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Molar extinction coefficients of solutions of some organic compounds

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Abstract. Molar extinction coefficients of aqueous solutions of some organic compounds, viz. formamide (CH_3NO), *N*-methylformamide (C_2H_5NO), *NN*-dimethylformamide (C_3H_7NO), *NN*-dimethylacetamide (C_4H_9NO), 1,4-dioxane ($C_4H_8O_2$), succinimide ($C_4H_5NO_2$) and solutions of acetamide (C_2H_5NO) and benzoic acid ($C_7H_6O_2$) in 1,4-dioxane ($C_4H_8O_2$) have been determined by narrow beam γ-ray transmission method at 81, 356, 511, 662, 1173 and 1332 keV. The experimental values of mass attenuation coefficients of these compounds have been used to calculate effective atomic numbers and electron densities. The additivity rule earlier used for aqueous solution has been extended to non-aqueous (1,4-dioxane) solutions.

Keywords. Molar extinction coefficients; effective atomic numbers; electron density.

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1. Introduction

The experimental determination of molar extinction coefficients of 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]. Reliable values of these coefficients for solutions are required in many scientific, engineering and chemical disciplines involving photon interactions. In view of promising advantages of molar extinction coefficients of solutions, Gagandeep *et al* [2] developed for the first time mathematical formulations of these coefficients for a number of aqueous solutions of soluble salts and made measurements at different γ-ray energies. Singh *et al* [3,4] continued to determine these coefficients for carbohydrates and amino acids by γ-ray transmission method. A review of X-ray and γ-ray attenuation in solutions has been given by Singh and Gerward [5].

In the present work, we report the molar extinction coefficient ε, of some compounds, viz. formamide (CH_3NO), *N*-methylformamide (C_2H_5NO), *NN*-

dimethylformamide (C_3H_7NO), *NN*-dimethylacetamide (C_4H_9NO), 1,4-dioxane ($C_4H_8O_2$), succinimide ($C_4H_5NO_2$) as estimated from the measured absorbance of γ radiations in their aqueous solutions and use of Beer–Lambert law and additivity rule. Extinction coefficients of acetamide (C_2H_5NO) and benzoic acid ($C_7H_6O_2$), insoluble in water, were determined for their solutions in 1,4-dioxane ($C_4H_8O_2$), to test the validity of additivity in non-aqueous solutions.

2. Theory

The amount of radiation absorbed may be measured in a number of ways. The transmittance T is defined as

$$T = \frac{I}{I_0}.$$

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

$$\mathrm{RD} = \log \frac{1}{T} = \log \frac{I_0}{I} = \log 100/\%T = 2 - \log \%T, \tag{1}$$

where I_0 and I are the intensities of γ radiations traversed through the cell without and with the solution.

Radiation density depends on the total quantity of the absorbing compound in the radiation path and is linearly dependent on the concentration of the absorbing species. This is most commonly expressed as Beer–Lambert law:

$$\mathrm{RD} = \varepsilon x c, \tag{2}$$

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 liter of the solution) of the absorbing species in the solution and ε is called the molar absorptivity or extinction coefficient (l $\mathrm{mol}^{-1}\mathrm{cm}^{-1}$ or mol^{-1} cm^2). Molar extinction coefficient, constant for a particular substance, is a measure of the amount of radiation absorbed per unit concentration per unit length and depends upon the wavelength of the incident radiation and is greater where the absorption is more intense.

A plot of radiation density vs. concentration should be linear, if Beer's law is being obeyed. Most substances obey Beer–Lambert law at low to moderate concentrations, although some exceptions are well-known. Once a plot of RD vs. concentration has been generated, the value of the extinction coefficient can be obtained from the slope of the lines, if path length is known. If radiation density is known, the corresponding concentration can be determined from calibration curve. The use of spectroscopic measurements to determine unknown concentrations is one of the most important steps in the field of chemical analysis.

The change in the radiation intensity $\mathrm{d}I$ due to interactions occurring during its passage through solution is given by

$$-\mathrm{d}I = \sigma I N \,\mathrm{d}x, \tag{3}$$

where N is the number of interaction centres per unit volume and σ is the interaction cross-section called the probability of interaction, i.e. the area, which has to be hit

by the photons in order to cause interaction. In terms of molar concentration, by using $N = N_{\mathrm{A}}c$, eq. (3) may be written as

$$-\mathrm{d}I = \sigma I N_{\mathrm{A}} c\,\mathrm{d}x, \tag{4}$$

where N_{A} is the Avogadro's number.

Integration of eq. (4) leads to

$$I = I_0 \mathrm{e}^{-\sigma N_{\mathrm{A}} c x}. \tag{5}$$

This expression is identical to 'Beer–Lambert law' which is used to describe radiation attenuation in homogeneous medium. For practical purposes, the following form is preferred:

$$I = I_0 \cdot 10^{-\varepsilon M c x}, \tag{6}$$

where $M = \sum_i n_i A_i$ is the molar mass (molecular weight), n_i and A_i are respectively the number of formula units and atomic weight of the ith element.

Effective molecular weight of the solution is given by the following formula:

$$M = x_1 M_1 + x_2 M_2, \tag{7}$$

where

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \quad \text{and} \quad n_1 = \frac{w_1}{M_1}, \quad n_2 = \frac{w_2}{M_2},$$

where M_1 and M_2 are the molar masses of component 1 and 2 respectively and w_1 and w_2 are the corresponding weight fractions.

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

$$\varepsilon = \sigma N_{\mathrm{A}}\ \log_{10} e = 0.4343 \sigma N_{\mathrm{A}} = 0.4343 M \mu_{\mathrm{m}}. \tag{8}$$

Thus, the molar extinction coefficient for any element and photon energy can readily be calculated from existing compilations of mass attenuation coefficients. The molar extinction coefficient, ε, for the chemical compound $A_x B_y$ is given by the simple relation:

$$\varepsilon = x\,\varepsilon_A + y\,\varepsilon_B, \tag{9}$$

where ε_A and ε_B are the molar extinction coefficients for the elements A and B. Equation (9) is easily extended to chemical compounds with more than two components.

The mass attenuation coefficient (μ_{m}) is proportional to the total molecular cross-section, $\sigma_{\mathrm{t,m}}$, through the relation

$$\sigma_{\mathrm{t,m}} = (\mu_{\mathrm{m}})\,\frac{M}{N_{\mathrm{A}}}. \tag{10}$$

The average total atomic cross-section $\sigma_{\mathrm{t,a}}$ can be expressed as

$$\sigma_{\mathrm{t,a}} = \sigma_{\mathrm{t,m}} \frac{1}{\sum_i n_i}. \tag{11}$$

Similarly, the average electronic cross-section, $\sigma_{\mathrm{t,el}}$, is given by

$$\sigma_{\mathrm{t,el}} = \frac{1}{N_{\mathrm{A}}} \sum_i \frac{f_i A_i}{Z_i} (\mu_m)_i \tag{12}$$

where $f_i = n_i / \sum_j n_i$ is the fractional abundance of element i with respect to the number of atoms.

The effective atomic number (Z_{eff}) is the ratio of atomic and electronic cross-sections:

$$Z_{\mathrm{eff}} = \frac{\sigma_{\mathrm{t,a}}}{\sigma_{\mathrm{t,el}}}. \tag{13}$$

The effective number of electrons per unit mass, i.e., electronic density N_{e} can be found from

$$N_{\mathrm{e}} = \frac{\mu_{\mathrm{m}}}{\sigma_{\mathrm{t,el}}} = \left(\frac{Z_{\mathrm{eff}}}{M}\right) N_{\mathrm{A}} \sum_i n_i. \tag{14}$$

3. Experimental details

The molar extinction coefficients were determined using narrow beam transmission geometry similar to that used by Singh *et al* [6]. A $2'' \times 2''$ NaI (Tl) crystal having energy resolution of 12.5% at 662 keV γ-rays from the decay of ^{137}Cs was used for the measurement of mass attenuation and molar extinction coefficients. The detector and source were both provided with adequate lead shielding. The sample–detector solid angle was $< 5.0 \times 10^{-5}$ Sr. The source and sample systems were mounted on composite stands of adjustable heights. The platform for the sample was capable of rotation around a vertical axis. With the help of this rotational arrangement, error caused by deviation in thickness was reduced to a minimum by taking average value of the intensities at four faces of the sample. With the help of screw arrangement, the platform having radioactive source was also made capable of movement in transverse direction to the incident beam for proper alignment. The measuring time as well as the sample thicknesses were selected in order to satisfy the ideal condition suggested by Creagh and Hubbell [7]. Radioactive sources, namely, ^{137}Cs, ^{133}Ba, ^{60}Co and ^{22}Na of each 5-mCi strength were obtained from isotope division of BARC, Mumbai. In order to check the performance of the experimental set-up, the linear attenuation coefficient of aluminum was calculated using it as a reference absorber material. At 662 keV, its value was found to be 0.199 cm^{-1}, which is in good agreement with theoretical value 0.202 cm^{-1} calculated with the help of XCOM program developed by Berger and Hubbell [8]. Recently, this well-known and much used program has been transformed to the window platform by Gerward *et al* [9]. The window version of XCOM is called WinXCOM. The samples contained in perspex boxes of different thicknesses were placed one by one between the source and the detector. The transmission intensity was measured by gating the channels at the full-width at half-maximum position of the photopeak. This minimizes the contributions of both small angle and multiple scattering events to

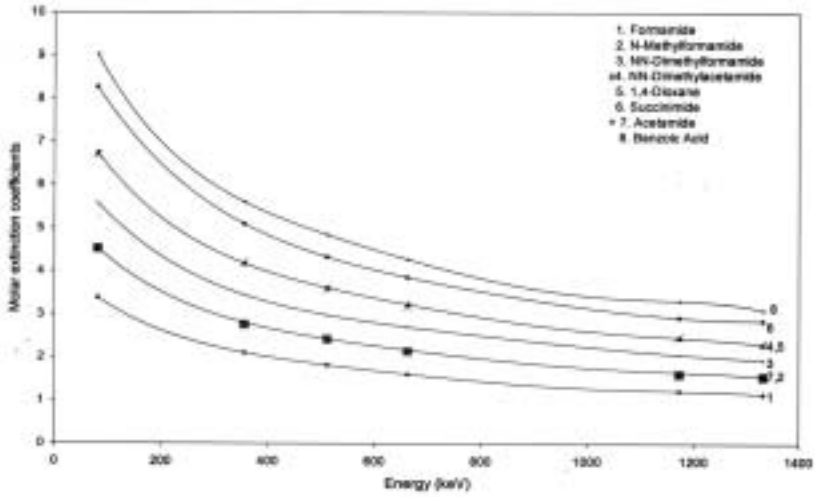

Figure 1. Plot of molar extinction coefficients vs. energy for pure form of compounds.

the measured intensity. The counting time was selected such that at least 10^5–10^6 counts were recorded under the photopeak so that the statistical uncertainty in the counts was below 0.3%. The stability and reproducibility of the experimental arrangement was tested before and after each set of runs in the usual manner.

4. Results and discussion

For each sample and selected γ-ray energy, the photon intensity was determined without and with absorber. The experimental molar extinction coefficients were determined using eq. (2). These values were compared with the theoretical ones obtained using eq. (8). The values of molar extinction coefficients for solutions of organic compounds in water and in 1,4-dioxane are shown in tables 1 and 2 respectively (which are available at http://www.ias.ac.in/pramana/v62/p1139/fulltext.pdf). The values of molar extinction coefficients of these compounds were fitted to the following expression:

$$\varepsilon = A_0 + A_1 E + A_2 E^2 + A_3 E^3 + A_4 E^4, \tag{15}$$

where E is the energy of incident photon in keV and A's are constants.

It was seen that lesser number of parameters in eq. (15) did not yield good fit, showing the trivial dependence upon the energy of the incident γ radiations. All the experimental values of ε were found to lie on the curve. As an illustration, a typical curve for pure forms of organic compounds is shown in figure 1 and the values of the constants for formamide (CH_3NO) are as given below:

$$A_0 = 4.0261, \quad A_1 = -0.0091, \quad A_2 = 1 \times 10^{-5},$$
$$A_3 = -1 \times 10^{-8} \quad \text{and} \quad A_4 = 3 \times 10^{-12}.$$

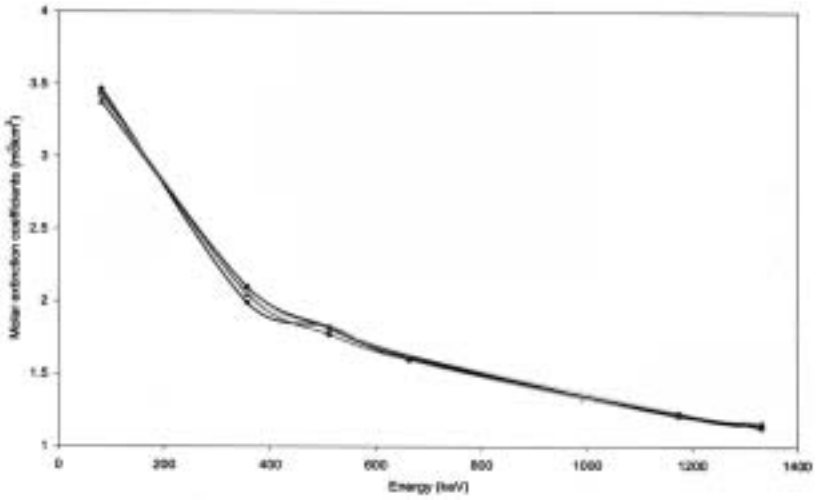

Figure 2. Plot of molar extinction coefficients vs. energy at various concentrations for formamide.

In $C_nH_{2n+1}NO$ series, starting from formamide to *NN*-dimethylformamide, the molar extinction coefficient of CH_2 group gets added to the molar extinction coefficient of the previous sample and we get ε for the next member of the series. It is observed that the group contributions are quite additive. In our previous paper by Singh *et al* [3] the values of the molar extinction coefficients of carbohydrates were also fitted to third-order polynomial for all the carbohydrates of $C_nH_{2n}O_n$ type. Value of molar extinction coefficient is independent of the concentration of the solution as illustrated in figure 2.

Using the present experimental data of mass attenuation coefficients of solutions and of H, C and O at different energies from El-Kateb and Abdul Hamid [10] the effective atomic numbers of solutions under study were determined from eq. (13). The values of effective atomic numbers and electron densities (eq. (14)) of all these organic compounds were found to be independent to the change in concentration of the solution and energy of the incident photon.

5. Conclusion

The results presented here provide a basis for studying photon interactions with solvated (hydrated) ions rather than bare ions in the solid form. Using the solution method one can verify the Beer–Lambert law and determine the mass attenuation coefficients, molar extinction coefficients, as well as effective atomic numbers and electron densities. In the present work, in addition to the additivity rule for aqueous solution, the additivity in other organic solvent has also been verified. The results will be useful for biological and health-orientated applications and the new measurements will be welcomed in order to update the experimental data files and to upgrade the theoretical vs. experimental data comparisons.

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Table 1. Molar extinction coefficients of aqueous solutions of some organic compounds.

Solution	Density of the solution	Molar extinction coefficients ($mol^{-1}cm^2$)					
		81 keV	356 keV	511 keV	662 keV	1173 keV	1332 keV
Formamide	1.0262						
CH_3NO	Expt.	3.467	1.992	1.828	1.625	1.215	1.137
Mol. Wt. = 45.04	Thr.	3.537	2.154	1.861	1.662	1.266	1.186
	1.0543						
	Expt.	3.434	2.051	1.774	1.599	1.226	1.145
	Thr.	3.499	2.136	1.845	1.648	1.256	1.176
	1.0809						
	Expt.	3.416	2.069	1.828	1.636	1.237	1.127
	Thr.	3.462	2.118	1.830	1.635	1.245	1.167
	1.1031						
	Expt.	3.418	2.101	1.830	1.598	1.209	1.172
	Thr.	3.429	2.103	1.816	1.622	1.236	1.158
	1.1334						
	Expt.	3.376	2.100	1.816	1.608	1.225	1.147
	Thr.	3.396	2.087	1.802	1.610	1.227	1.149
N-Methylformamide	1.0043						
C_2H_5NO	Expt.	4.663	2.823	2.509	2.223	1.567	1.601
Mol. Wt. = 59.07	Thr.	4.654	2.837	2.450	2.188	1.668	1.562
	1.0062						
	Expt.	4.570	2.818	2.355	2.174	1.583	1.581
	Thr.	4.615	2.822	2.437	2.178	1.660	1.555
	1.0083						
	Expt.	4.457	2.811	2.385	2.178	1.579	1.557
	Thr.	4.577	2.809	2.427	2.168	1.652	1.547
	1.0102						
	Expt.	4.520	2.735	2.428	2.159	1.647	1.546
	Thr.	4.541	2.794	2.414	2.158	1.644	1.539
	1.0110						
	Expt.	4.520	2.759	2.414	2.137	1.616	1.550
	Thr.	4.502	2.781	2.403	2.146	1.635	1.532
NN-Dimethylformamide	0.9849						
C_3H_7NO	Expt.	5.556	3.537	2.898	2.847	1.957	2.048
Mol. Wt. = 73.09	Thr.	5.768	3.517	3.038	2.714	2.066	1.936
	0.9730						
	Expt.	5.684	3.391	3.048	2.641	2.115	1.851
	Thr.	5.729	3.508	3.028	2.708	2.063	1.933
	0.9609						
	Expt.	5.582	3.407	3.052	2.719	2.012	1.943
	Thr.	5.688	3.498	3.022	2.698	2.057	1.927
	0.9552						
	Expt.	5.647	3.484	3.030	2.664	2.023	1.938
	Thr.	5.650	3.485	3.012	2.692	2.051	1.921
	0.9487						
	Expt.	5.581	3.437	2.974	2.700	2.064	1.944
	Thr.	5.609	3.476	3.003	2.683	2.044	1.915

Table 1. (Continued).

Solution	Density of the solution	Molar extinction coefficients ($mol^{-1}cm^2$)					
		81 keV	356 keV	511 keV	662 keV	1173 keV	1332 keV
NN-Dimethylacetamide	0.9808						
C_4H_9NO	Expt.	6.989	3.864	3.881	3.184	2.305	2.434
Mol. Wt. = 87.12	Thr.	6.898	4.199	3.625	3.239	2.467	2.312
	0.9696						
	Expt.	6.837	4.031	3.676	3.106	2.383	2.186
	Thr.	6.841	4.192	3.621	3.235	2.463	2.308
	0.9609						
	Expt.	6.641	4.212	3.693	3.309	2.499	2.329
	Thr.	6.799	4.185	3.613	3.231	2.459	2.304
	0.9515						
	Expt.	6.760	4.133	3.654	3.181	2.473	2.322
	Thr.	6.758	4.177	3.610	3.224	2.456	2.300
	0.9366						
	Expt.	6.694	4.214	3.567	3.175	2.476	2.319
	Thr.	6.716	4.170	3.602	3.220	2.452	2.297
1,4-Dioxane	1.0135						
$C_4H_8O_2$	Expt.	6.922	4.132	3.664	3.223	2.483	2.186
Mol. Wt. = 88.12	Thr.	6.946	4.237	3.656	3.268	2.490	2.333
	1.0281						
	Expt.	6.826	4.173	3.656	3.214	2.446	2.303
	Thr.	6.896	4.221	3.645	3.256	2.481	2.324
	1.0312						
	Expt.	6.795	4.131	3.595	3.220	2.435	2.306
	Thr.	6.847	4.202	3.632	3.244	2.472	2.315
	1.0327						
	Expt.	6.730	4.154	3.625	3.216	2.461	2.301
	Thr.	6.797	4.187	3.618	3.232	2.462	2.307
	1.0337						
	Expt.	6.771	4.158	3.610	3.210	2.462	2.302
	Thr.	6.751	4.172	3.604	3.220	2.454	2.299
Succinimide	1.0468						
$C_4H_5NO_2$	Expt.	7.899	4.785	4.139	3.152	3.267	2.950
Mol. Wt. = 99.09	Thr.	7.828	4.764	4.114	3.675	2.799	2.623
	1.0499						
	Expt.	7.828	4.899	4.380	3.795	2.871	2.956
	Thr.	6.811	4.755	4.106	3.668	2.794	2.618
	1.0536						
	Expt.	7.749	4.835	4.401	3.873	2.860	2.603
	Thr.	7.798	4.747	4.100	3.662	2.790	2.614
	1.0619						
	Expt.	7.201	4.481	4.077	3.683	2.371	2.281
	Thr.	7.781	4.738	4.093	3.656	2.785	2.609
	1.2659						
	Expt.	7.379	4.544	3.858	3.439	2.607	2.543
	Thr.	7.337	4.519	3.905	3.488	2.658	2.490

Table 2. Molar extinction coefficients of solutions of organic compounds in 1,4-dioxane.

Solution	Density of the solution	Molar extinction coefficients ($mol^{-1}cm^2$)					
		81 keV	356 keV	511 keV	662 keV	1173 keV	1332 keV
Acetamide	1.0299						
C_2H_5NO	Expt.	4.538	2.787	2.426	2.167	1.657	1.551
Mol. Wt. = 59.07	Thr.	4.523	2.796	2.425	2.158	1.644	1.540
	1.0308						
	Expt.	4.536	2.786	2.426	2.147	1.651	1.549
	Thr.	4.523	2.794	2.415	2.158	1.644	1.540
	1.0314						
	Expt.	4.538	2.786	2.423	2.166	1.652	1.532
	Thr.	4.523	2.794	2.414	2.157	1.643	1.540
	1.0325						
	Expt.	4.531	2.809	2.423	2.178	1.656	1.549
	Thr.	4.520	2.794	2.414	2.157	1.643	1.539
	0.9986						
	Expt.	4.527	2.798	2.420	2.166	1.657	1.559
	Thr.	4.502	2.781	2.403	2.147	1.635	1.532
	1.0308						
	Expt.	4.536	2.786	2.426	2.147	1.651	1.549
	Thr.	4.523	2.794	2.415	2.158	1.644	1.540
Benzoic acid	1.0468						
$C_7H_6O_2$	Expt.	9.008	5.788	4.991	4.482	3.412	3.198
Mol. Wt. = 122.13	Thr.	9.330	5.766	4.982	4.451	3.391	3.177
	1.0499						
	Expt.	9.323	5.771	4.982	4.461	3.395	3.182
	Thr.	9.319	5.760	4.976	4.445	3.386	3.173
	1.0536						
	Expt.	9.323	5.779	4.982	4.452	3.392	3.188
	Thr.	9.309	5.755	4.969	4.440	3.384	3.172
	1.0619						
	Expt.	9.308	5.756	4.986	4.446	3.383	3.188
	Thr.	9.298	5.744	4.965	4.434	3.379	3.167
	1.2659						
	Expt.	8.976	5.600	4.836	4.270	3.310	3.397
	Thr.	8.991	5.564	4.806	4.291	3.273	3.066