A Note on the Measurement of the Absorption Coefficient in Infra-red Region. Influence of the Thickness of Layer on the Measurement of Absorption Coefficient

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Introduction

In order to determine the absorption coefficient k (or absorption index κ) in infra-red region, the transmission method is usually used. In the most of the researches, it is assumed that the Beer's rule holds strictly, For the gases and dilute solutions, this assumption may be valid, but inadequate to the liquids and solids which are highly absorbing. The invalidity of the Beer's law is due to the boundary reflexion and to the multiple reflexion of the substance layer whose thickness is comparable to the wavelength.

Recently, Simon[1] has investigated the surface reflexion of the highly absorbing substances including carbon tetrachloride and has obtained the values of refractive indices and of the absorption indices from the reflexion coefficients.

We have calculated the transmission coefficient of the infra-red beam passing through a thin layer of liquid carbon tetrachloride according to the correct formula using Simon's data, and have compared this with the value calculated from simple Beer's law.

The effect of the thickness of the layer is very marked, and it is concluded that we cannot obtain the correct value of the absorption coefficient for the highly absorbing materials by the simple transmission method usually used.

The Formula of Transmission Coefficient for the Single Plane Layer

A plane electromagnetic wave of the wavelength λ is considered to be linearly polarized and to be propagated in the medium 1. An absorbing dielectric layer with plane boundary surface is placed as shown in Fig. 1.

1) I. Simon, *J. Opt. Soc. Am.*, 41, 336 (1951).

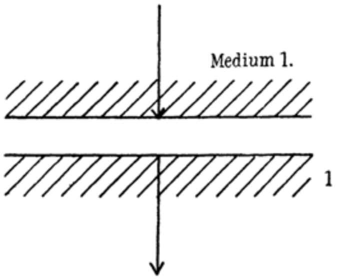

Fig. 1.

The direction of the propagation of incident wave is considered to be normal to the boundary surface. A part of the wave will be transmitted through the sheet characterized by refractive index n, absorption coefficient k ($=n\kappa$, where κ is absorption index) and thickness d. The medium 1 is considered to be non-absorbing and to be characterized by refractive index n_1.

The transmission coefficient of the sheet D^2 is expressed as follows[2]:

$$D^2=e^{-\frac{4\pi kd}{\lambda}}\times\frac{1+R_{12}{}^4-2R_{12}{}^2\cos 2\gamma}{1+R_{12}{}^4e^{-\frac{8\pi kd}{\lambda}}-2R_{12}{}^2e^{-\frac{4\pi kd}{\lambda}}\cos\left(\frac{4\pi nd}{\lambda}+2\gamma\right)}$$

$$=\frac{\sinh^2(-\ln R_{12})+\sin^2\gamma}{\sinh^2\left(\frac{2\pi kd}{\lambda}-\ln R_{12}\right)+\sin^2\left(\frac{2\pi nd}{\lambda}+\gamma\right)} \quad (1)$$

where

$$R_{12}{}^2=\frac{(n-n_1)^2+k^2}{(n+n_1)^2+k^2} \quad (2)$$

$$\tan\gamma=\frac{2n_1k}{(n^2-n_1{}^2)+k^2} \quad (3)$$

Transmission Coefficient for the Thin Layer of Liquid Carbon Tetrachloride

The calculation is made for the thin layer of carbon tetrachloride placed between rock salt plates.

The refractive indices and the absorption coefficients of carbon tetrachloride for the infra-red waves in the wave number 760–815 cm^{-1} region are tabulated in Table I. The data are taken from Simon's paper[1]. Using these values, the values of R_{12}, and $\tan\gamma$ are calculated. In this calculation, n_1 is taken to be 1.52. The calculated values are tabulated also in Table I.

Carbon tetrachloride shows marked absorption and dispersion in the region 760–815 cm^{-1} [1]. The suitable thickness of the layer for the measurement of the absorption coefficients by transmission method in this region would be, therefore, very small and

TABLE I

REFRACTIVE INDICES, ABSORPTION COEFFICIENTS AND RELATED CONSTANTS OF CARBONTETRACHLORIDE IN INFRA-RED REGION

$\tilde{\nu}$(cm.$^{-1}$)	n	k	R_{12}	$\tan\gamma$
760	1.30	1.20	0.40	−21.5
765	1.30	1.25	0.41	−76.1
770	1.30	1.25	0.41	−76.1
775	1.45	1.30	0.41	+ 2.65
780	1.85	1.75	0.51	+ 1.29
785	2.15	3.10	0.66	+ 0.79
790	1.70	3.50	0.74	+ 0.78
795	1.20	2.00	0.60	+ 1.94
800	0.80	0.80	0.44	− 2.38
805	0.85	0.45	0.34	− 0.99
810	0.95	0.25	0.25	− 0.52
815	1.05	0.15	0.16	− 0.41

The value of refractive index of rock salt is taken as $n_1=1.52$.

would be comparable to the wave-length. We have calculated the transmission coefficients D^2 for the layer of the thickness $d=2.5\times10^{-5}$ cm., 5×10^{-5} cm. and 10^{-4} cm. respectively. On the other hand, the values of hypothetical transmission coefficient $T^2=\exp(-4\pi kd/\lambda)$, are also calculated. These values are tabulated in Tables II, III, and IV. The values of $(-\ln D^2)$ and $4\pi kd/\lambda$ are also given in Tables II, III and IV.

TABLE II

TRANSMISSION COEFFICIENTS AND RELATED QUANTITIES FOR THE LAYER OF CARBON TETRACHLORIDE

$d=2.5\times10^{-5}$ cm.

$\tilde{\nu}$(cm^{-1})	D^2	$\exp(-4\pi kd/\lambda)$	$-\ln D^2$	$4\pi kd/\lambda$
760	0.818	0.751	0.201	0.287
765	0.796	0.740	0.228	0.301
770	0.796	0.740	0.228	0.303
775	0.740	0.728	0.301	0.317
780	0.635	0.674	0.454	0.395
785	0.394	0.465	0.931	0.766
790	0.377	0.418	0.976	0.873
795	0.624	0.605	0.471	0.502
800	0.884	0.812	0.123	0.208
805	0.935	0.892	0.067	0.114
810	0.955	0.938	0.046	0.064
815	0.964	0.963	0.037	0.038

2) M. Yasumi, This Bulletin, 24, 54 (1951).

TABLE III

$d=5\times10^{-5}$ cm.

$\tilde{\nu}$(cm^{-1})	D^2	$\exp(-4\pi kd/\lambda)$	$-\ln D^2$	$4\pi kd/\lambda$
760	0.663	0.563	0.411	0.575
765	0.639	0.547	0.448	0.603
770	0.635	0.546	0.454	0.606
775	0.565	0.530	0.571	0.634
780	0.442	0.452	0.892	0.792
785	0.182	0.217	1.70	1.53
790	0.160	0.174	1.83	1.75
795	0.444	0.367	0.812	1.00
800	0.761	0.657	0.273	0.417
805	0.886	0.799	0.121	0.224
810	0.902	0.880	0.103	0.127
815	0.936	0.927	0.066	0.076

TABLE IV

$d=10^{-4}$ cm.

$\tilde{\nu}$(cm^{-1})	D^2	$\exp(-4\pi kd/\lambda)$	$-\ln D^2$	$4\pi kd/\lambda$
760	0.415	0.317	0.879	1.15
765	0.391	0.301	0.939	1.20
770	0.390	0.298	0.942	1.21
775	0.348	0.281	1.06	1.27
780	0.224	0.206	1.50	1.58
785	0.044	0.047	3.12	3.06
790	0.030	0.030	3.51	3.50
795	0.187	0.135	1.68	2.00
800	0.553	0.434	0.592	0.834
805	0.725	0.639	0.322	0.448
810	0.797	0.776	0.227	0.254
815	0.866	0.858	0.144	0.153

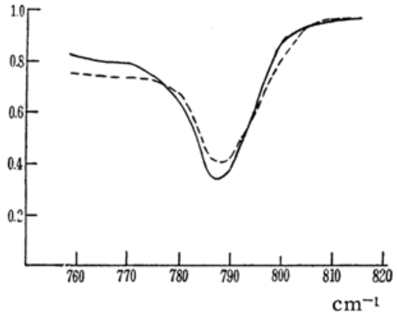

Fig. 2.

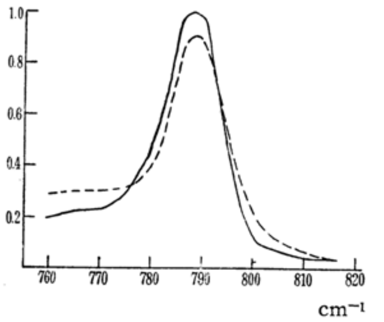

Fig. 3.

The values of D^2 and T^2 versus wave numbers for the thickness of $d=2.5\times10^{-4}$ cm. are illustrated in Fig. 2. The behavior of ($-\ln D^2$) and $4\pi kd/\lambda$ versus wave numbers are shown in Fig. 3.

Discussion

As shown in Tables I—III, and Figs. 2—3, it is concluded that the values of the transmission coefficients for the thin layer of carbon tetrachloride calculated with the exact formula are markedly different from the hypothetical transmission coefficient calculated with simple Beer's law. In the case of $d=10^{-4}$ cm., the maximum deviation amounts about 30%.

If we calculate the absorption coefficients from the values of D^2, which will be identical with the experimental transmission coefficients in ideal cases, according to simple Beer's law, the obtained values would be $-\ln D^2/(4\pi d/\lambda)$. As shown in Table I—III, the values of ($-\ln D^2$) are markedly different from $4\pi kd/\lambda$.

The situation will be more serious when the relative absorption coefficient is concerned, for the deviation will have plus sign in one wave-length region and minus sign in another region.

It can be said that the transmission method based upon the simple Beer's law cannot be applied for the highly absorbing substances and an erroneous conclusion would be drawn if we calculate absorption coefficient according to Beer's law.

It may not be unexpected that the absorption coefficient is dependent on the thickness of the layer and that the unexisting lines appear in some case or existing lines disappear in another case[3].

For the less absorbing materials the effect of the thickness will be less important, but for the lines whose absorption coefficient is about 0.5[4] the effect is not negligible[5].

Summary

The transmission coefficient of a thin layer of carbon tetrachloride is calculated according to the exact formula and compared with the

3) Earle K. Plyer and Nicola Aquista, *J. Opt. Soc. Am.*, **44**, 505 (1954).

4) e. g. k is ca. 0.6 for 8.90 μ of ethyl ether, 0.5 for 5.8 μ of ethyl acetate.

5) This conclusion is drawn from the calculation made by K. Kuratani.

value calculated by simple Beer's rule.

The usual transmission method which is based upon the Beer's law is inadequate to the determination of the absorption coefficient of highly absorbing substances such as carbon tetrachloride.

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