



CHAPTER II

PRINCIPLE, THEORETICAL AND PRACTICAL

BACKGROUND INFORMATION

2.1 Metallochromic Reagent(9)

This group of reagent may be classified into various types as follows:

2.1.1 Metal Indicator Metal indicators are substances that undergo a marked color change when the concentration of free metal ion in a solution changes. These indicators usually have properties typical of acid-base indicators. The anion of the indicator is a base capable of donating one or more electron pairs and can hence function as a ligand. This base can react with a hydrogen ion or a metal ion (or with other electrophilic species). Often the color of the metal complex is about the same as that of the free indicator anion, and the color change occurs when one or more hydrogen ions are replaced by a metal ion. It is possible to classify the metal indicators broadly according to their mode or mechanism of reaction into four types.

2.1.1.1 Metallochromic Indicators Metallochromic indicators are substances which react with metal ions to form colored products having the properties necessary in visual indicators. The color-species is usually due

to the formation of a chelate complex, but there are a few instances where inorganic anions such as iodide or thiocyanate form simple co-ordination complexes of sufficient absorption in the visible range of the spectrum. Metallochromic indicators can be classified on the basis of their structures to be: azo dyes, phthaleins, sulfo-phthaleins, triphenylmethane dyes, antraquinone dyes, and phenolic substances.

2.1.1.2 Fluorescence Indicators Fluorescence indicators have also been called "metallochromic indicators" (10) or "metallochromic fluorescent indicators" (11). These are similar to metallochromic indicators in their chelation properties and mechanism of reaction except that on formation of a chelate the fluorescence. Complexometric titrations with such indicators are usually performed with the solution subjected to ultraviolet illumination.

2.1.1.3 Diverse Metal-sensitive and Metal-specific Indicators A further group of metal indicators, which are themselves colorless. So the detection of the end-point is based on somewhat different principles. The color formation is attributed in some cases to charge transfer spectra or to alteration of the ligand field strength. The color of the uncomplexed indicator does not interfere, and hence, if necessary, a fairly high indicator concentration can be used. For most colorless



indicators, which as a rule are less sensitive than the indicator dyes, this visually detectable color intensity corresponds to a molarity between 10^{-4} and 10^{-6} (12). In selected cases, the action and sensitivity of such indicators may be improved by the addition of an organic solvent, such as alcohol or a ketone, to the titration medium.

2.1.1.4 Turbidity Indicators The end point of a complexometric titration can be detected by observing the appearance of a precipitate. Well known is the classical method of Liebig-Denigès(13): a solution of a cyanide is titrated with silver nitrate until a precipitate of silver argentocyanide is formed. Turbidity indicators are of little contemporary interest for chelometric titration.

2.1.2 Redox Indicators Redox indicators are applicable in some complexometric titrations, as the potential of a redox couple is markedly influenced by the presence of a complexing agent which forms a more stable complex with the oxidized species than with reduced species (or vice versa), or which in a more indirect way alters the ratio of the concentrations of the oxidized and reduced species. As the method can be applied only to special systems and as many of the indicators react slowly, the method has its limitations.

Metallochromic Indicators

Körbl and Přibil(9) introduced the term metallochromic indicator to designate a metal indicator that has acid-base activity and that functions in a complexometric titration by reacting with the metal ion to form a chelate substantially soluble in the titration medium. In the structure of such indicators one or more ligand groups must be joined directly to a resonance system. (Such indicators are usually so-called mordant or chrome dyes) The change in the spacing of low-lying π electron energy levels resulting from the chelation causes a shift in the wavelength of the absorption bands and hence a change in color. The extent of the shift may depend to some extent on the metal ion involved. For this reason, metallochromic indicators function in this way as acid-base indicators, pH has a profound effect on their mode of action and range of application. Sharper end points are usually obtained when an extremely small concentration of a metallochromic indicator is employed in a complexometric titration. For this reason the indicator in either its metallized or its free form need only be added in concentration of 10^{-6} - 10^{-5} M.(14) to give a color change that is still clearly detectable. The indicators are arranged principally according to their structures. Naphthylazo compounds constitute a large group, most of which have hydroxyl groups substituted adjacent to the azo bond, while a few also depend on carboxyl or arsonic

2.2 General Method for Preparation of Azo Dyes

The azo dyes are a distinct and clearly defined class, characterized by the presence of one or more azo (-N=N-) groups. It is strongly chromophilic and in combination with other groups, such as aryl -OH and $-\text{AsO}_3\text{H}_2$ furnishing replaceable H is likely to give chelating agents of value in spectrophotometric analysis. Amongst analogously constituted compounds with the same number of azo groups, those containing naphthalene nuclei have a darker color than those containing benzene nuclei (15).

The reaction of an aromatic amine with nitrous acid to yield a diazo compound and the coupling combination of the diazo compound with a suitable component to yield an azo derivative are two of the older reactions in organic chemistry. The former, diazotization, was discovered by Griess in 1858, while the latter, coupling reaction, was discovered by Kekule and Hidegh in 1870 (16).

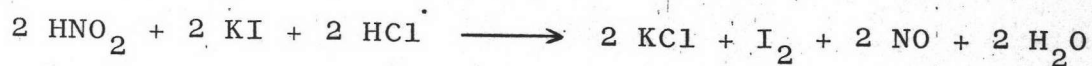
2.2.1 The Diazotization

There are many methods for the preparation of diazo compounds. But the most important one involves treating a primary aryl amine with nitrous acid in the presence of a mineral acid to form a diazonium salt as given in the equation:



Sodium nitrite is employed in theoretical

quantity, but the acid must be in order to prevent partial diazotization and the excess mineral acid also stabilizes the diazonium salt by inhibition of decomposition due to other reactions. The molar proportion of acid usually necessary is 2.5-3 and hydrochloric acid is usually employed because it gives, in general, the most soluble salts with aromatic amine. But at the same time hydrochloric acid reacts with nitrite to give chlorine gas, which of course, leads to side reactions. For this reason, the diazotization mixture should never contain more than 20% of free hydrochloric acid. If diazotization is to proceed satisfactorily the amine must be in solution in the aqueous acid or the amine hydrochloride must be in a very fine state of suspension. The addition of sodium nitrite is carried out at 0-5°C on account of the instability of diazonium salts, higher temperatures up to or even more than 20°C are permissible for some diazonium salts. Completion of diazotization and of slight excess of nitrous acid are tested for by moist potassium iodide starch paper.



The excess nitrous acid which interferes with subsequent reactions of the diazonium salt, can be destroyed by the addition of small amount of urea. Urea will react with nitrous acid giving off nitrogen, carbon dioxide and water. The ease of diazotization depends on the basicity of the amine and difficulties in diazotization can also arise

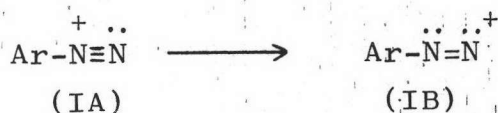
because of the large molecular weight of the amine, sparing solubility in aqueous acid, or oxidizability.

2.2.2 The Coupling Reaction

All coupling components used to prepare azo dyes possess one common feature, i.e., an active hydrogen atom bound to a carbon atom. Compounds of the following types can be used as azo coupling components compounds that possess phenolic hydroxy groups such as phenols and naphthols; aromatic amines, compounds that possess enolizable ketone groups of an aliphatic character, and heterocyclic compounds.

Analogous to aromatic halogenation, nitration, and sulfonation, the azo coupling reaction is an electrophilic aromatic substitution. The effect on the reaction rate of substituents on both the diazo and coupler components is in agreement with this mechanism. Thus the reaction is facilitated by electron-attracting groups in the diazo component, and by electron-donating groups in coupler components.

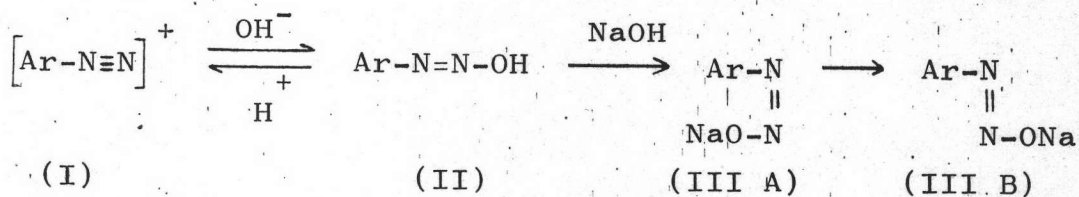
The diazonium ion may be represented by two resonance structures (IA) and (IB), of which (IA) makes the main contribution on account of its stability, but it may be the unstable structure (IB)



having a nitrogen atom with a sextet of electrons, which

enables the attachment to the anionoid carbon atom in the phenoxide ion to take place (17) with the formation of the azo linkage $\text{Ar-N=N-Ar}'$

The diazonium ion (I) reacts reversibly in water to form the aryldiazohydroxide (II), which exists in stereoisomeric forms and is a weak acid. In strongly alkaline solution the acid forms the diazotates (III A and III B), and the equilibrium between the ion (I), which is the effective coupling agent, and the diazohydroxide (II) will depend on the nature of the aryl group and the pH of the medium.



Coupling positions. The position of attachment of an azo group to a carbon atom in a coupling reaction is governed by a general rule, which follows from the mechanism of the reaction. The diazonium group attacks a position which has been activated as a site of high electron density. Coupling therefore takes place in the o- or p- position to the directing hydroxyl of amino group in the second component; if both these positions are occupied no coupling will take place, or one of the substituents will be displaced. Coupling never takes place in the m-position to the directing group(18). A few well-known coupling components are shown in Fig.2.1 together with the favored positions of coupling under the conditions normally used.

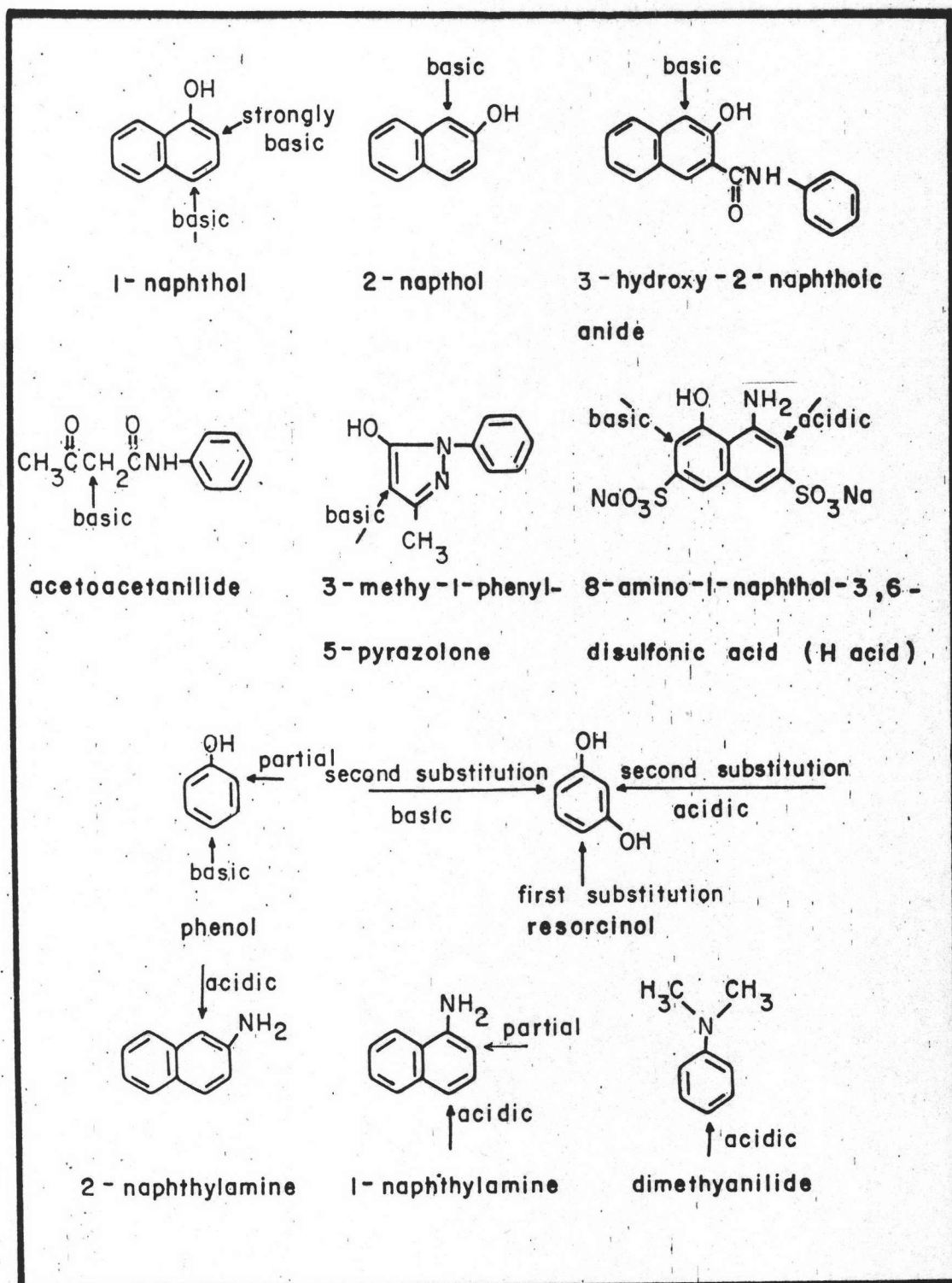


Fig.2.1 : Few well-known coupling components.

2.3 Visible Spectrophotometry

Methods based on the absorption of radiation are powerful and useful tools for the analytical chemist. In the visible region, it becomes apparent that virtually every element and many ions and molecules are either colored, can react with a colored substance, or can react to form a colored substance. Each of these situations presents the possibility of a quantitative analytical determination. Spectrophotometric methods are widely used for the quantitative determination of many trace substances, especially inorganic elements.

The basic principle of quantitative absorption spectroscopy lies in comparing the extent of absorption of a sample solution with that of a set of standards at a selected wavelength. With a spectrophotometer, the spectrum of the absorbing substance is determined, and a suitable wavelength is chosen. Generally, a wavelength close to that of maximum absorption is chosen for maximum sensitivity; but the wavelength chosen should also fall in a region where the absorbance does not change rapidly with change in wavelength.

Some common and important factors involved in the formation of absorbing compounds are:

a) pH. Since pH plays a very important role in complex formation, proper adjustment of pH or the use of a buffer often eliminates certain interfering reactions. The

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selectivity for certain metals is much improved in highly acidic media.

b) Reagent concentration The amount of reagent required is dictated by the composition of the absorbing complex formed. An optimum concentration of reagents should be determined, since either not enough reagent or too much reagent can cause deviation from Beer's Law.

c) Time Formation of the absorbing complex may be slow, in some cases requiring several minutes or a few hours for full color development after addition of the reagents.

d) Order of mixing reagents Frequently it is important to add the reagents in a specified sequence, otherwise full color development will not be possible or interfering reactions may occur.

e) Temperature The optimum temperature should be established in the procedure. Certain reactions require elevated temperature to decrease the time necessary for complete color development.

f) Stability If the absorbing complex formed is not very stable, the absorbance measurement should be made as soon as possible. If the absorbing complex is photosensitive, precautions should be taken in order to avoid its photodecomposition. Certain reagents may sometimes be added to help stabilize the absorbing complex.

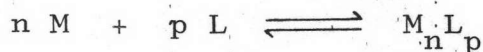
g) Masking The term masking refers to the

addition of a complexing agent to form a metal complex of such stability that, in this case, color-forming reactions with another reagent do not occur to any appreciable extent.

h) Organic solvent Many organic reagents or complexes are only slightly soluble in water. In such cases, it is necessary to add a water-miscible organic solvent to avoid precipitation or to aid color-development. In other cases, solvent extraction might be employed, for example, to separate the colored compound from excess reagent or from interfering substances.

i) Salt concentration High concentrations of electrolyte may be form the ion-association complexes that cause a shift in the maximum absorption. This is a type of masking effect and usually causes a decrease in the absorption.

The spectrophotometric method is particularly valuable for studying complexes of low stability. Consider the formation of a complex $M_n L_p$, where M is a metal ion and L is a ligand:



The molar ratio of the two compounds of a complex is important. In a quantitative determination, an excess of ligand should be added in order to force the equilibrium toward completion.

Continuous-Variation Method (Job Method).

The method of continuous variations is one of the most widely and numerous techniques for identifying complexes in solution by spectrophotometric measurements, first described by Job (19) and later extended in applicability to include successive complex formation by Vosburgh and Cooper (20). The molar ratios may also be varied by changing the concentrations of both components while the total number of moles of both components are kept constant. The absorbance of each solution is measured at a suitable wavelength and corrected for any absorbance of the mixture if no reaction has occurred. The corrected absorbance is then plotted against the volume fraction

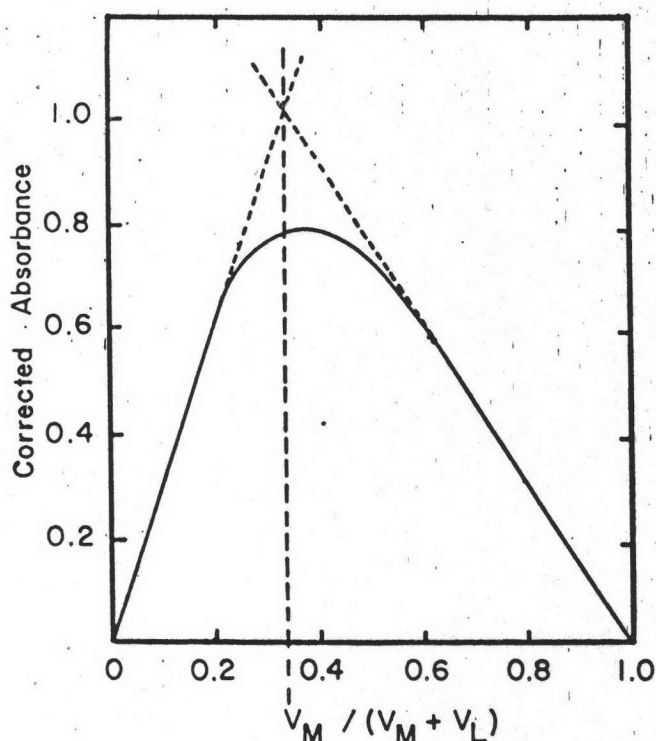


Fig. 2.2 Continuous variation plot for the complex ML_2

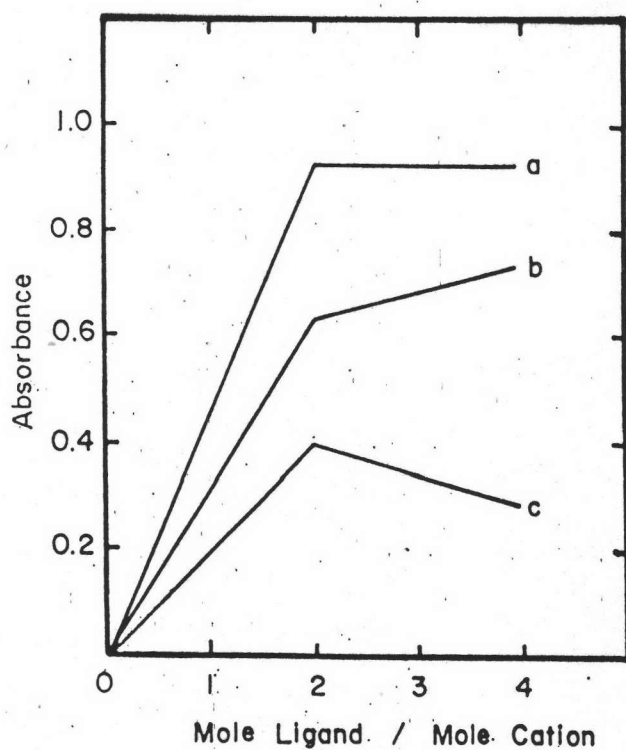
(which is equal to the mole fraction) of one of the reactants (V_M/V_{M+L}). A maximum (or a minimum if the complex absorbs less than the reactants) occurs at a volume ratio $V_M : V_L$ corresponding to the combining ratio of cation and ligand in the complex. To determine whether more than one complex forms between the reactants, the method is ordinarily repeated using different reactant concentrations and measurements at several wavelengths.

Mole-Ratio Method

Yoe and Jones (21) found that for a very stable complex, the concentration of one component is kept fixed and that of the other varied to give a series of $[L]/[M]$ ratios. The absorbances of these solutions, measured at an absorption maximum for the complex M_nL_p , increase linearly up to the molar ratio of the complex, at which virtually the whole amount of both components is complexed (assuming little dissociation). Further addition of component L cannot increase the absorbance, and the line becomes horizontal, or shows a break if component L absorbs at the same wavelength (Fig.2.3). In rare cases, an excess component L may cause a decrease in absorbance owing to the stepwise formation of higher-order complexes that have smaller ϵ values at this wavelength.

Slope-Ratio Method

Slope-ratio method was proposed by Aubrey E. Harvey, Jr. and Delmer L. Manning in 1950 (22). The method is



- (a) Component L does not absorb at the wavelength of maximum absorption for the complex.
- (b) Component L absorbs slightly at the wavelength of maximum absorption for the complex.
- (c) An excess of component L causes a decrease in absorbance of the complex.

Fig.2.3 Molar-ratio method, showing different curves.

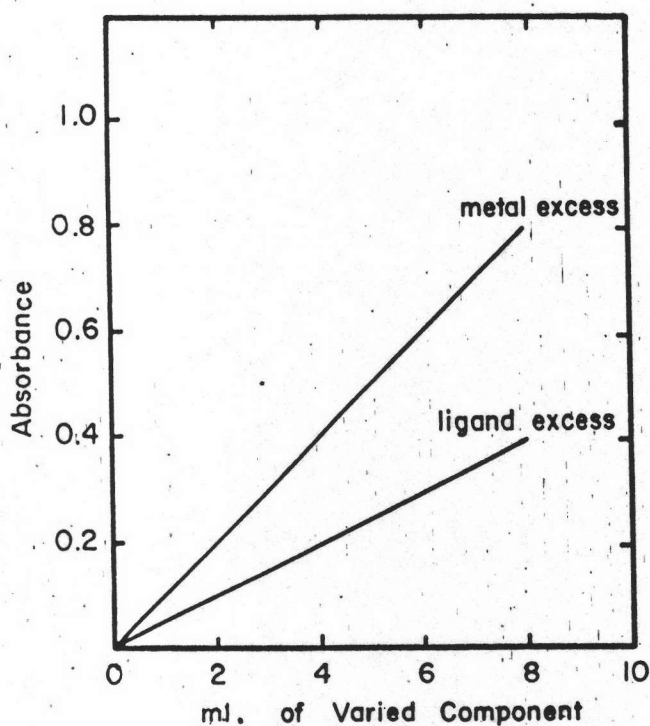
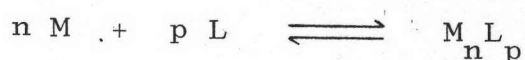


Fig.2.4 Slope-ratio method for the complex ML_2 .

particularly useful for weak complexes; it is applicable only to systems in which a single complex is formed. The method assumes that the complex formation reaction can be forced to completion in the presence of a large excess of either reactant and that Beer's Law is followed under these circumstances.

For the reaction



The following equation can be written, when L is present in very large excess :

$$[M_n L_p] \cong F_M / n$$

If Beer's Law is obeyed

$$A_n = \epsilon_b [M_n L_p] = \epsilon_b F_M / n$$

and a plot of A with respect to F_M will be linear. When M is very large with respect to L

$$[M_n L_p] \cong F_L / p$$

and
$$A_p = \epsilon_b [M_n L_p] = \epsilon_b F_L / p$$

The slope of the straight lines A_n / F_M and A_p / F_L are obtained under these conditions; the combining ratio between L and M obtained from the ratio of the slopes

$$\frac{A_n / F_M}{A_p / F_L} = \frac{S_M}{S_L} = \frac{\epsilon_b / n}{\epsilon_b / p} = p/n$$