Novel method for simultaneous measurement of film thickness and mass fraction of urea–water solution

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Quantitative knowledge of the film thickness and mass fraction of the urea–water solution is very crucial in many practical applications. Film thickness or mass fraction can only be determined individually by conventional measurement techniques. We develop a novel measurement method to measure the film thickness and mass fraction of urea–water solution simultaneously. The absorption coefficients of urea–water solution (5–50 wt%) are measured, a pair of optimized wavelengths is then chosen to achieve high measurement sensitivity. Cross validation is also performed and uncertainties of the technique are smaller than 0.68% for thickness measurements and 1.86% for mass fractions.

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Liquid film formation due to droplets impact on a solid surface is very common in many practical application processes, for example, thin-film spray cooling of electronic components[1], aqueous film forming foam in fire suppression system[2], water droplets collision with the surface of heat transfer tube in falling film evaporator[3], and thin films of urea–water solutions in the automotive exhaust gas pipe in selective catalytic reduction systems[4]. The measurement of multi-parameter (e.g., film thickness, mass fraction) of liquid films is very important to understand the film formation processes and optimize the application devices.

Film thickness and mass fraction of urea–water solutions can only be determined individually by conventional measurement techniques. Film thickness measurement techniques are mainly classified into two groups: electrical contact method and optical method. Electrical method depends on electrical properties, for example, resistance and conductance of the film. However, the measurement range and accuracy will be influenced by several factors, such as the waveform of film surface, probe structure, and coverage of the liquid film on the plate[5]. Optical method, especially laser diagnostic method, is an advantageous tool due to non-invasive, high response, and high sensitivity[6–10]. Yang *et al.*[11] studied the liquid film thickness, liquid-phase temperature, and vapor-phase temperature above the film for pure water. Gresizik *et al.*[12,13] determined the 2D information of liquid water film thickness deposited on a transparent quartz plate by spontaneous Raman scattering and laser-induced fluorescence from low concentrations of a dissolved tracer substance. However, these methods are invalid for the aqueous solutions, when the solute is also absorbed as the solvent in

the studied region. Mass fraction measurement of urea–water solution based on density or ultrasonic velocity has been widely used in $DeNO_x$ process in practical application, but the measurement accuracy is limited due to contact with the liquid film. Non-invasive optical method for mass fraction measurement based on refractive index of the solution can achieve high accuracy, but the film thickness cannot be determined simultaneously.

In this letter, a novel technique based on laser spectroscopy is developed to determine the film thickness and mass fraction of urea–water solution simultaneously. The absorption spectra of urea–water solution for mass fraction (5–50 wt%) are measured with a Fourier-transform infrared (FTIR) spectrometer. Based on sensitivity analysis, a pair of optimized laser wavenumber positions is chosen and cross validation is performed to obtain the uncertainties of the novel technique.

Because of hydrogen bonding, liquid water exhibits broad-band absorption from OH-stretch vibrational bands in the near-infrared region[14]. Yang *et al.* determined the accurate liquid-water absorption cross sections with a spectral resolution of 2 cm^{-1} at various temperatures (25–75 °C) in the near-infrared region from 5800 to 7800 cm^{-1}[15]. And a coarse transmission curve for single crystal for urea was presented by Halbout *et al.* in 1979[16]. Since both solvent (water) and solute (urea) are absorbed in the near-infrared region, the molecular absorption coefficients of the urea–water solutions are not proportional to the absorption cross sections of the pure water. Moreover, there were no accurate enough absorption cross sections available for urea in the studied region in earlier studies. Therefore, in our work here, a novel method is developed to determine mass fraction and film thickness of urea–water solutions when analyzing only the overall absorption
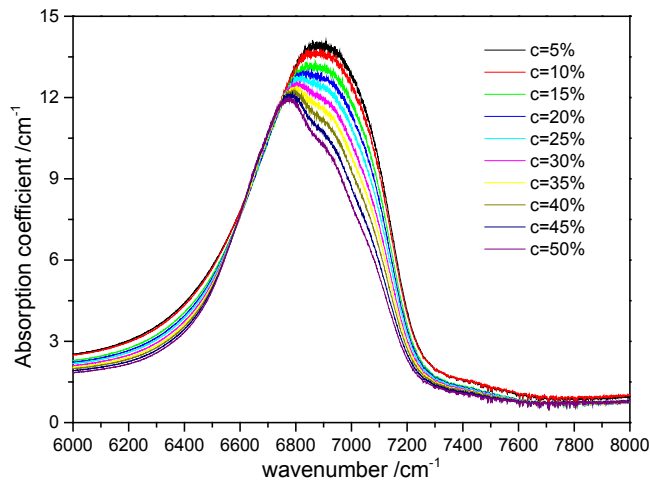
Fig. 1. Absorption spectrum of urea–water solution for mass fractions between 5 and 50 wt% measured via FTIR.

coefficients of the solutions, but without knowing the absorption cross section of the urea separately. Here, the wavelength- and mass fraction-dependent absorption coefficients $k(v, c)$ of urea–water solution were measured with a FTIR spectrometer (PerkinElmer Spectrum 100) with a spectral resolution of 0.25 cm^{-1} at room temperature. Urea–water solutions were prepared with for 5–50 wt% in a 1 mm pathlength quartz cuvette with two optical windows. The absorption spectra at different mass fractions are presented in Fig. 1. Since the central absorption wavenumber of urea (~6660 cm^{-1}) is smaller than pure water (~6892 cm^{-1}), the absorption feature of urea–water solution shifts toward longer wavelengths with increasing mass fractions. The standard deviation is smaller than 1% for three repeated experiments and 1.3% for the sample-to-sample variations.

Based on the Beer–Lambert law, the transmittance at a specific wavenumber position v_i is

$$\tau(v_i) = (I_t/I_0)_{v_i} = \exp(-k(v,c)d_1),\qquad (1)$$

where I_t and I_0 are the transmitted and incident intensities, respectively, d_1 (cm) is the length of the absorbing medium, that is, film thickness of the urea–water solutions, and $k(v, c)$ is a function of mass fraction c and wavenumber v. With the absorption coefficients derived from the spectra shown in Fig. 1, linear fit for $k(v, c)$ at a pair of wavenumber positions can be obtained as

$$k(v,c) = A_i + B_i c, \quad i = 1,2,\qquad (2)$$

where A_i and B_i are the respective fitting coefficients. Therefore, transmission is only a function of two unknown parameters, c and d_1. The ratio of the logarithm of the transmissions at two wavenumber positions can be formed as

$$R_{1/2} = \frac{\lg\left((I_t/I_0)_{v_1}\right)}{\lg\left((I_t/I_0)_{v_2}\right)} = \frac{k_1 d_1}{k_2 d_1} = \frac{k_1}{k_2}.\qquad (3)$$

Since $R_{1/2}$ is only a function of absorption coefficients, it can be expressed as a function of mass fraction c

$$R_{1/2} = \frac{k_1}{k_2} = \frac{A_1 + B_1 c}{A_2 + B_2 c},\qquad (4)$$

and mass fraction can be then obtained as

$$c = \frac{A_2 R_{1/2} - A_1}{B_1 - B_2 R_{1/2}}.\qquad (5)$$

The film thickness can be determined by inserting Eq. (5) into Eq. (1)

$$d_1 = \frac{\lg\left(I_t/I_0\right)}{A_1 + B_1 \dfrac{A_2 R_{1/2} - A_1}{B_1 - B_2 R_{1/2}}}.\qquad (6)$$

With the developed method, mass fraction and film thickness of the aqueous solutions can be determined simultaneously when the accurate absorption cross sections of the solute (urea in this work) are unknown.

Sensitivity analysis at different selected wavenumber position pairs is necessary to achieve high measurement sensitivity. The derivative of the absorption coefficients with respect to mass fraction dk/dc is depicted in Fig. 2. Four wavenumber positions (extrema: 7040.75 and 6719.75 cm^{-1}, zero: 6613.25 and 6761.00 cm^{-1}) at the curve are chosen and three pairs (6613.25/7040.75, 6719.75/7040.75, and 6761.00/7040.75 cm^{-1}) are then formed. The measurement sensitivity of the technique depends on the derivative of $R_{1/2}$ with respect to mass fraction $dR_{1/2}/dc$

$$dR_{1/2}/dc = \frac{A_2 B_1 - B_2 A_1}{\left(A_2 + B_2 c\right)^2}.\qquad (7)$$

The mass fraction dependence of the derivative $dR_{1/2}/dc$ for three pairs is shown in Fig. 3. $dR_{1/2}/dc$ increases
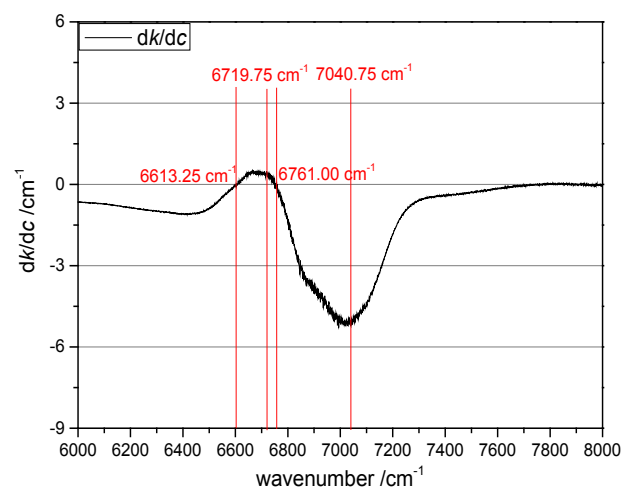

Fig. 2. Wavelength-dependent derivative with respect to mass fraction from 5 to 50 wt% for absorption coefficient of urea–water solution, dk/dc.
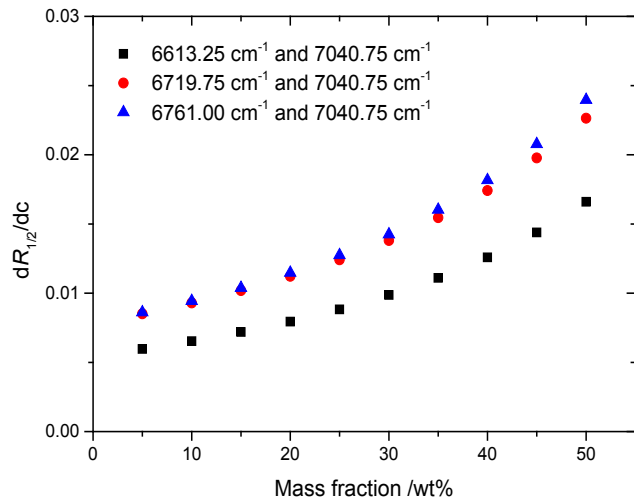
Fig. 3. Derivative of $R_{1/2}$ with respect to mass fraction for three wavenumber positions pairs.

with increasing mass fraction of the urea–water solution for all three pairs, it reveals that the measurement sensitivity increases with the increasing mass fraction. And the highest $dR_{1/2}/dc$ value is located at the third pair (6761.00/7045.75 cm^{-1}), hence, the pair is chosen as the most sensitive pair for the present work. The absorption coefficients and its linear fit curve are plotted in Fig. 4, where the respective fitting coefficients A_i and B_i in Eq. (2) can be determined. For the third pair, the fitting coefficient B_2 at 7045.75 cm^{-1} is negative. According to Eq. (7), $dR_{1/2}/dc$ increased with the increasing mass fraction c, and the trend is consistent with the results as shown in Fig. 3.

Cross validation method is employed in this work to determine the measurement accuracy of the chosen two wavenumber positions for the developed technique. The transmission data are chosen from the FTIR measurement at different mass fractions (5–50 wt%). For the
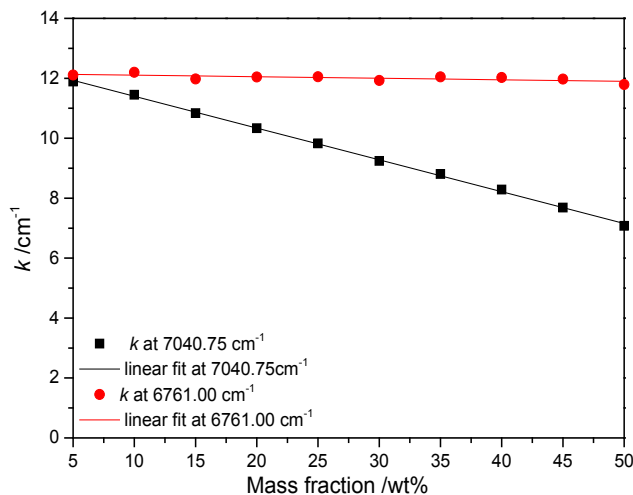

Fig. 4. Mass fraction dependence of urea–water solution absorption coefficient at two chosen wavenumber positions with linear fit curves.
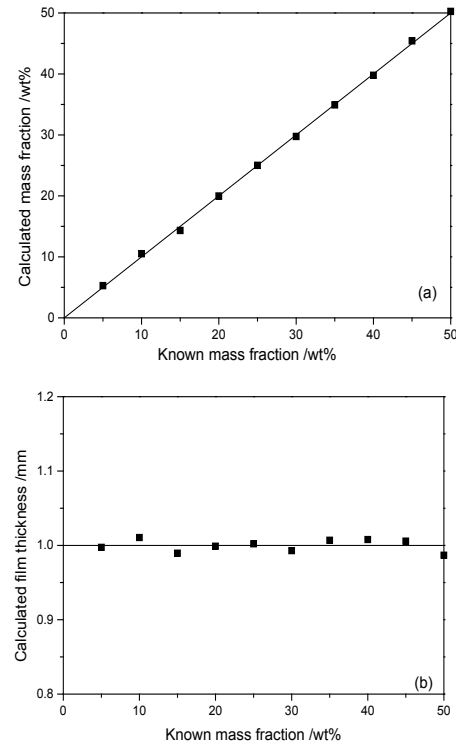

Fig. 5. Calculated (a) mass fraction and (b) film thickness of urea–water solution with cross validation method.

cross validation method, when the transmission data at one specific mass fraction are eliminated, all the transmission data at other mass fractions are used to determine the absorption coefficients. The fitting coefficients A_i and B_i, the film thickness, and the mass fraction at the known specific mass fraction of the urea–water solutions can then be determined, which are compared with the known parameters to determine the measurement accuracy.

As shown in Figs. 5(a) and (b), the calculated mass fraction and film thickness of urea–water solution are in good agreement with the known parameters. The maximum uncertainty of the method for mass fraction is 5.72%, when the known mass fraction is 5 wt%, and it is consistent with the result of sensitivity analysis given above, that is, the sensitivity increases with the increasing mass fraction. The mean uncertainty is 0.68% for the film thickness measurement.

In conclusion, we develop a novel technique for simultaneous measurement of liquid film thickness and mass fraction of urea–water solution. With sensitivity analysis, a pair of optimized wavenumber positions is chosen to achieve highest measurement sensitivity. Cross validation is also performed, the mean uncertainties of 0.68% for liquid film thickness and 1.86% for mass fraction are found with the novel technique. The proposed method is also valid for other aqueous solutions, that is, when the absorption cross sections of the solvent and solute are unknown. In future, simultaneous measurement of other characteristic parameter of liquid film, for example film temperate will also be studied.

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