the general science journal

Molar Extinction Rate Coefficient

Manjunath.R
#16/1, 8th Main Road, Shivanagar, Rajajinagar, Bangalore560010, Karnataka, India
*Corresponding Author Email: manjunath5496@gmail.com

In a typical absorption spectral measurement a monochromatic radiation is made to fall on a homogeneous absorbing substance. In such a situation a part of the radiation is reflected, a part is absorbed, and a part is transmitted. The intensity of incident radiation, I is equal to the sum of the intensities of reflected (I'"), absorbed (I') and transmitted (I") radiation.

$$I = I''' + I' + I''$$

In most cases of homogeneous nonmetallic substances, such as transparent substances, the loss of radiant intensity due to reflection may not exceed 4%. This fraction can be, and is therefore, usually ignored. Thus, for all practical purposes, we may write:

$$I = I' + I''$$

If temperature, composition, and other factors including wavelength are kept constant, then the rate of absorption of intensity of incident monochromatic radiation on passage through a homogenous absorbing substance, – dI/dt, where I is the incident radiant intensity and t the time, is directly proportional to the intensity of incident monochromatic radiation, namely, that

$$-dI / dt = k\, I$$

$$d\ln I = -k \cdot dt$$

The constant of proportionality, k, appearing in the above equation is called the absorption rate coefficient, and this is a characteristic of the absorbing substance. Further, the negative sign signifies that incident radiant intensity decreases with time. Since at t=0 we have the original intensity I, the intensity I" at any time t can be found from equation above by integration between these limits. We obtain thus

$$\ln (I''/ I) = -k \cdot t$$

$$\ln (I/ I'') = k \cdot t$$

When monochromatic radiation travels in a homogeneous substance of refractive index η a distance ℓ with a velocity (c/ η), then the time taken by radiation is:

$t = \eta\, \ell / c$, where $c = 3\times 10^{10}$cm/s is the speed of light in vacuum.

The last equation may be written also as

$\log (I / I'') = k''\, \eta\, \ell /c$ in which case $k'' = k /2.303$ is the extinction rate coefficient of the substance.

The ratio of the intensities of transmitted and incident radiation gives the transmittance, T, expressed as:

$$T = I'' / I$$

From the transmittance, one can calculate the quantity known as absorbance. Absorbance is the amount of light absorbed by a substance. It is calculated from T using the following equation:

$$\text{Absorbance} = -\log T = \log (I / I'')$$

$$\text{Absorbance} = k''\, \eta\, \ell /c$$

A plot of absorbance versus thickness 'ℓ' is expected to a straight line passing origin with slope = k" η /c. When homogeneous solutions of chemical species are considered, it is clearly desirable to modify this expression to include the concentration of absorbing chemical species. Thus, the extinction rate coefficient in above equation is in turn related to the concentration of absorbing chemical species.

$$k'' = k_M C$$

where k_M, called the molar extinction rate coefficient, is a proportionality constant determined by the nature of the absorbing chemical species and the wavelength of light used.

$$\text{Absorbance} = (k_M \eta \ell / c) C$$

$$k_M = (c / \eta \ell C) \times \text{absorbance}$$

The molar extinction rate coefficient is a measurement of how fast a chemical species absorbs light at a given wavelength. It is an intrinsic property of the chemical species, also a measure of the rate of the electronic transition. The larger the molar extinction rate coefficient, the faster the electronic transition. The absorbance is measured with some form of spectrophotometer. At present spectrophotometers utilizing photoelectric cells are available which give absorbance directly. Once absorbance for a given solution is measured and the thickness of the cell used is known, the molar absorption rate coefficient of the given solution for the given wavelength can readily be calculated by knowing the refractive index of the solution and the concentration of absorbing chemical species. At low concentrations, less than 10^{-3} M, absorbance is linear and proportional to concentration of absorbing chemical species with slope = $k_M \eta \ell / c$.

A plot of absorbance versus concentration is not always expected to a straight line passing origin.

In practice, the following effects may lead to deviations from linearity:

- Fluorescence and Phosphorescence;
- Light scattering including Raman;
- Photochemical reactions;
- Presence of large amounts of strong electrolytes;
- Non- monochromatic nature of the radiation;
- Changes in refractive index at high analyte concentration;
- Stray light effect;
- Shifts in chemical equilibrium as a function of concentration;
- Complexation, association or dissociation.

According to Beer Lambert's law,

$$\text{Absorbance} = \varepsilon \ell C$$

where ε, called the molar extinction coefficient, is a measurement of how strong a chemical species absorbs light at a given wavelength.

Since Absorbance = $(k_M \eta \ell / c) C$:

$$(k_M \eta \ell / c) C = \varepsilon \ell C$$

From this it follows that

$$k_M \eta / c = \varepsilon$$

or

$$k_M / \varepsilon = c / \eta$$

Since η is always less than c. Therefore:

$$k_M \text{ is} > \text{than } \varepsilon$$

Which means: rate of absorption is always greater than the strength of absorption.

(k_M / ε) values for liquids at 20 °C (589.29nm)

Benzene	$\eta = 1.501$	$k_M / \varepsilon = 1.99 \times 10^8$
Carbon tetrachloride	$\eta = 1.461$	$k_M / \varepsilon = 2.05 \times 10^8$
Carbon disulfide	$\eta = 1.628$	$k_M / \varepsilon = 1.84 \times 10^8$
Ethanol (ethyl alcohol)	$\eta = 1.361$	$k_M / \varepsilon = 2.204 \times 10^8$
10% Glucose solution in water	$\eta = 1.3477$	$k_M / \varepsilon = 2.22 \times 10^8$
20% Glucose solution in water	$\eta = 1.3635$	$k_M / \varepsilon = 2.200 \times 10^8$
60% Glucose solution in water	$\eta = 1.4394$	$k_M / \varepsilon = 2.08 \times 10^8$
sucrose	$\eta = 1.3344$	$k_M / \varepsilon = 2.24\times 10^8$

Amount of radiant intensity absorbed,

$$I' = (I - I'')$$

Since $I'' = I \exp(-2.303 k_M \eta \ell C/ c)$. Consequently we may write without further hesitation that

$$I' = I (1 - \exp(-2.303 k_M \eta \ell C/ c))$$

The fluorescence intensity (F) is proportional to the amount of radiant intensity absorbed:

$$F = I' Q = I \varphi (1 - \exp(-2.303 k_M \eta \ell C/ c))$$

where φ = fluorescence quantum yield. The fluorescence quantum yield (φ) gives the efficiency of the fluorescence process. It is defined as the ratio of the number of photons emitted to the number of photons absorbed. When $(2.303 k_M \eta \ell C/c) < 0.05$, which can be achieved at low concentrations of analyte, the fluorescence intensity can be expressed as:

$$F = (2.303I \varphi k_M \eta \ell /c) C$$

At low concentrations, less than 10^{-5} M, fluorescence intensity is linear and proportional to concentration of analyte with slope = $2.303 I \varphi k_M \eta \ell /c$.

For substances other than solutions the absorbance is given by:

$$\text{Absorbance} = k'' \eta \ell /c$$

When discussing the mass extinction rate coefficient, this equation is rewritten:

$$\text{Absorbance} = (k_\mu \eta \ell /c) \rho$$

where ρ = density of absorbing chemical species and k_μ = mass extinction rate coefficient. The mass extinction rate coefficient is a measurement of how fast a chemical species absorbs light at a given wavelength, per unit mass. The molar extinction rate coefficient is closely related to the mass extinction rate coefficient by the equation:

$$\text{Molar extinction rate coefficient} = \text{mass extinction rate coefficient} \times \text{molar mass}$$

$$k_M = k_\mu \times \text{molar mass}$$

At low densities, less than 10^{-3} g /cm^3, absorbance is linear and proportional to density of absorbing chemical species with slope = $k_\mu \eta \ell / c$.

REFERENCES:

- Reusch, William. "Visible and Ultraviolet Spectroscopy".
- Reusch, William. "Empirical Rules for Absorption Wavelengths of Conjugated Systems".
- Zitzewitz, Paul W. (1999). Glencoe Physics. New York, N.Y.: Glencoe/McGraw-Hill.