-method is very hazardous for the study of outer-sphere complexes. Inspection of the pertinent literature [17,18] also reveals several striking discrep-

Table 2. Results of the L-method at various ionic strengths I and various wavelengths. For comparison, results of the M-method and solubility method (see Ref. 15) are also given.

Constant	Method	$I = 1$ M			$I = 2$ M			$I = 4$ M		
		300 nm	320 nm	340 nm	300 nm	320 nm	340 nm	300 nm	340 nm	470 nm
$\varepsilon_1\beta_1$ M^{-2} cm^{-1}	L	1210	660	300	1010	570	260	980	290	< 40
	M	1280			1040			1000		
β_1 M^{-1}	L	0.18	0.12	0.08	0.13	0.09	0.04	0.15	0.09	0.3
	M	1.74			—					
	Soly	1.42			1.8			1.1		

ancies — often referred to as "unexplained" — which can be derived from the use of this dubious method. A few examples will be given.

Evans and Nancollas [2] used the reliable M-method in their study of hex-amminecobalt halide (and other) systems. Their results were criticized by King et. al.[19] who using the L-method obtained β_1 values more than a hundred times lower. That the discrepancy is due to the L-method was pointed out by Larsson and Tobiasson,[7] but it is more often ascribed to the difference in ionic strength. The results of Evans and Nancollas [2] have been confirmed with other methods.[20,21]

Tanaka et al.[22] obtained low β_1 values, using the L-method, on similar systems. The wavelength was varied, but the variation was sometimes as low as 2 nm. It seems more reasonable to conclude from the data given [22] that there is a variation of β_1 with the wavelength than that there is not.

Inner- and outer-sphere complex formation. Outer-sphere complexes normally affect only the charge-transfer bands in the ultraviolet, leaving the visible spectrum unaffected. As was correctly suggested by Smithson and Williams,[23] this behaviour provides a means to distinguish outer- from inner-sphere complexes. However, the misconception has been occasionally raised [22,24,25] that the degrees of outer- and inner-sphere complex formation on the same system can be determined separately by spectrophotometry, or, generally, that different methods of measurement, even when correctly applied, can give different results. The idea has been rejected repeatedly.[10,19,26]

Nevertheless, the spectrophotometric L-method has recently been used on a number of systems to determine a constant for ML-formation, on the one hand in the ultraviolet region, on the other in a visible band.[25,27–29] The constants are, for reasons presented above, different at the different wavelengths. The interpretation given, however, is [25,27–29] that in UV the sum of the constants for the inner-sphere complex and the outer-sphere complex is obtained, while the measurements in the visible region yield only the outer-sphere complex constant. That this separation is not possible is obvious from an inspection of eqn. (1) (p. 3570). If inner- and outer-sphere ML complexes were formed (but no higher complexes) eqn. (1) would read

$$\varepsilon = \frac{\varepsilon_0 + (\varepsilon_{1i}\beta_{1i} + \varepsilon_{1o}\beta_{1o})[L]}{1 + (\beta_{1i} + \beta_{1o})[L]} \tag{8}$$

where i and o stand for inner- and outer-sphere, respectively. The denominator of eqn. (8) is derived from the stoichiometry of the system and is thus completely wavelength-independent. All that happens at higher wavelengths is that $\varepsilon_{1o} \approx \varepsilon_0$. Plots according to eqn. (3) (cf. Ref. 25) would at any wavelength give $(\beta_{1i} + \beta_{1o})$.

CONCLUSIONS

The previous sections clearly show that the L-method is unreliable. The data interpretation may be wrong due to one or more of several reasons: unjustified neglect of higher complexes, accidental reduction of eqn. (1), influence of experimental errors. The result is usually the same: higher complexes escape discovery, β_1 comes out too low.

It should be mentioned, that in a system where polynuclear complexes cannot be excluded also the M-method would be objectionable.

Although only absorbance measurements have been discussed here, it is evident that many of the conclusions drawn are in principle valid for any method that measures some quantity P, where

$$P = \sum_{n=0}^{N} P_n [ML_n] \tag{9}$$

especially if P is studied vs. the ligand concentration. Other optical methods (cf. Ref. 10) ion exchange and kinetic methods are examples.

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