Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Course Code: CHD-103

Course Title: Selected Instrumentation in Chemistry (Section B)

Unit: UV-Visible Spectroscopy

Module Name: Derivation of Beer-Lambert's law, deviations from Beer's law

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Notes

Beer-Lambert's law

- A combination of Lambert's law and Beer's law results in the Beer-Lambert's law.
- It governs the absorption of light by absorbing media like solutions.
- This law states that "The fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path."

$$A = \varepsilon cl$$

Lambert's law of transmission of light (derivation)

- The law states that:

When a monochromatic light is passed through a pure homogeneous medium, the decrease in the intensity of light with thickness of the absorbing medium at any point X is proportional to the intensity of the incident light.

$$-\frac{dI}{dx} \propto I$$

- $-\frac{dI}{dx} = kI$ (i)
- Where, dI is the small decrease in intensity of the light passing through a small thickness dx.
- k is the constant of proportionality called the absorption coefficient.
- The intensity I at any point X at a distance x from the start of the medium, can be found in terms of the original intensity I_o as follows:
- Equation (i) can be rewritten as:
- $dI/I = -k\,dx$ (ii)
- When x=0, $I = I_o$
- Integrating equation (ii) between the limits x=0 to x and $I = I_o$ to I ,we get
- $\int_{I}^{I_o} dI/I = \int_{x=0}^{x=x} -k dx$
- $\ln I/I_o = -kx$ (iii)
- $I/I_o = e^{-kx}$
- Or $\mathbf{I = I_o\, e^{-kx}}$ (iv)
- This equation expresses how the original intensity I_o is reduced to intensity I after passing through a thickness x of the medium.
- Equation (iii) can be written as
- $2.303 \log I/I_o = -kx$
- $\log I/I_o = -kx/2.303$
- $\log I/I_o = k' x$ (v)
- $I = I_o\, 10^{-k'x}$ (vi)
- Where $k' = k/2.303$ is called extinction coefficient of the substance i.e. the absorbing medium.
- This quantity is now called absorption coefficient or absorptivity of the substance.
- $\log I/I_o$ is called absorbance of the medium .

Beer's Law

- Beer's law states that:
- When a monochromatic light is passed through a solution, the decrease in the intensity of light with the thickness of the solution is directly

proportional not only to the intensity of the incident light but also to the concentration c of the solution.

- Mathematically we have
- $-dI/dx \propto I \times c$ (i)
- $-dI/dx = \varepsilon I c$ (ε is pronounced as epsilon)
- Where ε is a constant of proportionality and is called molar absorption coefficient. Its value depends upon the nature of the absorbing solute and the wavelength of the light used.
- Equation (i) can be rewritten as
- $dI/I = -\varepsilon\, c\, dx$
- Integrating this equation between the limits x=0 to x and $I = I_o$ to I ,we get
- $\int_{I}^{I_o} dI/I = \int_{x=0}^{x=x} -\varepsilon\, c\, dx$
- $\ln I/I_o = -\varepsilon\, c\, dx$ (ii)
- $I/I_o = e^{-\varepsilon c x}$ (iii)
- $I = I_o e^{-\varepsilon c x}$ (iv)
- This equation expresses how the intensity of a monochromatic light falls from I_o to I on passing through a thickness x of a solution of concentration c.
- $2.303 \log I/I_o = -\varepsilon c x$
- $\log I/I_o = -\varepsilon c x/2.303$
- $\log I/I_o = -\varepsilon' c x$ (v)
- $I = I_o \times 10^{-\varepsilon' c x}$
- $\varepsilon' = \varepsilon/2.303$ was earlier called molar extinction coefficient of the absorbing solution. Now this quantity is called molar absorption coefficient or molar absorptivity of the absorbing solution.

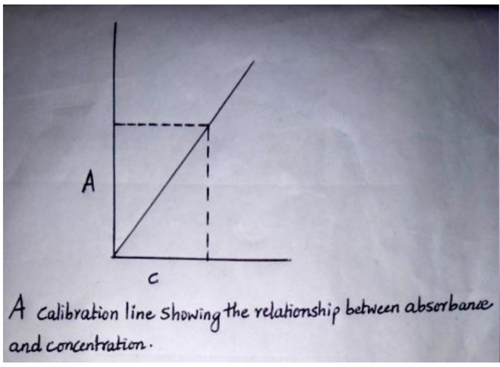
Deviations from Beer's law

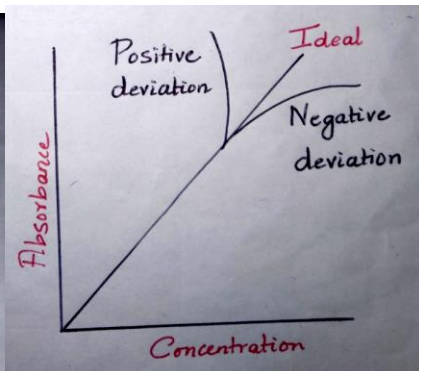
- The linear relationship between optical density and concentration of solution is not observed at concentrations above 10^{-2} M.
- Hence concentrated solutions do not obey Beer-Lambert's equation.
- The law is not obeyed if the absorbing species reacts with the solvent, dissociates or associates in solution.

- The molecules of the absorbing species should remain as simple molecules and should not undergo any change in molecular condition.
- Temperature fluctuations and entry of stray light into the absorbing system also lead to deviations from Beer- Lamberts law.
- The light incident on the absorbing medium should be monochromatic otherwise minor deviations from Beer-lamberts law are observed.
- Hence monochromators have to be used to produce monochromatic beams.
- The molar extinction coefficient depends on the refractive index of the absorbing medium.
- At high concentrations these changes are considerable but at concentrations below 10^{-2}M, these changes can be neglected.
- When Beer-Lambert law is obeyed, calibration plot will be obtained as a straight line passing through the origin.
- If there are deviations from Beer-Lambert's law, the calibration plot will curve either:

- Upward (positive deviation)

  OR
- Downward (negative deviation)





Validity of Beer-Lambert's law

- The Beer-Lambert's law is strictly applicable to dilute solutions whose concentrations are below 10^{-2} M.
- Such solutions obey the equation O.D = $-\log_{10} T = \varepsilon cl$
- According to which optical density is proportional to the concentration of the solution and transmittance is inversely proportional to the concentration.

REFERENCES

- Dr. Madan R.L., (2014), '*Chemistry for Degree Students B.Sc. Third Year*', S. Chand.