

Molar extinction coefficients of some carbohydrates in aqueous solutions

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Abstract. Molar extinction coefficients of some carbohydrates viz. L-arabinose ($C_5H_{10}O_5$), D-glucose ($C_6H_{12}O_6$), D-mannose ($C_6H_{12}O_6$), D-galactose ($C_6H_{12}O_6$), D(-) fructose ($C_6H_{12}O_6$) and maltose ($C_{12}H_{24}O_{12}$) in aqueous solutions have been determined at 81, 356, 511, 662, 1173 and 1332 keV by gamma ray transmission method in a narrow beam good geometry set-up. These coefficients have been found to depend upon the photon energy following a 4-parameter polynomial. These extinction coefficients for different sugars having the same molecular formula have same values varying within experimental uncertainty. Within concentration ranges studied, Beer–Lambert law is obeyed very well.

Keywords. Molar extinction coefficients; interaction cross-sections.

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1. Introduction

The study of absorption of gamma radiations in materials of common use and of biological importance has been an important subject in the field of radiation physics and is potentially useful in the development of semi-empirical formulations of high accuracy, possibly along the lines detailed by Jackson and Hawkes [1]. Carbohydrates play a vital role in the lives of plants and animals, both as structural elements and in the maintenance of functional activity. These in the form of sugar and starch represent a major part of the total caloric intake for humans, plants, animal life and for many microorganisms and are necessary for the growth of body tissues. Since radioactive sources such as ^{137}Cs (662 keV), ^{60}Co (1173 and 1332 keV), ^{133}Ba (81 and 356 keV) and ^{22}Na (511 keV) are used in biological studies, radiation sterilization, and industry [1,2] a thorough knowledge of the interaction of photons with biologically important substances such as amino acids, carbohydrates and fatty acids is desirable. Extensive data on mass attenuation coefficients of gamma rays in some compounds and mixtures of dosimetric and biological importance have been compiled by Hubbell [3] in the energy range 1 keV to 20 MeV. An updated version of the

attenuation coefficients for elements having atomic numbers from 1 to 92 and for 48 additional substances has also been compiled by Hubbell and Seltzer [4]. Gopinathan *et al* [5,6] and Gopinathan *et al* [7,8] have studied total attenuation cross-sections for several amino acids and sugars only in the solid form for limited energies. In a pioneering work, Teli *et al* [9–11] determined gamma ray attenuation coefficients of magnesium chloride, zinc sulphate and sodium chloride at 123 keV. Later on, attenuation in solutions of ferrous sulphate and ammonium chloride at 123 and 662 keV was studied by Teli and Chaudhary [12,13]. However, Gerward [14] noted the basic flaw in the formulation developed by them as the densities of solutions required for the estimation of mass attenuation coefficients were arrived at theoretically, by taking the volume of the solution as the sum of the volumes of its constituents, which in the light of prevalence of strong solute/solvent interactions is untenable. He developed alternative method for the determination of the density of the solutions. Kaur *et al* [15] and Singh *et al* [16] reformulated the equation used by Teli *et al* [9] and established the solution method as another method to obtain the mass attenuation coefficients of the solid solutes from their solutions. Gagandeep *et al* [17] reported attenuation coefficients of solutions of three carbohydrates namely glucose, maltose and sucrose in the energy region, in which the influence of all photon interaction processes can be seen. In this paper we report the molar extinction coefficient ϵ , of carbohydrates namely L-arabinose, D-glucose, D-mannose, D-galactose, D(-) fructose and maltose at 81, 356, 511, 662, 1173 and 1332 keV, calculated from the radiation densities gathered for their aqueous solutions.

2. Theory

2.1 Molar extinction coefficients

Lambert developed the equation for attenuation of a photon beam as a function of the thickness of a homogeneous medium. Beer developed the equation for the effect of concentration. According to Beer–Lambert law, the probability that a photon will be absorbed in a medium is directly proportional to the concentration of the absorbing molecule and to the thickness of the sample.

The absorbance or radiation density (RD) of a solution is defined by the equation:

$$\text{RD} = \log \frac{I_0}{I}, \quad (1)$$

where I_0 is the intensity of the incident beam impinging on a cell containing the solution and I that of the transmitted beam. The radiation density is related to the concentration of the solution as

$$\text{RD} = \epsilon xc, \quad (2)$$

where x (cm) is the path length of the cell, c (mol/L) is the molar concentration (number of moles of the solute dissolved per litre of the solution) of the absorbing species in the solution and ϵ is a constant of proportionality called the molar extinction coefficient. Molar extinction coefficient depends upon the wavelength of the incident radiation and is greatest where the absorption is most intense. Its dimensions are $1/(\text{concentration} \times \text{path length})$

Molar extinction coefficients

and is normally convenient to express it in $\text{L mol}^{-1} \text{cm}^{-1}$. Alternative units are $\text{cm}^2 \text{mol}^{-1}$. This change in units emphasizes the point that ϵ is a molar cross-section for absorption analogous to the mass attenuation coefficient μ/ρ and, the greater the cross-section of the molecule for absorption, the greater its ability to block the passage of the incident radiation. The relation (2) may be used to determine the concentration of solution from experimental RD values, if ϵ for solution is known.

The change in the radiation intensity dI due to its interactions occurring during the passage through material is given by

$$-dI = \sigma IN dx, \quad (3)$$

where N is the number of interaction centres per unit volume and σ is the interaction cross-section having the dimensions of area (m^2) called the probability of interaction and may be visualized as the area, which has to be hit by the photons in order to cause interaction.

Equation (3) may be written in terms of molar concentration by using $N = N_A c$, where N_A is the Avogadro constant,

$$-dI = \sigma I N_A c dx. \quad (4)$$

Integration leads to

$$I = I_0 e^{-\sigma N_A c x}. \quad (5)$$

This expression is essentially identical to the so-called 'Lambert-Beer law' which is used to describe radiation attenuation in homogeneous solutions. For practical purposes, the following form is preferred:

$$I = I_0 \cdot 10^{-\epsilon c x}. \quad (6)$$

Comparing eqs (5) and (6), we have

$$\epsilon = \sigma N_A \log_{10} e = 0.4343 \sigma N_A = 0.4343 M \frac{\mu}{\rho}, \quad (7)$$

where M is the molar mass (g/mol) or numerically

$$\frac{\sigma}{\text{barn}} = 3823 \frac{\epsilon}{\text{L mol}^{-1} \text{cm}^{-1}}. \quad (8)$$

The above equations have been derived for a solution of an absorbing compound in a practically transparent solvent. Deviations from Beer's law are expected to occur whenever the absorption of the solvent cannot be neglected.

The mixture rule can then be applied, giving the following a more accurate relation:

$$\text{RD} = \log \frac{I_0}{I} = \epsilon_w c_w x + \epsilon_s c_s x, \quad (9)$$

where ϵ_w and ϵ_s are the molar extinction coefficients of pure water (solvent) and solid solute, c_w and c_s are their respective molar concentrations. Under normal circumstances, we expect no deviations from Beer's law as formulated in eq. (9). This equation can be rewritten in the following form to determine molar extinction coefficient of the solute in the aqueous solution

$$\varepsilon_s = (1/c_s x)[RD - \varepsilon_w c_w x]. \quad (10)$$

The molar extinction coefficient of pure water can also be determined as follows:

$$\varepsilon_w = (1/c_w x) \log I_0/I, \quad (11)$$

where I is the intensity of radiation passing through water.

3. Experimental details

The details of the narrow beam transmission experiment set-up is as discussed in our paper [16]. The signal from the detector ($1.5'' \times 1.5''$ NaI (Tl) crystal having energy resolution of 12% at 662 keV gamma ray from the decay of ^{137}Cs) after suitable amplification was recorded in EG&G ORTEC 4 K plug-in-card coupled to a PC/AT. The sample detector solid angle was $< 0.5 \times 10^{-4}$ Sr. The results were obtained for those thicknesses of the samples that satisfied the condition $2 < \ln(I_0/I) < 4$ as suggested by Creagh and Hubbell [18]. The radioactive sources ^{137}Cs (662 keV), ^{60}Co (1173 and 1332 keV), ^{133}Ba (81 and 356 keV) and ^{22}Na (511 keV) of strength 5 mCi each were obtained from Bhabha Atomic Research Centre, Mumbai, India. The stability and reproducibility of the arrangement was tested before and after each set of runs in the usual manner. The experiments were performed in an air-conditioned room to avoid possible shifts of the photopeaks. To minimize the contribution of both small angle scattering and multiple scattering events to the measured intensity, the transmitted intensity was measured by gating the channels at the full-width at half-maximum position of the photo peak. A sufficient number of counts were collected under the photo peak to limit the statistical error to less than 1%. To study the effect of concentration of the solution on molar extinction coefficients, the perspex containers of fixed thicknesses were filled with different solutions having different concentrations. The intensity measurements were taken with the solution filled perspex box and with an empty (i.e. air filled) box, alternatively placed in the path of the beam.

4. Results and discussion

The radiation density values obtained at various concentrations and plotted against concentration of the solution (figure 1) are linear, the values of the slope equal to the ε values. These values for the various sugars studied are given in table 1 and agree very well with the average values of the ε obtained at each concentration from eq. (2). Molar extinction coefficients remain constant with concentration of the solution and vary with wavelength of the incident radiation so average values of ε were taken. Clearly Beer-Lambert law in aqueous solutions is obeyed. These values have also been compared with theoretical values of molar extinction coefficients of solutes calculated from the following relation:

$$\varepsilon_s = N_A \sigma_s \log_{10} e, \quad (12)$$

where N_A is the Avogadro number and σ_s is the interaction cross-section of solute.

The experimental values of molar extinction coefficients of carbohydrates of type $\text{C}_n\text{H}_{2n}\text{O}_n$ were fitted to the following expression

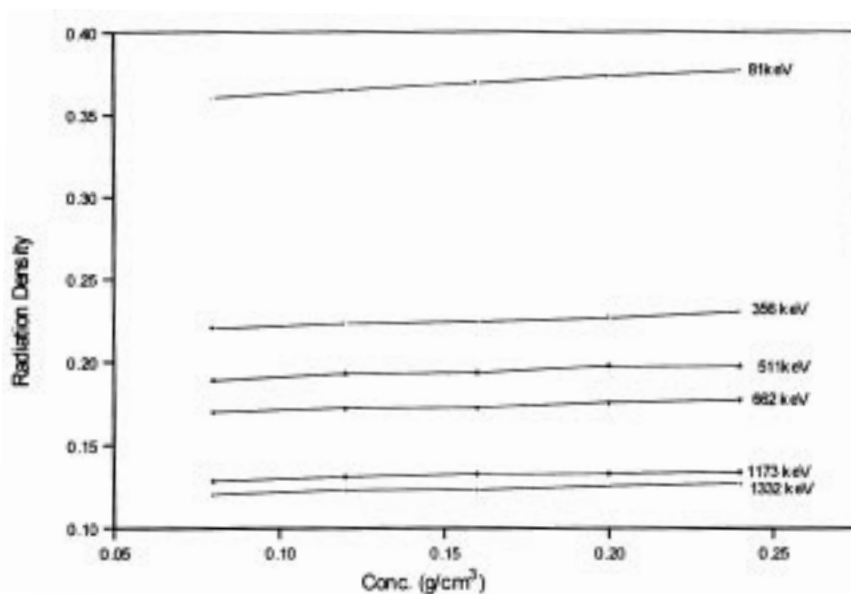


Figure 1. Radiation density vs. concentration for maltose.

Table 1. Molar extinction coefficients ϵ ($\text{mol}^{-1} \text{l cm}^{-1}$) of carbohydrates in aqueous solutions.

Solute	Conc. range	Molar extinction coefficient	81 (keV)	356 (keV)	511 (keV)	662 (keV)	1173 (keV)	1332 (keV)
L-arabinose $\text{C}_5\text{H}_{10}\text{O}_5$	0.08–0.24	Avg. exp.	0.0114	0.0071	0.0061	0.0054	0.0042	0.0038
		Thr.	0.0113	0.0070	0.0060	0.0054	0.0041	0.0038
		From slope	0.0115	0.0071	0.0060	0.0054	0.0041	0.0038
D-glucose $\text{C}_6\text{H}_{12}\text{O}_6$	0.08–0.24	Avg. exp.	0.0135	0.0085	0.0072	0.0063	0.0049	0.0044
		Thr.	0.0136	0.0084	0.0072	0.0064	0.0049	0.0046
		From slope	0.0136	0.0084	0.0071	0.0065	0.0049	0.0045
D-mannose $\text{C}_6\text{H}_{12}\text{O}_6$	0.08–0.24	Avg. exp.	0.0138	0.0084	0.0073	0.0063	0.0050	0.0045
		Thr.	0.0136	0.0083	0.0072	0.0064	0.0049	0.0046
		From slope	0.0138	0.0084	0.0072	0.0064	0.0048	0.0045
D-galactose $\text{C}_6\text{H}_{12}\text{O}_6$	0.08–0.24	Avg. exp.	0.0135	0.0084	0.0073	0.0064	0.0050	0.0044
		Thr.	0.0136	0.0083	0.0072	0.0064	0.0049	0.0046
		From slope	0.0135	0.0083	0.0072	0.0064	0.0051	0.0045
D(-) fructose $\text{C}_6\text{H}_{12}\text{O}_6$	0.08–0.24	Avg. exp.	0.0137	0.0086	0.0073	0.0065	0.0050	0.0044
		Thr.	0.0136	0.0083	0.0072	0.0064	0.0049	0.0046
		From slope	0.0139	0.0086	0.0071	0.0064	0.0050	0.0045
Maltose $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$	0.08–0.24	Avg. exp.	0.0271	0.0170	0.0145	0.0131	0.0098	0.0089
		Thr.	0.0272	0.0167	0.0144	0.0129	0.0098	0.0092
		From slope	0.0274	0.0167	0.0145	0.0129	0.0097	0.0093

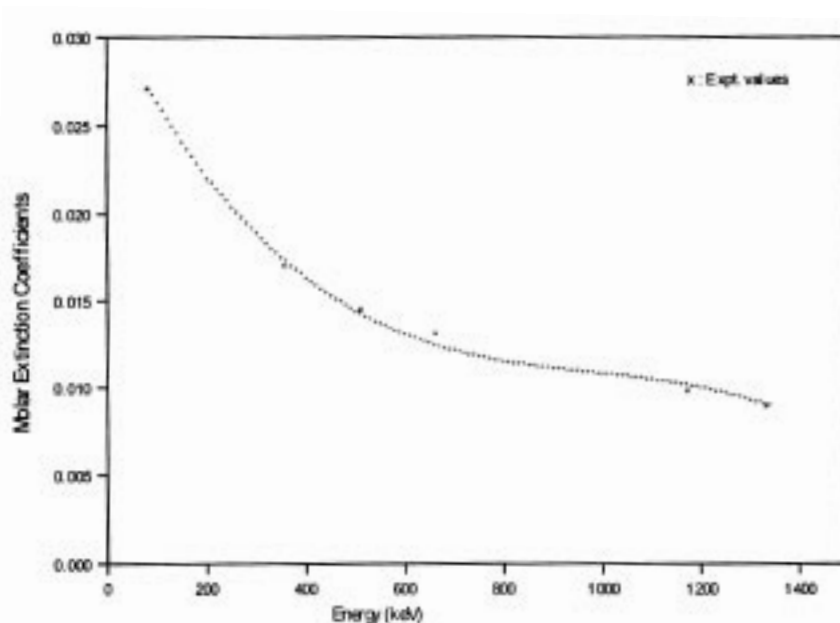


Figure 2. Polynomial fitting of molar extinction coefficients for $C_{12}H_{24}O_{12}$.

Table 2. Values of interaction cross-sections of carbohydrates in aqueous solutions.

Solute	Interaction cross-section (b/molecule)	81 (keV)	356 (keV)	511 (keV)	662 (keV)	1173 (keV)	1332 (keV)
L-arabinose	Avg exp.	43.70	27.12	23.23	20.55	15.89	14.44
$C_5H_{10}O_5$	Thr.	43.32	26.58	22.92	20.51	15.61	14.63
D-glucose	Avg exp.	51.88	32.62	27.68	24.34	18.69	16.91
$C_6H_{12}O_6$	Thr.	51.95	31.90	27.54	24.60	18.76	17.57
D-mannose	Avg exp.	52.72	32.09	27.81	24.14	19.25	17.11
$C_6H_{12}O_6$	Thr.	51.95	31.88	27.91	24.60	18.72	17.57
D-galactose	Avg exp.	51.57	31.94	28.04	24.37	18.95	16.81
$C_6H_{12}O_6$	Thr.	51.95	31.86	27.52	24.60	18.72	17.57
D(-) fructose	Avg exp.	52.33	32.69	27.73	24.68	19.18	16.96
$C_6H_{12}O_6$	Thr.	51.95	31.86	27.53	24.59	18.74	17.58
Maltose	Avg exp.	103.52	64.94	55.39	50.04	37.59	33.85
$C_{12}H_{24}O_{12}$	Thr.	103.90	63.79	55.01	49.28	37.47	35.18

$$\epsilon = A_0 + A_1E + A_2E^2 + A_3E^3, \tag{13}$$

where E is the energy of incident photon in MeV and A 's are constants. Parameters fitted for CH_2O i.e. $n = 1$ type carbohydrates are:

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$$\begin{aligned}A_0 &= 2.63 \times 10^{-3}, \\A_1 &= -4.79 \times 10^{-6}, \\A_2 &= 4.70 \times 10^{-9}, \\A_3 &= -1.62 \times 10^{-12}.\end{aligned}$$

The values of the constants for all other carbohydrates are multiple of these values. A typical curve for maltose ($C_{12}H_{24}O_{12}$) is shown in figure 2. All the experimental values of ϵ lies on this curve. These values of molar extinction coefficients of carbohydrates correspond to interaction cross-sections in the range of 14–103 b/molecule. As interaction cross-sections are found to depend upon energy of incident photons and not on concentration of the solution, the average values of interaction cross-sections of carbohydrates are shown in table 2.

Reviewing the data for various sugars having the same molecular formula, it is found that the ϵ values remain the same and are thus independent of the nature of the sugar. It may thus be said, the extinction coefficients are independent of the nature of the binding between the various atoms and are nearly totally given by number and nature of atoms.

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