1 Comparison between transmittance equations of optical cell for calculating optical
2 constants of liquid materials

3 Dong Li^{*1,2}, Yangyang Wu¹, Changyu Liu¹, Xiaoxue Zhang¹, Hanbing Qi^{1,2}, Minghu
4 Jiang²

5 ¹School of Architecture and Civil Engineering, Northeast Petroleum University,
6 Fazhan Lu Street, Daqing 163318, China

7 ²School of Mechanical Science and Engineering, Northeast Petroleum University,
8 Fazhan Lu Street, Daqing 163318, China

9 **ABSTRACT** A method for determining the optical constants of liquid
10 materials by using transmittances of optical cell filled with liquid materials was
11 introduced, and three equations for calculating the transmittance of optical cell were
12 comparatively investigated. The transmittance spectrograms at normal incidence of
13 optical cell filled with water at different thicknesses were measured in spectral range
14 2-2.5 μm , and optical constants of water were calculated based on the measured
15 spectrum, which are used to validate these equations. The results show that the
16 method in this work can effectively calculate the optical constants of liquid materials.
17 Considered the multiple transmission through the glass, the equations have a better
18 ability to calculate the total transmittance of optical cell filled with liquid material
19 compared with omitting the multiple transmission.

20 **Key words:** liquid materials; optical constants; transmittance calculation; inversion
21 calculation

*Corresponding authors. Tel.: +86 459 6507763 E-mail: Lidonglvyan@126.com

1. Introduction

Optical constants are basic optical property of liquid materials, which play an important role in fundamental and applied research [1-4], such as physics, chemistry and engineering et al. However, the optical constants of liquid materials can not directly measured by using experimental technology, which are often inversed based on spectrum data of optical cell filled with liquid materials. There are a lot of inversion methods to determine the optical constants of liquid materials, in which the single thickness transmittance method (or single optical path-length transmission method) and the double-thickness transmittances method (or double optical path-length transmission method) are more attractive.

The single thickness transmittance method was developed by Jones and his coworkers in the 1970s [5, 6], then improved by Bertie and Keefe [7-9], and the recent studies of Keefe et al. have brought a large contribution to the fundamental aspect of the single thickness transmittance method [10-14]. The single thickness transmittance method calculates the optical constants of liquid materials based on the transmittance of optical cell filled with liquid materials and Kramers-Kronig dispersion relationship. However, the major technical limitation of the single thickness transmittance method is that the integral in Kramers-Kronig dispersion relationship should be calculated from zero to infinity, or in other words the value of refractive index at a given wave-number could be computed only if extinction index is know for all wavenumbers [15].

The double-thickness transmittances method was proposed by Tuntomo and Tien [16], which iteratively calculates the optical constants of liquid materials by using transmittances of liquid materials with two different thicknesses. Although the transmittance of liquid materials is hardly measured because the liquid materials are filled in the optical cell, there are two methods to determine the transmittance of liquid materials by using the transmittance of optical cell filled with liquid materials, which are equivalent method and effective method[16, 17]. However, transmittance of liquid materials attained by the equivalent method or effective method are not same with the absolute transmittance of neat liquids. Otanicar et al. [18] improved the double-thickness transmittances method proposed by Tuntomo and Tien, which iteratively calculates optical constants of liquid materials by using transmittances of optical cell filled with liquid materials at two different thicknesses, but in the transmittance calculation of optical cell filled with liquid materials the overall medium was divided into discrete elements, and in fact there is no vacuum inter-space among the three-layer system[19, 20]. Li et al. [19, 20] proposed a novel inversion model of optical constants based on continuous absorbing layers consisting of multiple reflections that is more suitable for liquid measurement, which effectively improves the Otanicar's method. Li et al. [21] developed a novel double-thickness transmittances method to determine optical constants of liquid materials by using transmittances of optical cell filled with liquid materials at two different thicknesses based on search or intelligence arithmetic methods, which also considered continuous absorbing layers consisting of multiple reflections.

In the inversion methods of optical constants of liquid materials based on transmittance spectrum of optical cell, the equation of the total transmittance at normal incidence of optical cell filled with liquid material is a key to the calculation precision. There are three equations to calculate the total transmittance at normal incidence of optical cell filled with liquid materials, including Li's equation [19, 20], Li's equation [21] and Kameya's equation [17]. The equations of Li [19-21] considered the multiple transmission through the glass and liquid materials, but the equation of Kameya only considered the multiple transmission through the liquid materials. To the authors' knowledge, there are none references about the comparison of three equations.

In this work, the comparison of three equations was investigated. Based on the transmittance spectrograms of optical cell with water at different thicknesses measured in spectral wavelength range 2-2.5 μm at normal incidence, optical constants of water were calculated to validate these equations with the data of reference.

2. Experimental

2.1 Transmittance measurement

Spectrophotometric measurements at normal incidence were made by using a Bruke V70 FTIR spectrometer. Light from the FTIR's internal light source was focused through an iris, collimated, and passed into a Michelson interferometer that caused each wavelength to be modulated. This modulated beam was then passed through optical cell or without, and focused onto an HgCdTe or RT-DLaTGS

detector. The detector signal was analyzed with the manufacture's software (OUPS version6.5), which uses Mertz phase correction and boxcar apodization without zero filling to provide spectrally resolved transmitted intensity. The experiment was made at ambient temperature.

The total transmittance T_f of optical cell filled with liquid materials can be measured as follows:

$$T_f = \frac{I}{I_0} \quad (1)$$

Where, I_0 and I are the incident (baseline) and transmitted intensities, respectively. The incident intensity was measured when the optical cell filled with liquid materials was removed from the beam's path. The transmitted intensity was measured when the optical cell filled with liquid materials was placed in the optical path.

The total transmittance T_e of optical cell without liquid materials can be measured as follows:

$$T_e = \frac{I}{I_0} \quad (2)$$

Where, I_0 and I are the incident (baseline) and transmitted intensities, respectively. The incident intensity was measured when the optical cell filled without liquid materials was removed from the beam's path. The transmitted intensity was measured when the optical cell filled without liquid materials was placed in the optical path.

2.2 Transmittance calculation

The optical cell used in the experiment is a sandwich system, which is consisted of two glass slabs and a liquid material layer, so the total transmittance T_f at normal incidence of optical cell filled with liquid material can be calculated by[21]

$$T_f = \frac{T_g^2 T_l}{1 - R_g - R_g R_l + R_g^2 R_l + T_l^2 R_g R_l} \quad (3)$$

Where, R_g and R_l are the reflectance of glass and liquid material layer at normal incidence, respectively. T_g and T_l are the transmittance of glass and liquid material at normal incidence, respectively.

The reflectance of glass and liquid material layer at normal incidence are given by the following forms.

$$R_g = \rho_1 + \frac{(1-\rho_1)^2 \rho_1 \exp\left[-\frac{8\pi k_g L_g}{\lambda}\right]}{1 - \rho_1^2 \exp\left[-\frac{8\pi k_g L_g}{\lambda}\right]} \quad (4a)$$

$$R_l = \rho_2 + \frac{(1-\rho_2)^2 \rho_2 \exp\left[-\frac{8\pi k_l L_l}{\lambda}\right]}{1 - \rho_2^2 \exp\left[-\frac{8\pi k_l L_l}{\lambda}\right]} \quad (4b)$$

Where, ρ_1 and ρ_2 are the interface reflectance for surface between air and glass, and for surface between liquid material and glass, respectively. k_g and k_l are the extinction coefficients of glass and liquid material, respectively. L_g and L_l are the thickness of glass slab and liquid material layer, respectively. λ is the wavelength.

The transmittance of glass and liquid material layer at normal incidence are given by:

$$T_g = \frac{(1-\rho_1)(1-\rho_2) \exp\left[-\frac{4\pi k_g L_g}{\lambda}\right]}{1 - \rho_1 \rho_2 \exp\left[-\frac{8\pi k_g L_g}{\lambda}\right]} \quad (5a)$$

$$T_l = \frac{(1-\rho_2)^2 \exp\left[-\frac{4\pi k_l L_l}{\lambda}\right]}{1 - \rho_2^2 \exp\left[-\frac{8\pi k_l L_l}{\lambda}\right]} \quad (5b)$$

Where, T_g and T_l are the transmittance of glass and liquid material at normal incidence, respectively.

The interface reflectance ρ_1 and ρ_2 are calculated based on Fresnel's relations.

$$\rho_1 = \frac{(n_g - 1)^2 + k_g^2}{(n_g + 1)^2 + k_g^2} \quad (6a)$$

$$\rho_2 = \frac{(n_g - n_l)^2 + (k_g - k_l)^2}{(n_g + n_l)^2 + (k_g + k_l)^2} \quad (6b)$$

Where, n_g and n_l are the refractive index of glass and liquid material, respectively.

Li et al. gave the equation for calculating the total transmittance T_f at normal incidence of optical cell filled with liquid material, which is given by[19,20]

$$T_f = \frac{T_g^2 \exp\left(\frac{-4\pi k_l L_l}{\lambda}\right)}{1 - \left[\rho_2 + \frac{\rho_1 (1 - \rho_2)^2 \exp\left(\frac{-8\pi k_g L_g}{\lambda}\right)}{1 - \rho_1 \rho_2 \exp\left(\frac{-8\pi k_g L_g}{\lambda}\right)} \right]^2 \exp\left(\frac{-8\pi k_l L_l}{\lambda}\right)} \quad (7)$$

Kameya et al. gave the equation for calculating the total transmittance T_f at normal incidence of optical cell filled with liquid material, which is given by[17]

$$T_f = (1 - \rho_1)^2 (1 - \rho_2)^2 \exp\left(\frac{-4\pi k_l L_l}{\lambda}\right) \left[1 + \frac{2\rho_1 \rho_2}{1 - \rho_1 \rho_2} + (\rho_1 + \rho_2)^2 \exp\left(\frac{-8\pi k_l L_l}{\lambda}\right) \right] \quad (8)$$

2.3 Method for optical constants of liquid material

Dong et al. developed a novel method to determine the optical constants of liquid materials[21], which calculates optical constants of liquid materials by using transmittances of optical cell filled with liquid materials at two different thicknesses, and a calculation procedure based on iteration technique was adopted as the following steps:

Step 1. Given the k_l values and the normal transmittances of liquid material are established by equation (9).

$$T_{l,m1} = T_{f,m1} \quad (9a)$$

$$T_{l,m2} = T_{f,m2} \quad (9b)$$

Where, $T_{f,m1}$ and $T_{f,m2}$ is the normal transmittance measurement values of optical cell filled with liquid material, whose thickness of liquid material is L_1 and L_2 in

wavelength λ , respectively. $T_{l,m1}$ and $T_{l,m2}$ is the normal transmittance values of liquid material, whose thickness of liquid material is L_1 and L_2 , respectively.

Step 2. Determine the ρ_3 values by equation (10).

$$\rho_3 = \frac{1 - \sqrt{T_{l1}^2 + T_{l1} \left[\exp\left(\frac{4\pi k_l L_1}{\lambda}\right) - \exp\left(-\frac{4\pi k_l L_1}{\lambda}\right) \right]}}{1 + T_{l1} \exp\left(-\frac{4\pi k_l L_1}{\lambda}\right)} \quad (10)$$

Step 3. Find the k_l values by deducing equation (11a and 11b).

$$k_l = -\frac{\lambda \ln\left(1 + \frac{\sqrt{1 + 4(\rho_3 c)^2}}{2c}\right)}{4\pi L_2} \quad (11a)$$

$$c = \frac{T_{l2}}{(1 - \rho_3)^2} \quad (11b)$$

Step 4. Determine the ρ_3 values by equation (12), and then find the new n_l values by equation (13) [22, 23].

$$\rho_3 = \frac{(n_l - 1)^2 + k_l^2}{(n_l + 1)^2 + k_l^2} \quad (12)$$

$$n_l = \frac{2n_g(1 + \rho_3) + \sqrt{a}}{2(1 - \rho_3)} \quad (n_g < n_l) \quad (13a)$$

$$n_l = \frac{2n_g(1 + \rho_3) - \sqrt{a}}{2(1 - \rho_3)} \quad (n_g > n_l) \quad (13b)$$

Where a is defined as:

$$a = [2n_g(1 + \rho_3)]^2 - 4(1 - \rho_3) \times [(1 - \rho_3)n_g^2 - \rho_2(k_g + k_l)^2 + (k_g - k_l)^2]$$

(14)

Step 5. Determine the normal transmittance calculation values $T_{l,c1}$ and $T_{l,c2}$ of optical cell filled with liquid material by equation (15) using the calculated n_l and k_l , and then determine the normal transmittances of liquid material using the equation (16).

$$T_{l1} = \frac{(1 - \rho_3)^2 \exp\left(-\frac{4\pi k_l L_1}{\lambda}\right)}{1 - \rho_3^2 \exp\left(-\frac{8\pi k_l L_1}{\lambda}\right)} \quad (15a)$$

$$T_{l2} = \frac{(1-\rho_3)^2 \exp\left(-\frac{4\pi k_l L_2}{\lambda}\right)}{1-\rho_3^2 \exp\left(-\frac{8\pi k_l L_2}{\lambda}\right)} \quad (15b)$$

$$T_{l,m1} = T_{l,m1} + T_{m1} - T_{l,c1} \quad (16a)$$

$$T_{l,m2} = T_{l,m2} + T_{m2} - T_{l,c2} \quad (16b)$$

Step 6. Analyze the calculation errors of the normal transmittance of optical cell filled with liquid material between measured and calculated values. And the normal transmittance of optical cell filled with liquid material is established by the Eq. 3. If the errors are rational, the optical constants calculation is finished, otherwise returns to step 2.

3. Result and Discussions

3.1 Experimental measurements

The experimental media is water, and the window material of optical cell is ZnSe glass whose layer thickness is 2mm. The experimental transmittance spectrum measured in wavelength 2.0-2.5 μm for the optical cell filled with and without water are shown in Fig. 1, in which water thickness is 0.19, 0.39 and 0.5 mm, respectively. Measurements were made with a resolution of 4 cm^{-1} in air and at room environment. To attain good repeatability of measured transmittance spectrum of optical cell, each sample was measured three times. And the uncertainty of transmittance measurement is lower than 1.5%, which is shown in Fig. 2.

Fig. 1 Transmittances of optical cell filled with and without water

Fig. 2 Uncertainty of transmittance measurements

The optical constants of water are attained by the experimental method in this work using experimental values from Fig. 1. In the inversion calculation, the optical constants of ZnSe glass are shown in the Fig. 3[24], and transmittance spectrum of optical cell filled with water at thickness 0.19 and 0.39 mm are used in the inversion calculation. The extinction coefficients and refractive index of water with the data attained from the reference [25] are plotted in Fig. 4.

Fig. 3 optical constants of ZnSe glass

Fig. 4 optical constants of water

From the Fig. 4, it is stated that k calculation results of water are agreement with most values in the reference, and the smallest and biggest deviation between the experimental and the reference value in k calculation spectra is 0.58% at wavelength 2.17 μm , 49.06% at wavelength 2.27 μm . As shown in the figure, the most n calculation values also have a good agreement with the reference data, and the smallest and biggest deviation between the experimental and the reference value in n calculation spectra is 0.30% at wavelength 2.17 μm , 5.18% at wavelength 2.0 μm . This results indicates that the inversion method in this work can effectively calculate the optical constants of liquid materials.

3.2 Transmittance spectrum of optical cell

The transmittance spectrum of optical cell filled with water at thickness 0.19, 0.39 and 0.50 mm are calculated by using the equations (Eq.3, Eq.7 and Eq.8) combined with optical constants of water in Fig. 4, which are shown in Fig. 5 with the experimental data.

Fig. 5 Transmittance spectrum of optical cell filled with different thickness water
(a: 0.19mm; b: 0.39mm; c: 0.50mm.1: Li(Eq.3); 2: Li (Eq.7); 3: Kameya (Eq.8))

As shown in the Fig. 5 (a1, b1 and c1), the transmittance spectrum calculated by using the Eq. 3 with optical constants of water in this work are nearly same with the experimental data of optical cell filled with water at thickness 0.19 and 0.39mm, but the transmittance spectra at thickness 0.50mm is slightly different with the experimental data of optical cell filled with water. The reason is that the experimental transmittance spectrum of optical cell filled with water at thickness

0.19 and 0.39mm were directly used to calculate the optical constants of water. It is also found that the calculated transmittance spectrum by using the Eq. 3 with optical constants of water from Bertie are more similar with the experimental data when the optical constants of water attained by Bertie et al. are closer with this work.

From Fig. 5 (a2, b2 and c2), the transmittance spectrum calculated by using the Eq. 7 with optical constants of water in this work are slightly different with the experimental data of optical cell filled with water at thickness 0.19 and 0.39mm, but the transmittance spectra at thickness 0.50mm has a better agreement with the experimental data of optical cell filled with water. And the transmittance spectrum calculated by using the Eq. 7 are similar with the results calculated by using the Eq. 3 with optical constants of water from Bertie compared with the experimental data. This results show that the Eq.3 and Eq.7 are nearly same precision to determine the total transmittance at normal incidence of optical cell filled with water, but which also indicates that the Eq. 7 has a better ability to calculate the total transmittance of optical cell filled with liquid material when the liquid materials layer is thicker.

However, as shown in Fig. 5 (a3, b3 and c3), the transmittance spectrum calculated by using the Eq. 8 with optical constants of water in this work or from Bertie are obviously different with the experimental data of optical cell filled with water at thickness 0.19, 0.39 and 0.5mm, which indicates that the Eq. 8 is different with the Eq.3 and Eq.7. The reason is that the Eq. 8 neglected the multiple transmission through the glass, and the Eq.3 and Eq.7 considered the multiple transmission.

For better illuminating the deviation between the experimental and the simulated transmittance calculated with different equations, the relative error is defined as:

$$er(\lambda) = \sqrt{\frac{\sum(T_{i,0.19}-T_{exp,0.19})^2+(T_{i,0.39}-T_{exp,0.39})^2+(T_{i,0.50}-T_{exp,0.50})^2}{3}} \quad (17)$$

Where, $er(\lambda)$ is the relative error in wavelength λ . $T_{i,0.19}$, $T_{i,0.39}$ and $T_{i,0.50}$ is the simulated transmittance in wavelength λ at liquid layer thickness 0.19, 0.39 and 0.50mm, respectively. i denotes that the simulated transmittance is calculated by using the Eq. 3, Eq. 7 and Eq. 8 with optical constants of this work and Bertie, respectively. $T_{exp,0.19}$, $T_{exp,0.39}$ and $T_{exp,0.50}$ is the simulated transmittance in wavelength λ at liquid layer thickness 0.19, 0.39 and 0.50mm, respectively.

Fig. 6 Relative errors between experimental and simulated transmittance

(a: Li (Eq.3); b: Li (Eq.7); c: Kameya (Eq.8))

Fig. 6 shows the relative error between the experimental and the simulated transmittance. It is clearly shown that the relative errors by using the Eq. 3 and Eq. 7 with optical constants of water in this work are smaller than 5% in measured spectral range, but the relative errors by using Eq. 8 are beyond than 5% in measured spectral range. It is also found that the relative errors by using the Eq. 3 and Eq. 7 with optical constants of water attained from Bertie have a nearly same tendency. However the relative errors by using Eq. 8 with optical constants of water attained from Bertie are

obviously different with the two other equations, which indicates that the Eq. 8 has a weak precision to determine the total transmittance of optical cell filled with liquid material compared with the two other equations.

4. Conclusions

In the present work, three equations for calculating the transmittance of optical cell filled with liquid materials were introduced, and a method to determine the optical constants of liquid materials was investigated. The transmittance spectrograms of optical cell with different thicknesses of water were measured in spectral range 2-2.5 μm at normal incidence, which are used to validate the methods.

The method in this work can effectively calculate the optical constants of some liquid materials by using the transmittance spectrum of optical cell filled with liquid materials. The biggest deviation between the experimental and the reference value in refractive index and extinctions index spectra is 49.06% and 5.18%, respectively. Considered the multiple transmission through the glass, the equations have a better ability to calculate the total transmittance of optical cell filled with liquid material. However, neglected the multiple transmission through the glass, the equation has a poor ability to calculate the total transmittance of optical cell filled with liquid material.

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